Supporting Information

Secondary phosphine oxide-triggered selective oxygenation of a benzyl ligand on palladium

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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 (the water contents of the deuterated solvents ($CDCl_3$, CD_3CN, acetone-d_6, toluene-d_8, and CD_3OD) are <0.5% (chemical purities are 99.5%)). Hyflo Super-Cel was obtained from Nacalai. [PdBnCl(cod)],[1] phenylmethylphosphine oxide,[2] phenyl(*t*-butyl)phosphine oxide,[2] dimethylphosphine oxide,[3] di-*t*-butylphosphine oxide,[4] and ethylene-1,2-bis(phenylphosphine oxide)[5] were prepared as reported previously.

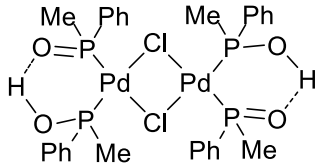
Physical and Analytical Measurements. NMR spectra were recorded on either a Bruker AV-300N (300 MHz (^{1}H), 75 MHz (^{13}C), 121 MHz (^{31}P)) or a JEOL JNM-AL400 (100 MHz (^{13}C)) spectrometer. All ^{1}H and ^{13}C chemical shift values (δ) were expressed relative to a residual solvent signal as a reference. ^{31}P NMR chemical shift values (δ) were reported in relative to triphenylphosphine as an external reference. 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.

General Procedure for the Oxygenation of a Benzyl Ligand in [PdBnCl(cod)] with Secondary Phosphine Oxides under O_2. All the reactions were performed in sealed J. Young valve NMR tubes (528-LPV-8) unless otherwise indicated. Either 1,1,2,2-tetrachloroethane or trimethylphenylsilane was used as an internal standard for each reaction. [PdBnCl(cod)] (10.0 mg, 29 μmol) and a secondary phosphine oxide (58 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon, and O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. The reaction was monitored by ^{1}H and ^{31}P NMR. Yields of the oxygenated compounds (BnOOH, BnOH and PhCHO) were determined based on the integrations of corresponding methylene or aldehyde proton signals in ^{1}H NMR spectra (δ 4.90, 4.57, and 9.94 ppm, respectively). The formation of complex **2** (or **3**) was confirmed based on ^{1}H and ^{31}P NMR analysis.

Isolation of Complex 2a. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.1 mg, 29.6 μmol) and diphenylphosphine oxide (12.1 mg, 59.8 μmol) were dissolved in CD_3CN (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. Yellow crystals were precipitated. After removal of the supernatant solution, the crystals were washed with hexane (three times) and dried under vacuum to give **2a** (12.3 mg, 11.2 μmol, 77%)**.** The NMR data were consistent with those reported previously.[6]

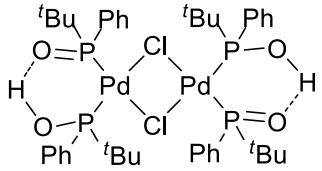
Isolation of Complex 2b. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol) and phenylmethylphosphine oxide (8.7 mg, 62.0 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. O_2

(10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2, and was filtered by a Hyflo Super-Cel and washed with $CHCl_3$. The filtrate was evaporated to dry, and the residue was reprecipitated from $CHCl_3$/hexane. After removal of the supernatant solution, the yellow precipitate was washed with hexane (three times) and dried under vacuum to give **2b** as a mixture of diastereomers (7.2 mg, 8.5 μmol, 59%).



Selected data for complex **2b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.19 (m, 20H, Ph), 2.05–1.79 (m, 12H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.8 (br d, $^1J_{PC}$ = 54.8 Hz), 131.2–130.8 (m), 130.4–130.3 (m), 129.9–129.7 (m), 128.6–128.3 (m), 21.0–20.5 (m). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 78.0. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{35}Cl_2O_4P_4Pd_2$ $[M+H]^+$ 842.8938, found 842.8969. Anal. Calcd for $C_{28}H_{34}Cl_2O_4P_4Pd_2$: C, 39.93; H, 4.07. Found: C, 39.87; H, 4.10.

Isolation of Complex 2c. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol) and phenyl-*t*-butylphosphine oxide (12.0 mg, 65.9 μmol) were dissolved in acetone-d_6 (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. A yellow solid was precipitated. After removal of the supernatant solution, the solid was washed with hexane (three times), and dried under vacuum to give **2c** (9.0 mg, 8.9 μmol, 61%) as a mixture of two main diastereomers (ca. 2.1:1).

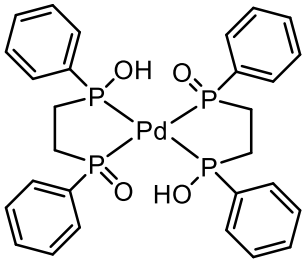


Major diastereomer of complex **2c**: ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 8H, Ph), 7.24 (t, J = 6.8 Hz, 4H, Ph), 7.11 (t, J = 7.4 Hz, 8H, Ph), 1.28 (s, 36H, ^{t}Bu). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.0 (dd, $^1J_{PC}$ = 57.0 Hz, $^3J_{PC}$ = 6.0 Hz), 131.8 (t, J_{PC} = 5.5 Hz), 130.3, 127.7 (t, J_{PC} = 5.3 Hz), 40.3 (dd, $^1J_{PC}$ = 50.5 Hz, $^3J_{PC}$ = 8.8 Hz), 27.4. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 96.3. Selected data for minor diastereomer of complex **2c**: ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 7.5 Hz, Ph), 7.61 (d, J = 7.2 Hz, Ph), 7.47–7.36 (m, Ph), 1.25 (s, 9H, ^{t}Bu), 1.24 (s, 9H, ^{t}Bu), 1.15 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 132.2 (t, J_{PC} = 4.9 Hz), 130.7, 127.9 (t, J_{PC} = 5.5 Hz), 27.3. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 96.9 ($^2J_{PP}$ = 21.8 Hz), 96.0 ($^2J_{PP}$ = 21.8 Hz), 95.2. HRMS (ESI): *m*/*z* calcd

for $C_{40}H_{57}ClNaO_4P_4Pd_2$ $[M\text{-}HCl+Na]^+$ 997.0867, found 997.0912. Anal. Calcd for $C_{40}H_{58}Cl_2O_4P_4Pd_2$: C, 47.54; H, 5.79. Found: C, 47.24; H, 5.72.

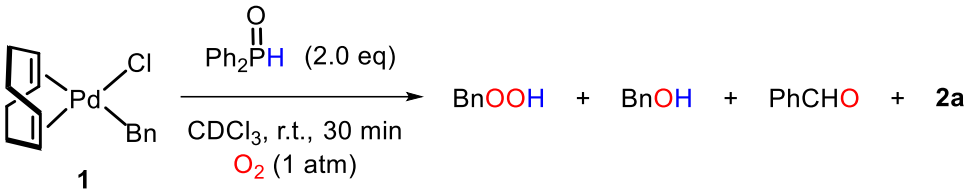
Isolation of Complex 2d. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol) and dimethylphosphine oxide (5.8 mg, 64 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2, and was filtered by a Hyflo Super-Cel and washed with $CHCl_3$. The filtrate was evaporated to dry, and the residue was reprecipitated from $CHCl_3$/hexane. After removal of the supernatant solution, the precipitate was washed with hexane (three times) and dried under vacuum to give **2d** as a pale yellow solid (5.4 mg, 9.1 μmol, 62%)**.** The NMR data for **2d** were consistent with those reported previously.[7]

Isolation of Complex 3. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.1 mg, 29 μmol) and ethylene-1,2-bis(phenylphosphine oxide) (8.4 mg, 59 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. Hexane was added to the reaction mixture to precipitate a pale yellow solid. After removal of the supernatant solution, the solid was washed with hexane (three times), and dried under vacuum to give **3** (10.2 mg, 15.4 μmol, 53%).



Complex **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.06 (m, 20H, Ph), 2.45 (br d, $^2J_{PH}$ = 21.7 Hz, 4H), 1.80 (br d, $^2J_{PH}$ = 24.6 Hz, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 140.0 (d, $^1J_{PC}$ = 55.5 Hz), 130.8 (d, $^2J_{PC}$ = 39.0 Hz), 130.3, 127.7 (d, $^3J_{PC}$ = 6.6 Hz), 34.9 (d, $^1J_{PC}$ = 61.5 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 129.8. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{31}O_4P_4Pd$ $[M+H]^+$ 661.0218, found 661.0161. Anal. Calcd for $C_{28}H_{30}O_4P_4Pd{\cdot}CHCl_3$: C, 44.64; H, 4.00. Found: C, 45.06; H, 3.94.

Table S1. Oxygenation of a benzyl ligand in the presence of Ph_2PHO[a]

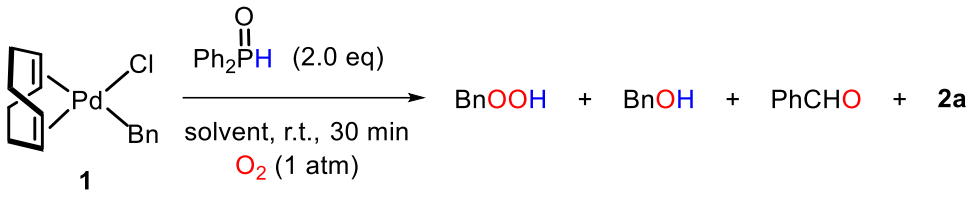


Entry	Yield (%)[b]			
	BnOOH	BnOH	PhCHO	**2a**
1	94	3	2	62
2	87	2	3	77
3	92	2	2	71
4	93	2	1	75
5	88	3	0	72
6	94	3	3	71
Avg	91	3	2	71
SD	2.8	0.5	1.1	4.7

[a] Reaction conditions: complex **1** (29 μmol), diphenylphosphine oxide (58 μmol), $CDCl_3$ (0.50 mL), under O_2, r.t., 30 min, in a NMR tube. [b] NMR yield. In the $^{31}P\{^1H\}$ NMR spectra, several small signals were observed at 75–84 ppm in addition to the signal for complex **2a** (78.3 ppm).

Effect of Solvents. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol) and diphenylphosphine oxide (11.8 mg, 58 μmol) were dissolved in a solvent (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. The reaction was monitored by ^1H and ^{31}P NMR. The results were summarized in Table S1.

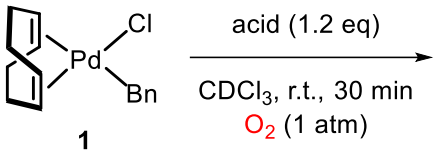
Table S2. Effect of solvents[a]



Entry	Solvent	Yield (%)[b]			
		BnOOH	BnOH	PhCHO	**2a**
1	$CDCl_3$	93	2	1	75
2[c]	$CDCl_3/H_2O$	95	0	0	54
3	CD_3CN	84	2	1	77[d]
4	acetone-d_6	61	0	2	74[d]
5	toluene-d_8	88	3	0	80[d]
6	CD_3OD	62	2	0	79[d]

[a] Reaction conditions: complex **1** (29 μmol), diphenylphosphine oxide (58 μmol), solvent (0.50 mL), under O_2, r.t., 30 min, in a NMR tube. [b] NMR yield. [c] $CDCl_3/H_2O$ = 0.45 mL/0.05 mL. [d] Isolated yield.

