Aza-metallacycle with a heptavalent Re (d^0) center

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Supporting Information

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1. Experimental details

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were purged with an argon flow before use. Other reagents were used as purchased. $ReOCl_3(PPh_3)_2$,[1] 2-ethynyl-5-methylaniline,[2] and 4-amino-3-ethynylbenzonitrile,[2] were prepared according to literature methods. A Synapt G2-Si was used for high-resolution mass spectroscopy (HRMS). Microanalyses were performed by Element Vario EL. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were collected on a Bruker Avance II (400 MHz) or a Bruker Avance III (500 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4.

Synthesis of complex 1a. A mixture of $ReOCl_3(PPh_3)_2$ (300 mg, 0.36 mmol) and 2-ethynyl aniline (51 mg, 0.43 mmol) in acetone (20 mL) was stirred for 5 hours at room temperature. The product was filtered to give a green solid. The solid was washed with isopropanol (5 mL), methanol (5 mL) and ether (10 mL × 2). Then it was dried under vacuum. Yield: 152 mg, 61%. $^{31}P\{^1H\}$ NMR (162.0 MHz, CDCl$_3$): δ = 9.9. ^1H NMR (400 MHz, CDCl$_3$): δ = 7.88-7.77 (m, 7H, Ph), 7.65 (t, J = 4.0 Hz, 3H, Ph), 7.56-7.52 (m , 6H, Ph), 7.39 (t , J = 8.0 Hz, 1H, Ph), 6.68 (d, J = 8.0 Hz, 1