Oxygenation in the Presence of either HCl or *n*-Bu$_4$NCl. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol) and either HCl (44.0 μL, 35.2 μmol, 0.80 M dioxane solution) or *n*-Bu$_4$NCl (9.7 mg, 34.8 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. Trimethylphenylsilane (15 μL, 87 μmol) was added as an internal standard. O_2 (10 mL) was passed through the solution using a syringe over 25 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. The reaction mixture was immediately analyzed by ^{1}H NMR. The results were summarized in Scheme S1.



1

acid (1.2 eq)

$CDCl_3$, r.t., 30 min

O_2 (1 atm)

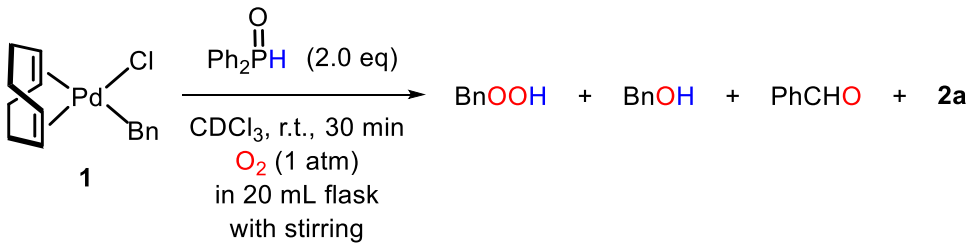
BnOOH + BnOH + PhCHO

	conv. of **1**			
HCl	37%	0%	0%	2%
n-Bu$_4$NCl	17%	0%	2%	5%

Scheme S1. Oxygenation in the presence of either HCl or *n*-Bu$_4$NCl.

Oxygenation of a Benzyl Ligand under O_2 in 20 mL Flask. In a 20 mL round-bottom flask equipped with a three-way cock and a magnetic stirring bar, [PdBnCl(cod)] (10.0 mg, 29 μmol) and diphenylphosphine oxide (11.8 mg, 58 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred at room temperature for 30 min under O_2. The reaction was monitored by ^1H and ^{31}P NMR. The results were summarized in Table S3.

Table S3. Oxygenation of a benzyl ligand under O_2

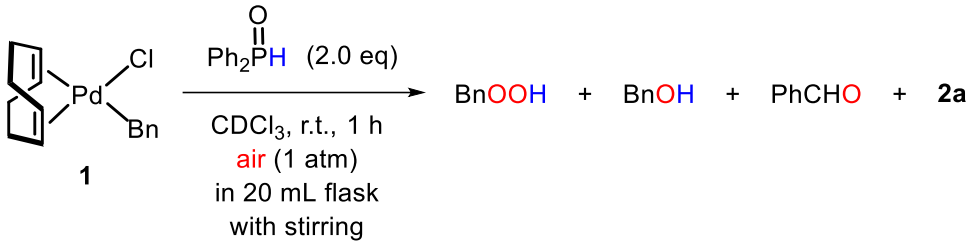


Entry	Yield (%)[b]			
	BnOOH	BnOH	PhCHO	**2a**
1	82	6	1	72
2	91	3	6	92
3	87	3	6	74
Avg	87	4	4	79
SD	3.7	1.4	2.4	9

[a] Reaction conditions: complex **1** (29 μmol), diphenylphosphine oxide (58 μmol), $CDCl_3$ (0.50 mL), under O_2, r.t., 30 min, in a 20 mL flask. [b] NMR yield.

Oxygenation of a Benzyl Ligand under Air in 20 mL Flask. In a 20 mL round-bottom flask equipped with a three-way cock and a magnetic stirring bar, [PdBnCl(cod)] (10.0 mg, 29 μmol) and diphenylphosphine oxide (11.8 mg, 58 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. Air (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred at room temperature for 1 h under air. The reaction was monitored by ^{1}H and ^{31}P NMR. The results were summarized in Table S4.

Table S4. Oxygenation of a benzyl ligand under air

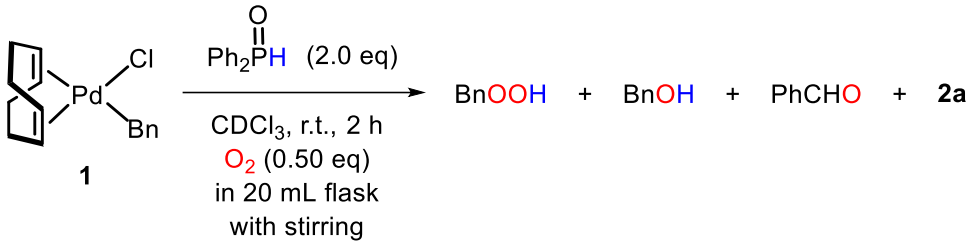


Entry	Yield (%)[b]			
	BnOOH	BnOH	PhCHO	**2a**
1	85	3	3	75
2	86	4	5	78
3	80	4	6	81
Avg	84	4	5	78
SD	2.6	0.5	1.2	2.4

[a] Reaction conditions: complex **1** (29 μmol), diphenylphosphine oxide (58 μmol), $CDCl_3$ (0.50 mL), under air, r.t., 1 h, in a 20 mL flask. [b] NMR yield.

Oxygenation of a Benzyl Ligand with O_2 (0.50 eq) in 20 mL Flask. In a 20 mL round-bottom flask equipped with a three-way cock and a magnetic stirring bar, [PdBnCl(cod)] (10.0 mg, 29 μmol) and diphenylphosphine oxide (11.8 mg, 58 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. O_2 (355 μL, 14.5 μmol) was introduced in the gas phase in the flask using a syringe. The reaction mixture was stirred at room temperature for 2 h. The reaction was monitored by ^1H and ^{31}P NMR. The results were summarized in Table S5.

Table S5. Oxygenation of a benzyl ligand with O_2 (0.50 eq)

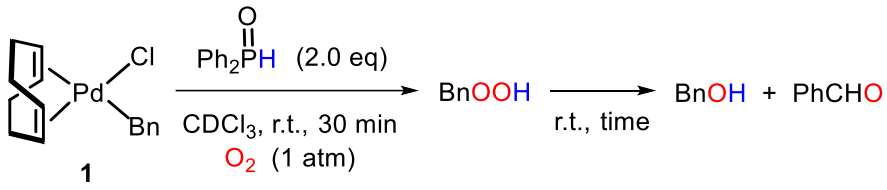


Entry	Yield (%)[b]			
	BnOOH	BnOH	PhCHO	**2a**
1	0	75	6	53
2	0	51	2	56
3	9	44	6	39
4	12	62	6	47
5	0	54	5	48
6	0	56	5	49
7	0	51	7	48
Avg	3	56	5	49
SD	4.8	9.2	1.5	4.9

[a] Reaction conditions: complex **1** (29 μmol), diphenylphosphine oxide (58 μmol), $CDCl_3$ (0.50 mL), O_2 (14.5 μmol), r.t., 2 h, in a 20 mL flask. [b] NMR yield.

Conversion of Benzyl Hydroperoxide into Benzyl Alcohol and Benzaldehyde. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol), diphenylphosphine oxide (11.8 mg, 58 μmol), and trimethylphenylsilane (15 μL, 87 μmol) as an internal standard were dissolved in $CDCl_3$ (0.50 mL) under argon. O_2 (10 mL) was passed through the solution using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. The conversion of formed benzyl hydroperoxide into benzyl alcohol and benzaldehyde was monitored by ^1H NMR. The results were summarized in Table S2.

Table S6. Conversion of formed benzyl hydroperoxide into benzyl alcohol and benzaldehyde[a]

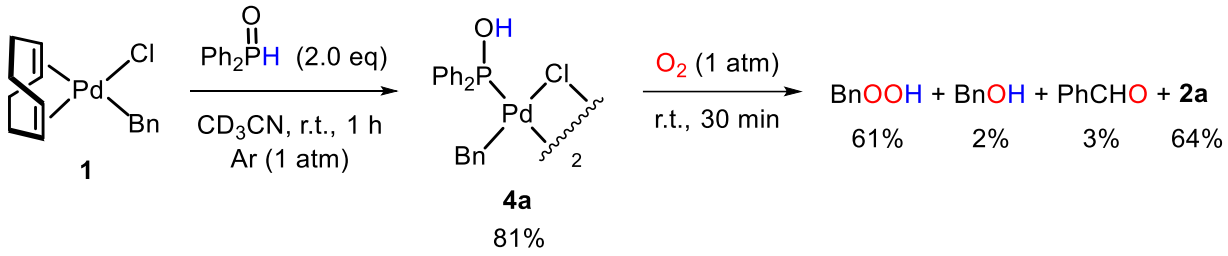


Time	Yield (%)[b]			
	BnOOH	BnOH	PhCHO	**2a**
0 min	94	3	2	62
3 h	91	4	4	61
6 h	91	4	5	60
48 h	33	18	28	59

[a] Reaction conditions: complex **1** (29 μmol), diphenylphosphine oxide (58 μmol), $CDCl_3$ (0.50 mL), under O_2, r.t., 30 min, in a NMR tube. [b] NMR yield.

Observation of Complex 4a. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol), diphenylphosphine oxide (11.8 mg, 58 μmol), and trimethylphenylsilane (15 μL, 87 μmol) as an internal standard were dissolved in CD_3CN (0.50 mL) under argon, and the reaction mixture was left at room temperature. After 1 h, a series of new signals corresponding to complex **4a** was observed. O_2 (10 mL) was passed through the reaction mixture using a syringe over 30 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. The ^1H NMR signals for **4a** disappeared, and oxygenated organic compounds and **2a** were obtained. However, in the abovementioned reaction, unidentified compounds were observed in the $^{31}P\{^1H\}$ NMR spectrum (δ 99.7 and 78.8 ppm) in addition to **4a** (δ 104.3 ppm) at the first step. The reaction of **1** with 1.0 equiv of diphenylphosphine oxide under Ar could suppress the byproduct formation. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol), diphenylphosphine oxide (5.9 mg, 29 μmol), and trimethylphenylsilane (15 μL, 87 μmol) as an internal standard were dissolved in CD_3CN (0.50 mL) under argon, and the reaction mixture was left at room temperature. After 1 h, **4a** was observed in 91% yield in the ^1H NMR spectrum.

Complex **4a**: ^1H NMR (300 MHz, CD_3CN) δ 7.76–6.91 (m, 10H, Ph), 2.98 (d, $^3J_{PH}$ = 3.0 Hz, 4H, CH_2Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, at -40 °C) δ 145.1 (d, J_{PC} = 2.5 Hz), 135.7 (d, J_{PC} = 54.2 Hz), 132.3, 132.2 , 131.8, 128.9, 128.4, 124.6, 30.9. $^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN) δ 104.3. ^1H-^{31}P HMQC spectrum of the reaction mixture containing **4a** prepared from **1** and 2.0 equiv of diphenylphosphine oxide (in CD_3CN) was shown in Figure S1. Because **4a** is very air-sensitive, a clear IR spectrum was not obtained.



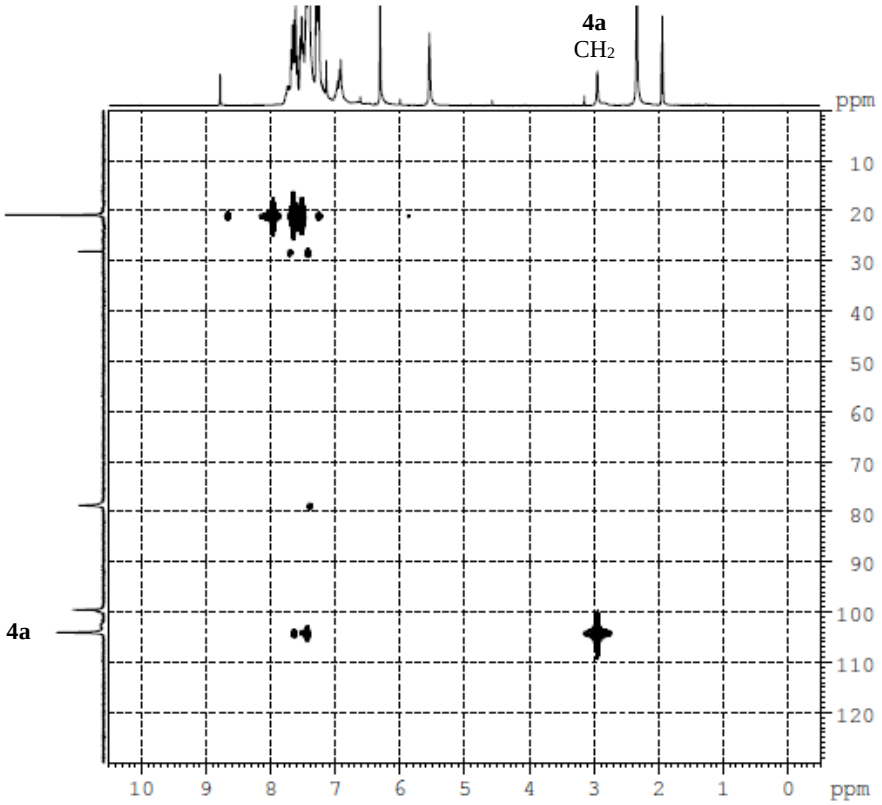
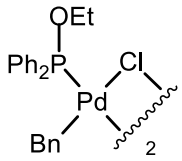


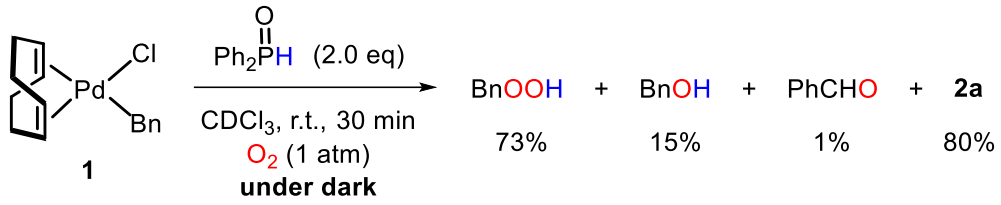
Figure S1. ^{1}H-^{31}P HMQC spectrum of the reaction mixture containing **4a** prepared from **1** and 2.0 equiv of diphenylphosphine oxide (in CD_3CN).

Synthesis of Complex 5. In a J. Young valve NMR tube, [PdBnCl(cod)] (10.0 mg, 29 μmol) and diphenylethoxyphosphine (6.3 μL, 29 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. The reaction mixture was stirred by shaking at room temperature for 1 h, and was filtered by a Hyflo Super-Cel and washed with $CHCl_3$. The filtrate was evaporated to dry, and the residue was reprecipitated from $CHCl_3$/hexane. After removal of the supernatant solution, the precipitate was washed with hexane (three times) and dried under vacuum to give **5** as a yellow solid (7.6 mg, 8.2 μmol, 56%).



Complex **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–6.94 (m, 30H, Ph), 3.93 (quintet, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.0 Hz, 4H), 3.10 (s, 4H), 1.26 (t, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.8, 134.6 (d, $^1J_{PC}$ = 52.5 Hz), 131.9 (d, $^2J_{PC}$ = 13.5 Hz), 131.0 (d, $^4J_{PC}$ = 2.4 Hz), 129.0 (br), 128.3 (d, $^3J_{PC}$ = 11.3 Hz), 128.1 (br), 124.8 (br), 65.4, 31.0 (br), 16.5 (d, $^3J_{PC}$ = 9.8 Hz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 114.5. HRMS (ESI): m/z calcd for $C_{42}H_{44}ClO_2P_2Pd_2$ [M-Cl]$^+$ 891.0579, found 891.0556. Anal. Calcd for $C_{42}H_{44}Cl_2O_2P_2Pd_2$: C, 54.45; H, 4.79. Found: C, 54.34; H, 4.82.

Oxygenation under Dark Conditions. In a J. Young valve NMR tube wrapped with an aluminum foil, [PdBnCl(cod)] (10.1 mg, 29 μmol) and diphenylphosphine oxide (11.8 mg, 58 μmol) were dissolved in $CDCl_3$ (0.50 mL) under argon. Trimethylphenylsilane (15 μL, 87 μmol) was added as an internal standard. O_2 (10 mL) was passed through the solution using a syringe over 25 sec. The reaction mixture was stirred by shaking at room temperature for 30 min under O_2. The aluminum foil was removed, and the reaction mixture was immediately analyzed by ^1H and ^{31}P NMR. The results were summarized in Scheme S2.



Scheme S2. Oxygenation under dark conditions.

Crystallographic Study of 2a and 5. Single crystals suitable for X-ray diffraction measurements obtained from $CHCl_3$/hexane for both **2a** (colorless block, by vapor diffusion) and **5** (yellow block, by liquid-liquid diffusion) were mounted using a cryoloop. The diffraction data were collected with a Rigaku Saturn CCD detector ($Mo_{K\alpha}$, λ = 0.71069 Å). Molecular structures of **2a** and **5** are shown in Figures S2 and S3, respectively. Crystal data are listed in Table S3. The structures were solved by direct methods using SHELXS-97 and refined by least squares on F^2, SHELXL-2013.[8] Non-hydrogen atoms were anisotropically refined except for disordered ones, which were isotropically refined. All hydrogen atoms including OH moieties in **2a** were positioned geometrically and refined using a riding model. Refinements were continued until all shifts were smaller than one-tenth of the standard deviations of the parameters involved.

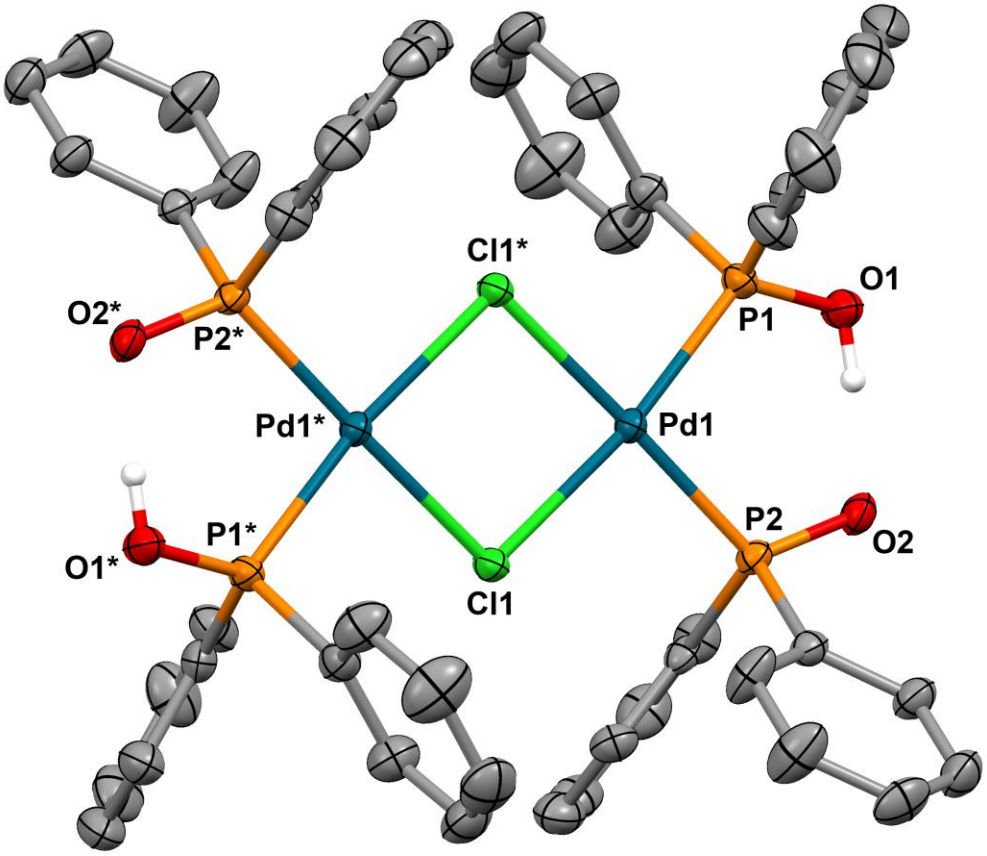


Figure S2. Molecular structure of **2a** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity except for those on oxygen atoms. Selected atomic distances (Å): Pd1–Cl1 = 2.4200(9), Pd1-Cl1* = 2.4286(9), Pd1-P1 = 2.2543(10), Pd1-P2 = 2.2490(9), P1-O1 = 1.542(3), P2-O2 = 1.539(2), O1···O2 = 2.418(4).

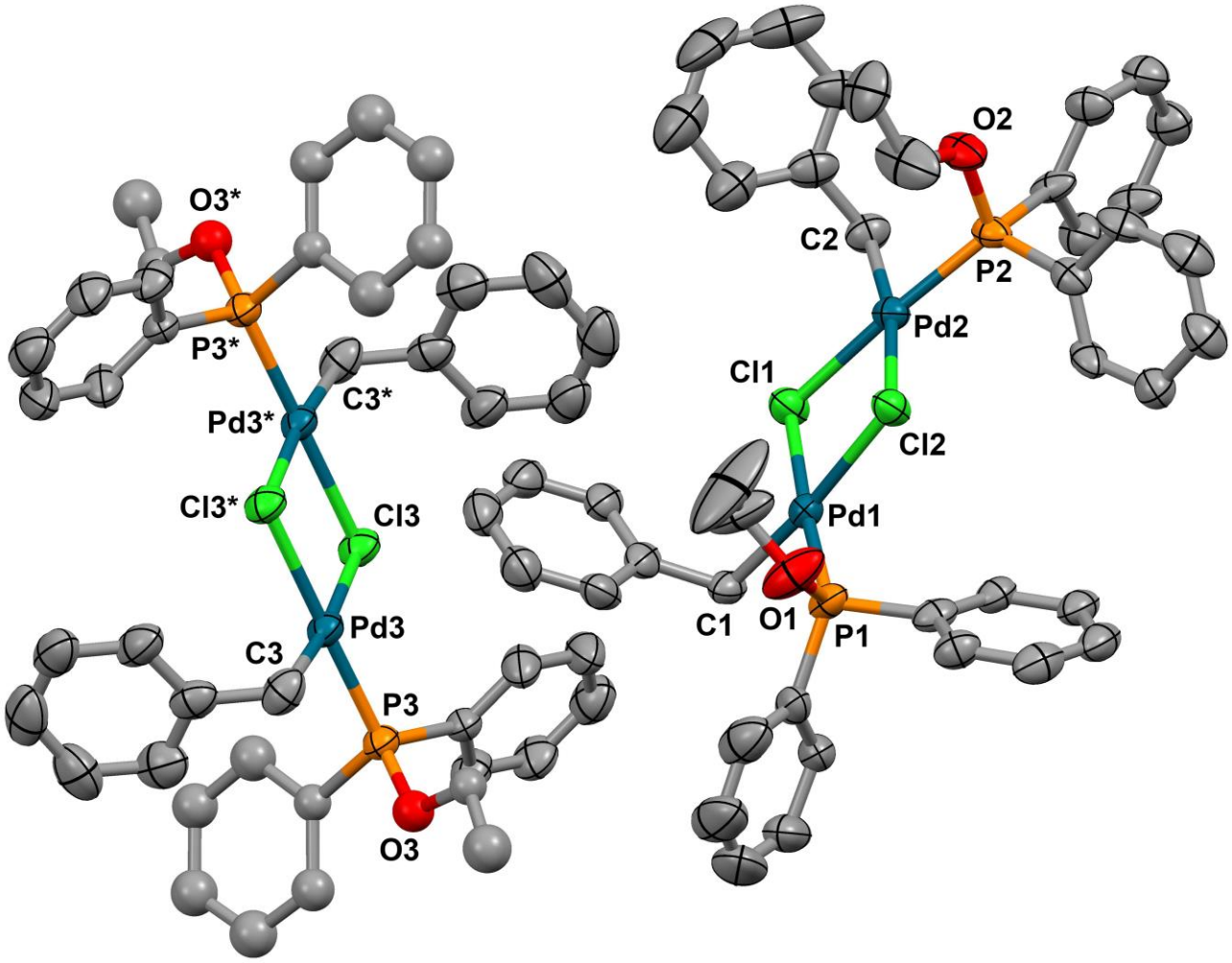


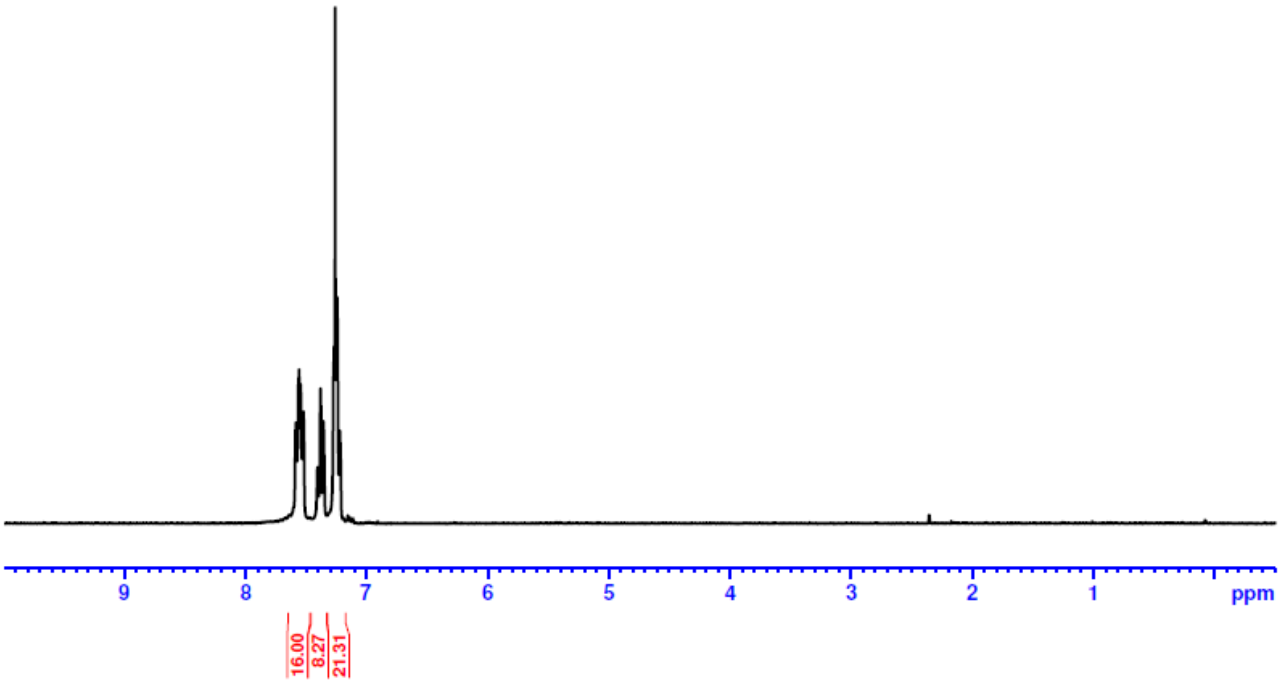
Figure S3. Molecular structure of **5** with 50% probability ellipsoids. Hydrogen atoms and a water molecule (a solvent molecule) are omitted for clarity. *Cis*-**5** (right) and *trans*-**5** (left) were observed in a 2:1 ratio in the unit cell. The ethoxy and phenyl groups in *trans*-**5** were treated as disordered. Selected atomic distances (Å): Pd1–Cl1 = 2.4227(18), Pd1-Cl2 = 2.4548(16), Pd2-Cl1 = 2.4300(17), Pd2-Cl2 = 2.4502(17), Pd3-Cl3 = 2.4480(18), Pd3-Cl3* = 2.4178(16), Pd1-P1 = 2.2218(18), Pd2-P2 = 2.2090(16), Pd3-P3 = 2.2036(16), Pd1-C1 = 2.071(5), Pd2-C2 = 2.082(6), Pd3-C3 = 2.064(7).

Table S7. Summary of crystal data, collection data, and refinement of **2a** and **5**

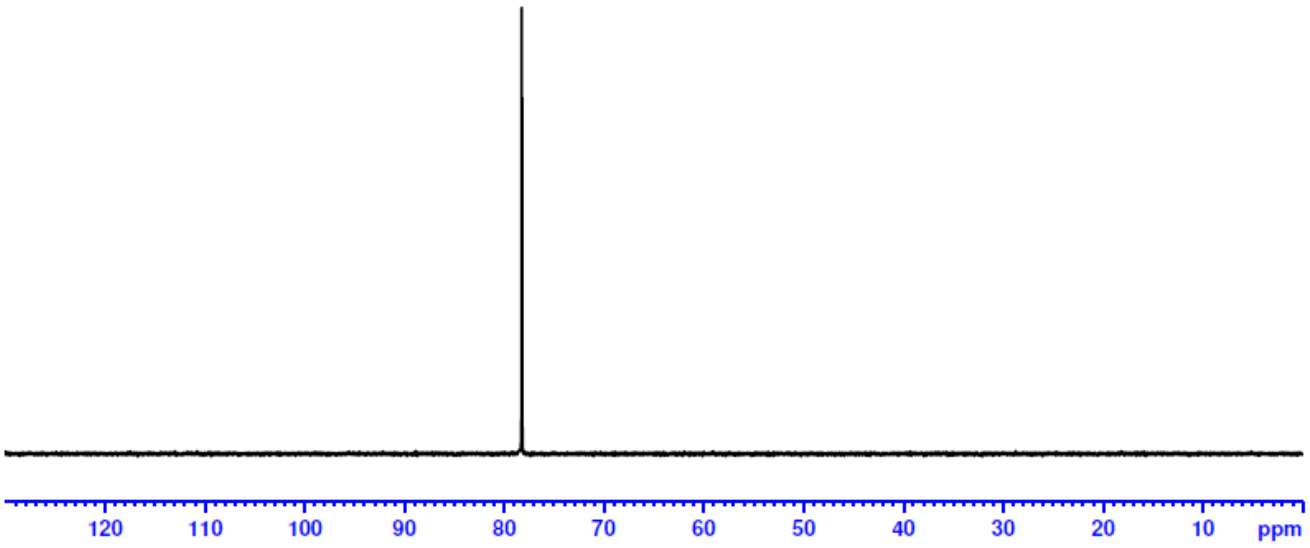
	2a	**5**
formula	$C_{48}H_{42}Cl_2O_4P_4Pd_2$	$C_{42}H_{44}Cl_2O_{2.67}P_2Pd_2$
Fw	1090.40	937.13
crystal size, mm	0.20 × 0.03 × 0.02	0.09 × 0.07 × 0.04
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a, Å	11.8642(15)	10.050(4)
b, Å	13.1675(15)	13.715(5)
c, Å	17.343(2)	23.780(8)
α, deg	68.772(6)	78.415(7)
β, deg	78.937(8)	81.104(7)
γ, deg	63.277(5)	86.079(7)
V, Å^3	2254.4(5)	3170(2)
Z	2	3
D (calcd), g cm^{-3}	1.606	1.473
data collection temp, K	153(2)	163(2)
μ (Mo Kα), mm^{-1}	1.102	0.71075
$2\theta_{max}$, deg	54.0	55.0
no. of measd reflns	17758	31106
no. of unique reflns	9460	14267
no. of obsd reflns ($I > 2\sigma(I)$)	7335	9848
no. of variables	543	674
R_1[a] ($I > 2\sigma(I)$)	0.0398	0.0591
wR_2[a] ($I > 2\sigma(I)$)	0.0762	0.1521
R_1[a] (all data)	0.0569	0.0894
wR_2[a] (all data)	0.0861	0.1888
GOF	1.080	1.094

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

Complex **2a**

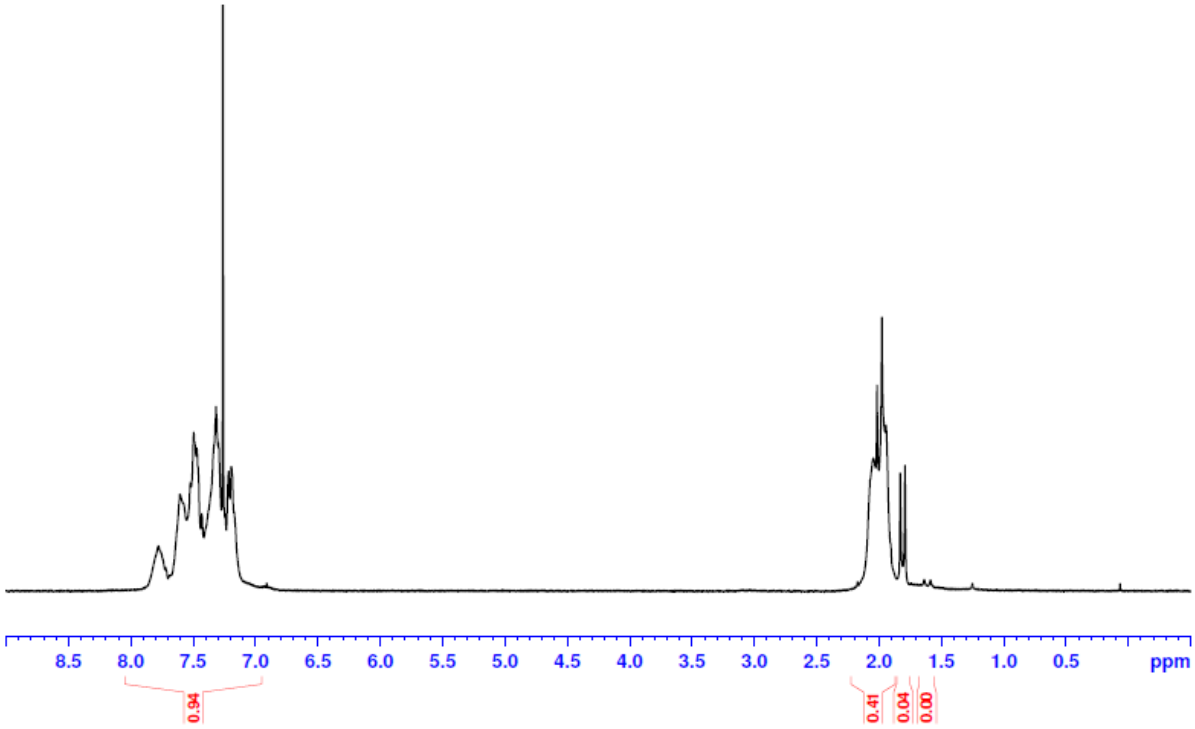


^{1}H NMR (300 MHz, $CDCl_3$)

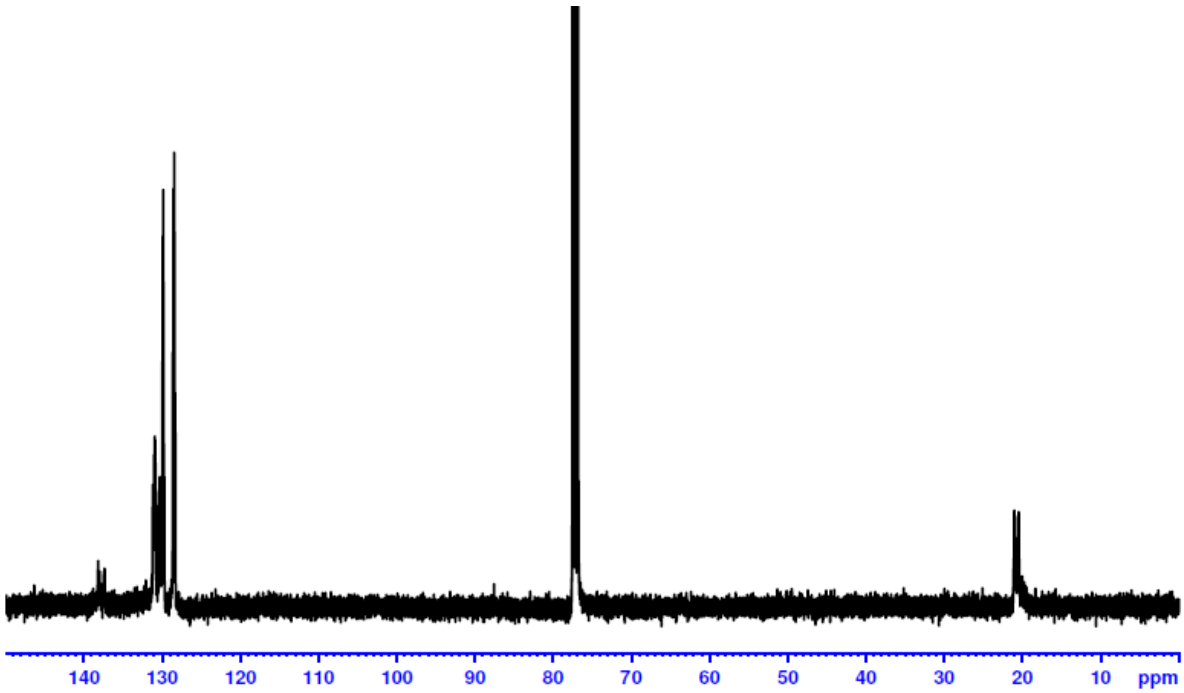


$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

Complex **2b**

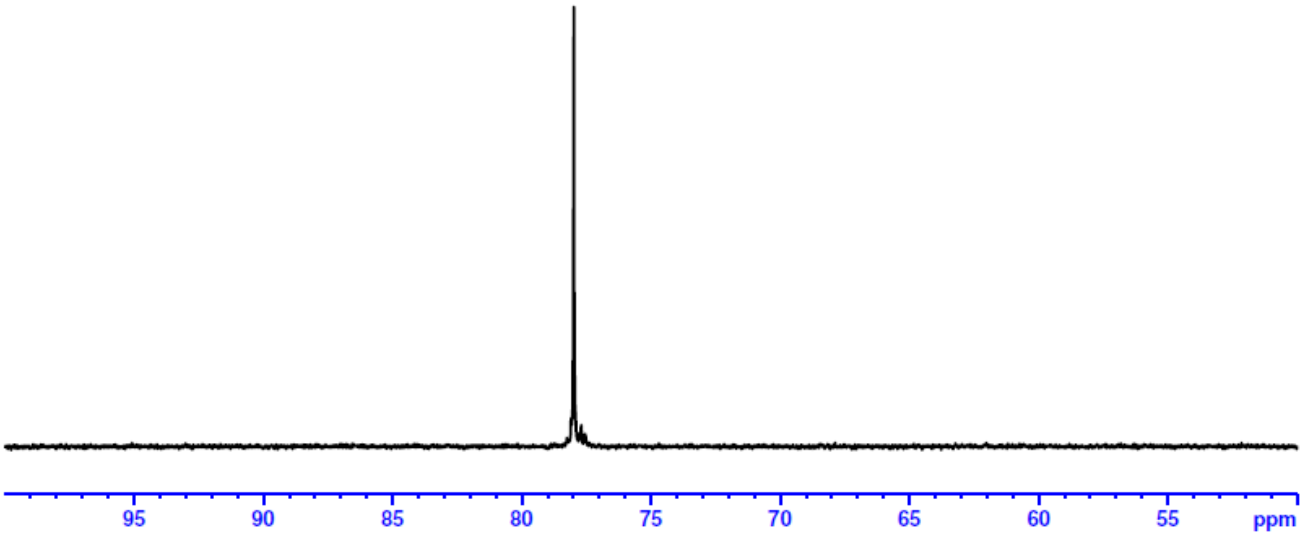


^{1}H NMR (300 MHz, $CDCl_3$)



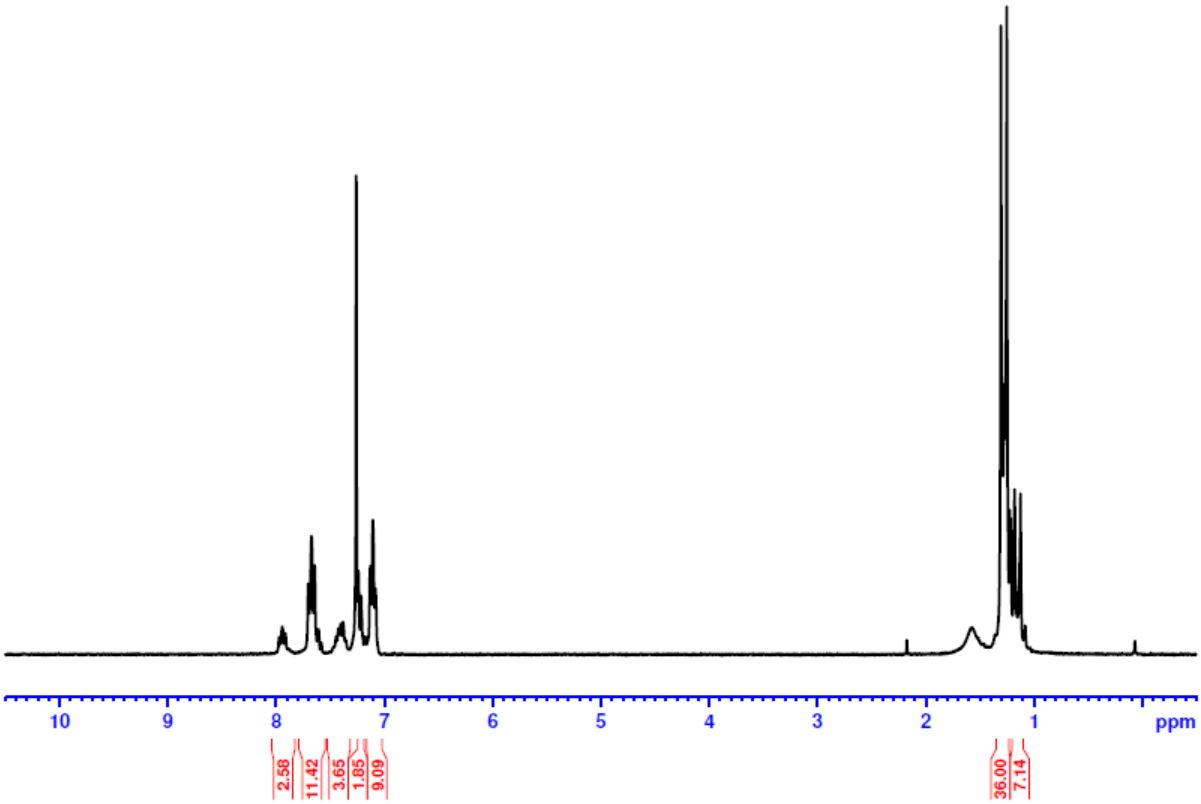
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

Complex **2b** (continued)

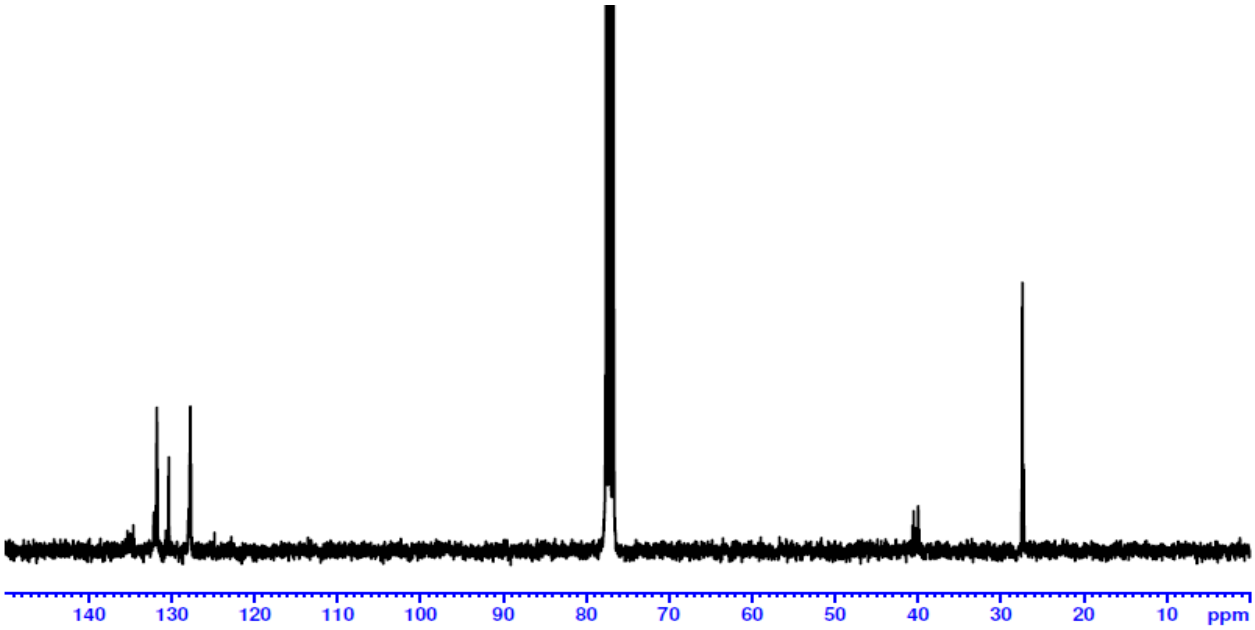


$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

Complex **2c**

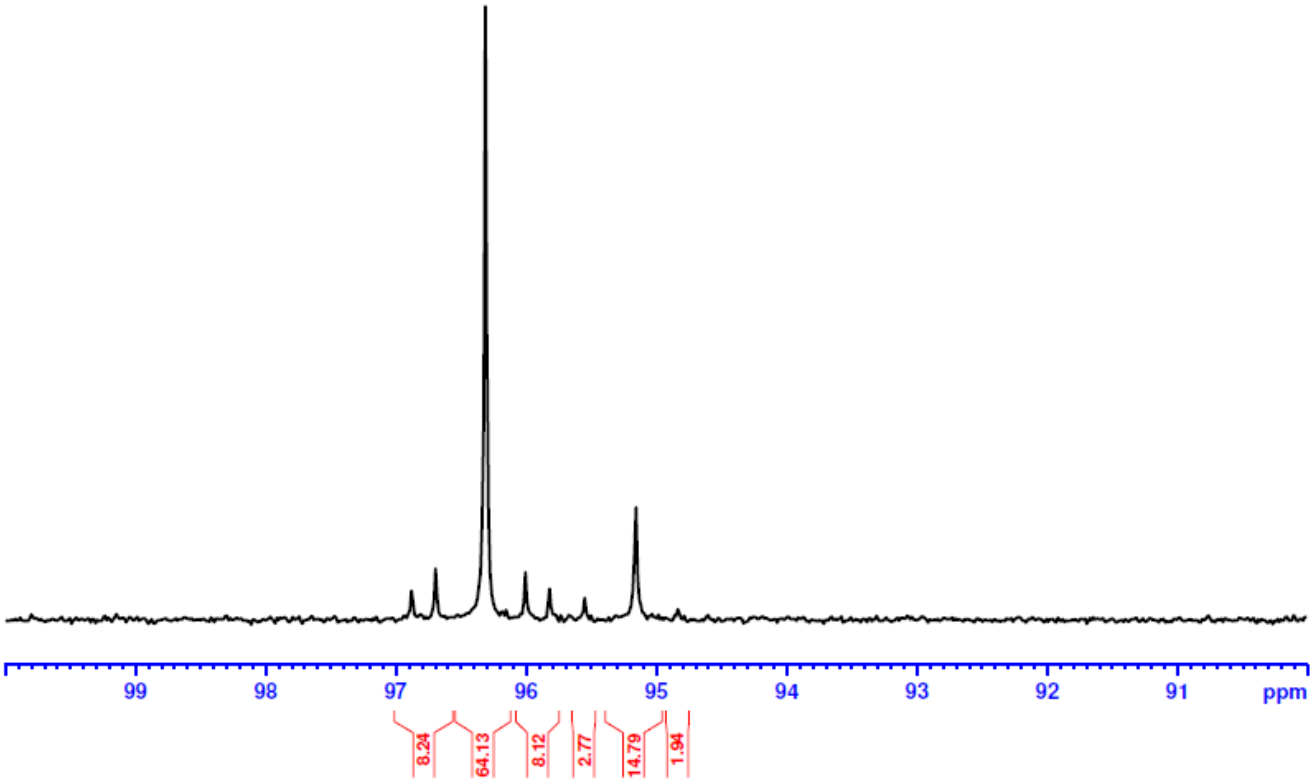


^{1}H NMR (300 MHz, $CDCl_3$)



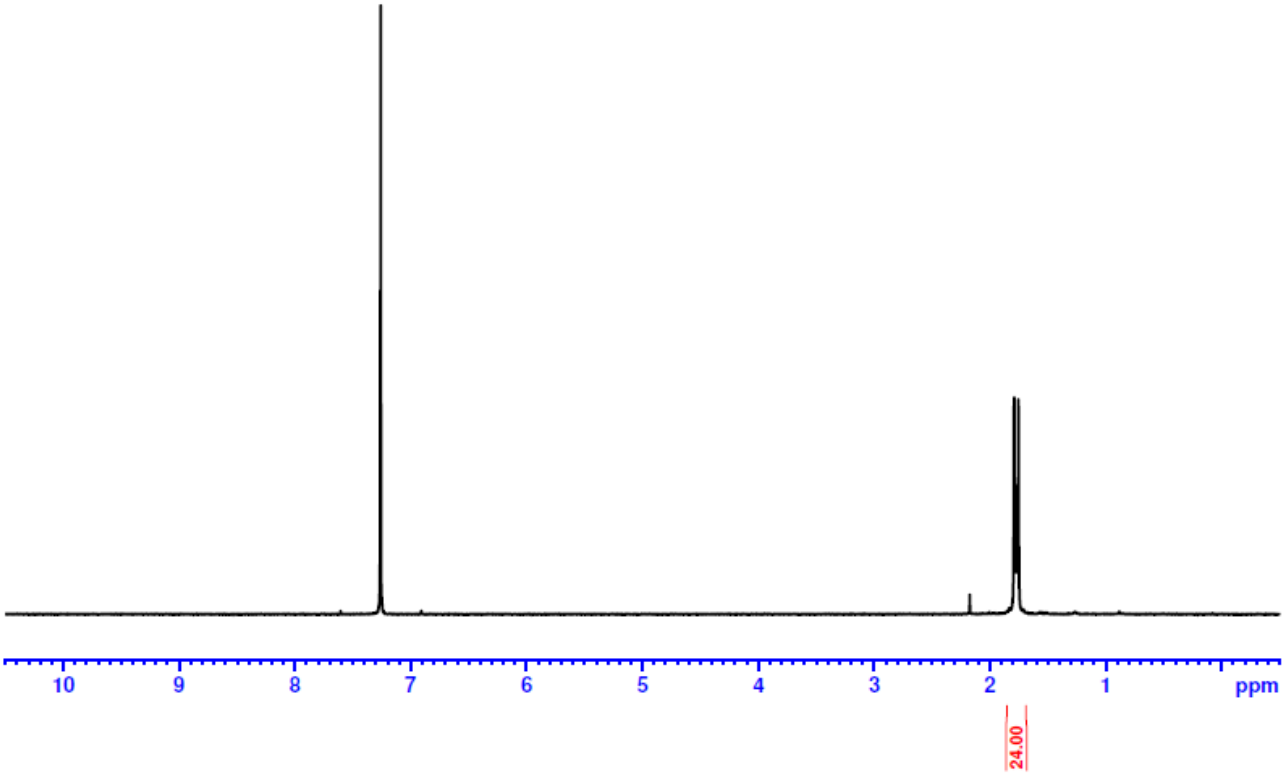
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

Complex **2c** (continued)

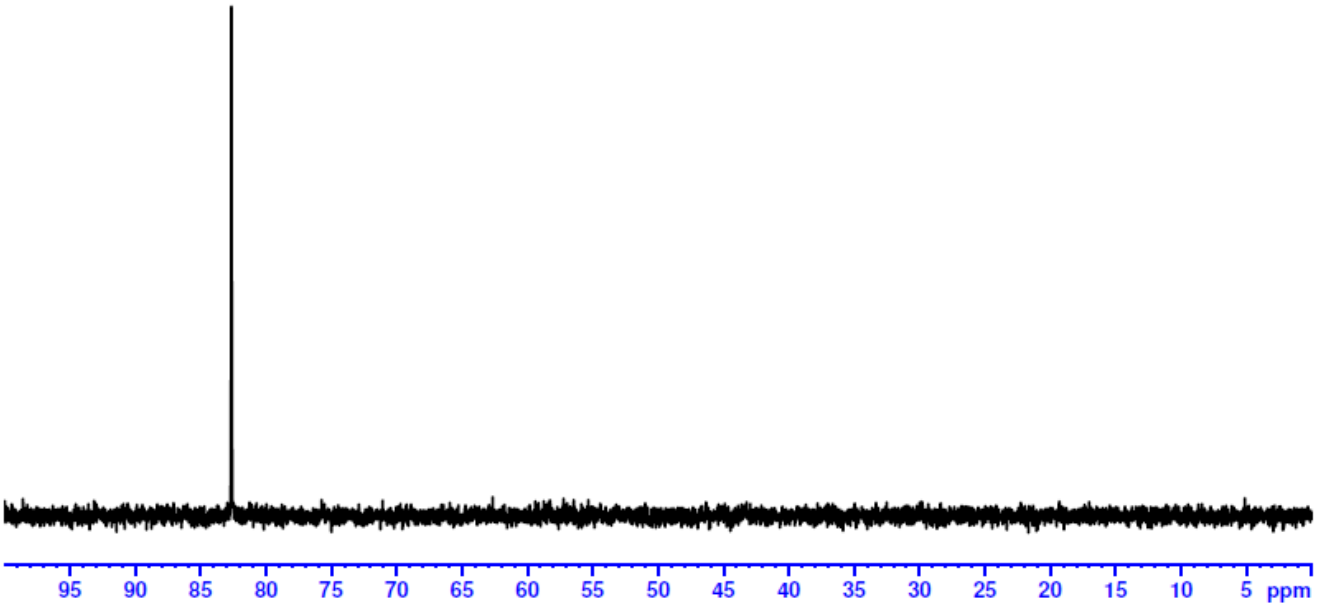


$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

Complex **2d**

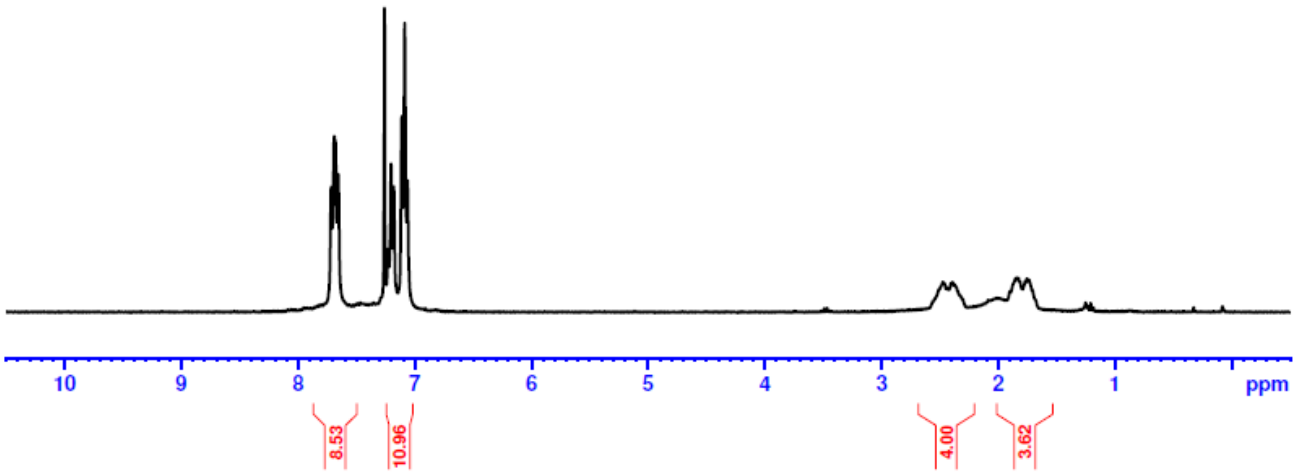


^{1}H NMR (300 MHz, $CDCl_3$)

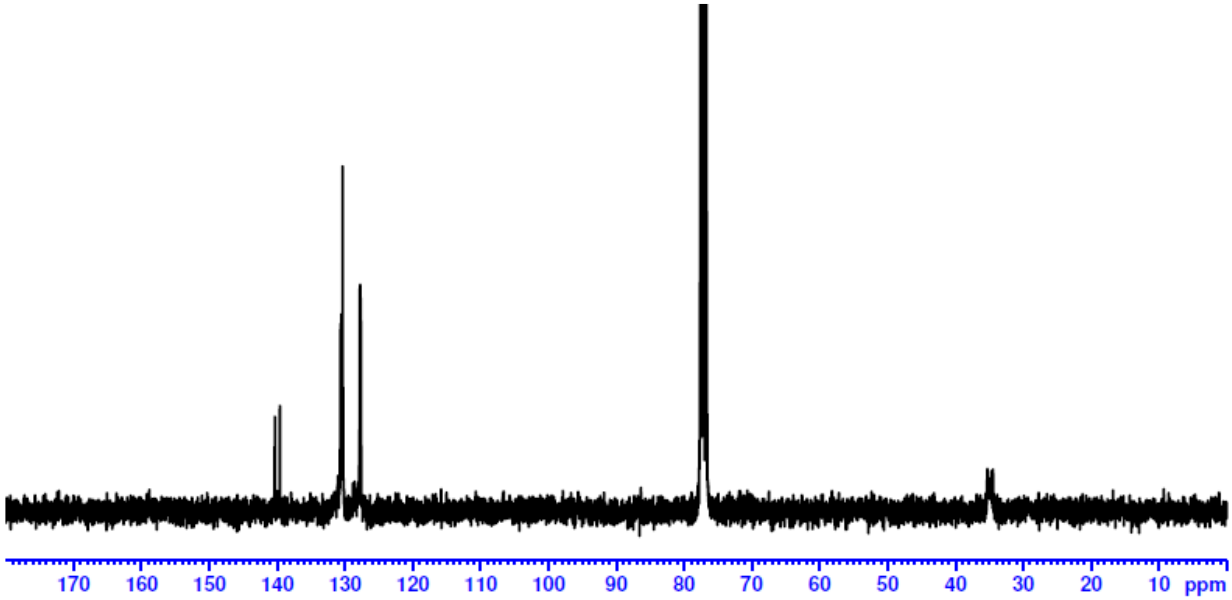


$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

Complex **3**

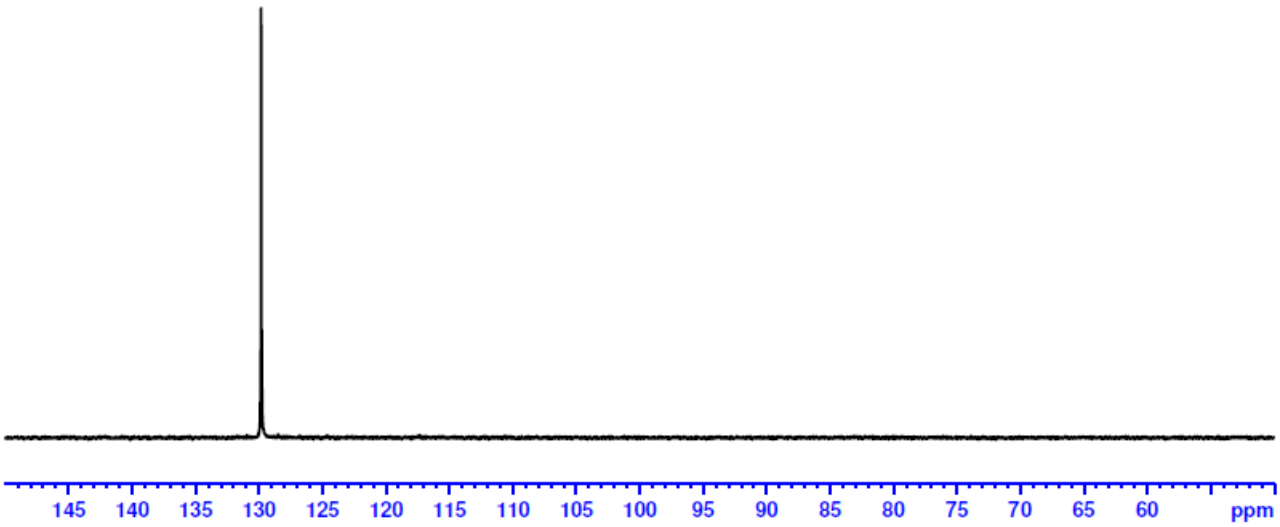


^{1}H NMR (300 MHz, $CDCl_3$)



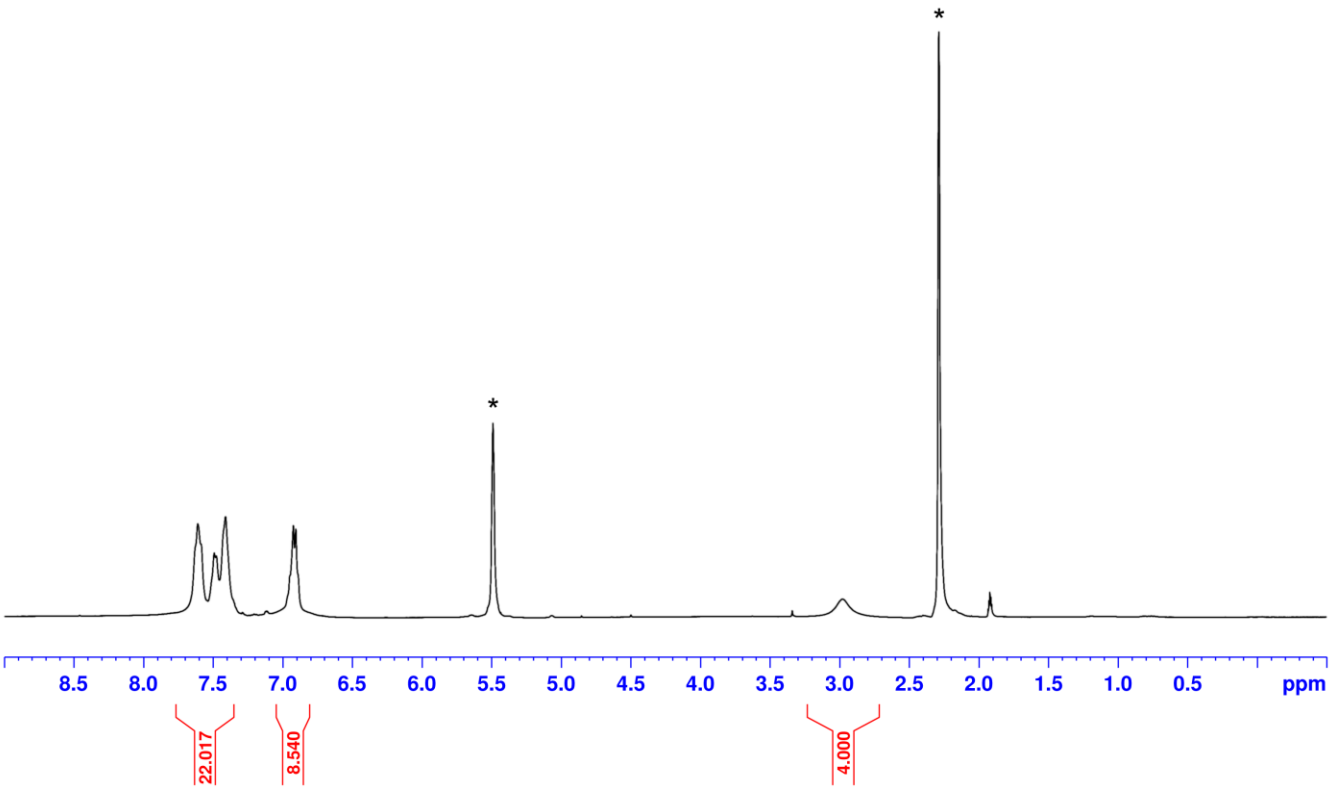
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

Complex **3** (continued)

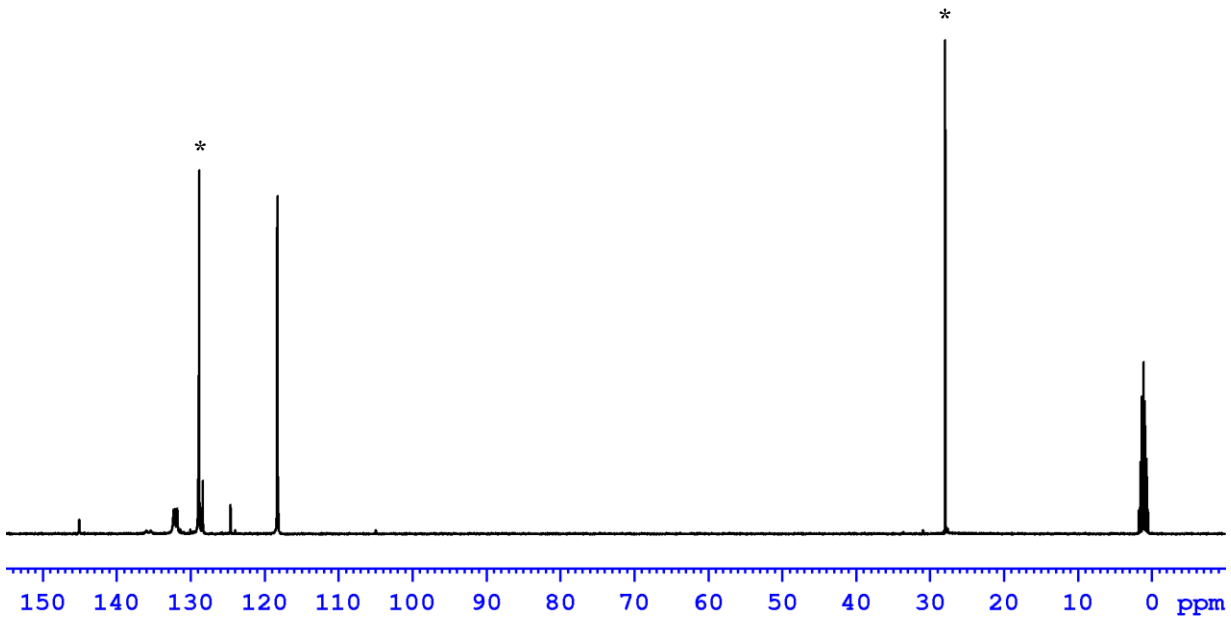


$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

Complex **4a**

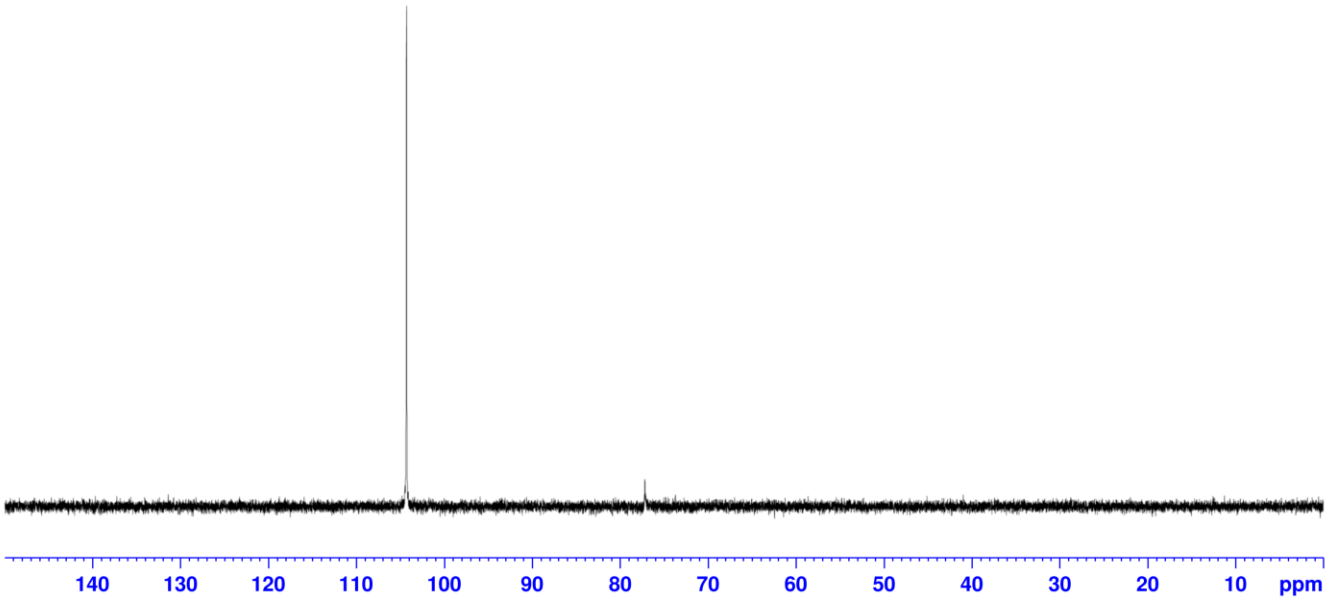


^{1}H NMR (400 MHz, CD_3CN, at -40 °C) (* = free cod)



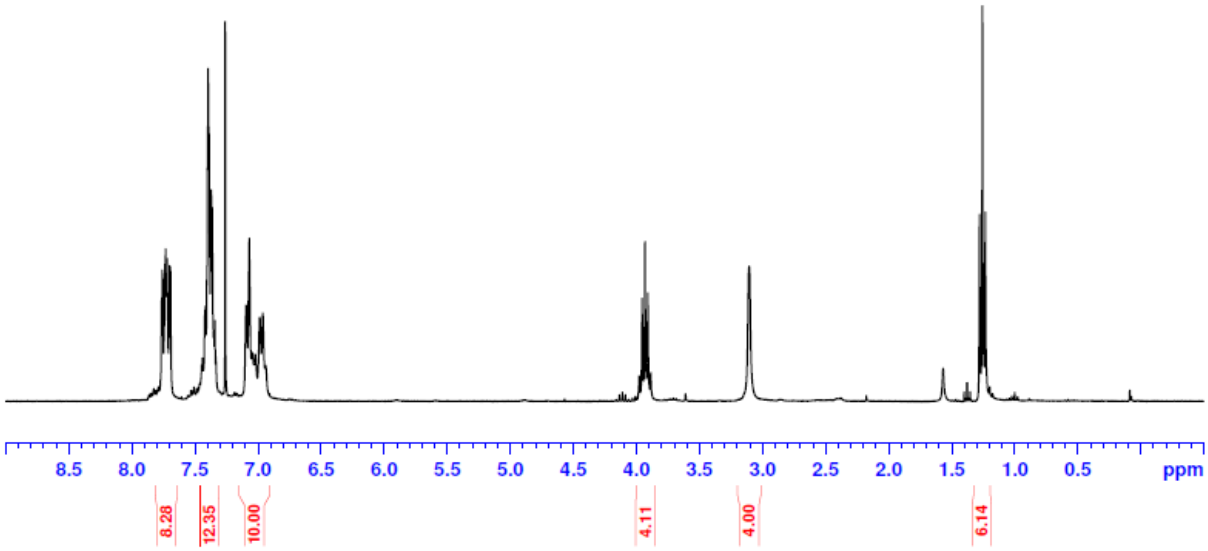
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN, at -40 °C) (* = free cod)

Complex **4a** (continued)

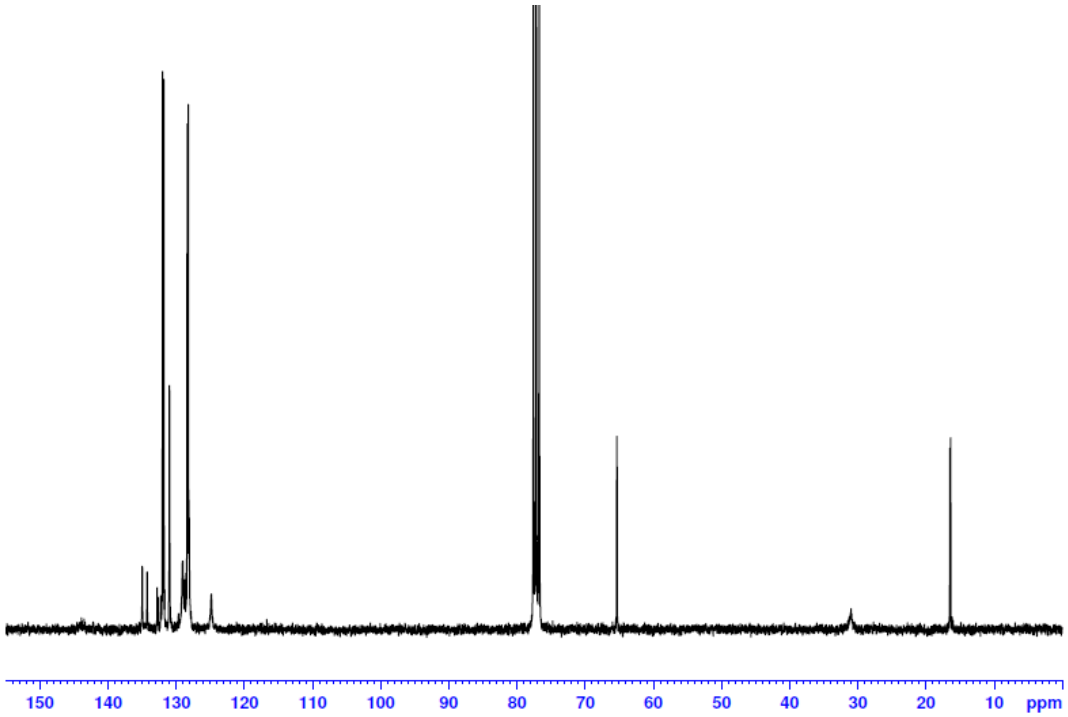


$^{31}P\{^{1}H\}$ NMR (161 MHz, CD_3CN)

Complex **5**

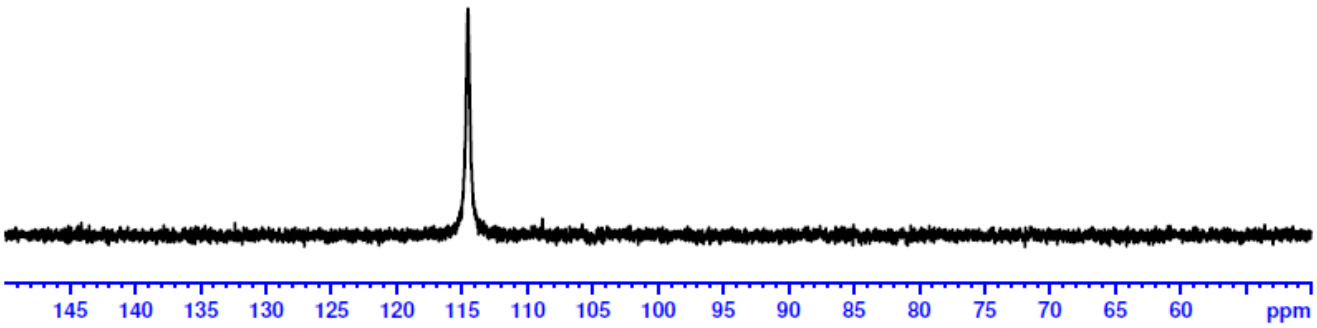


^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

Complex **5** (continued)



$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

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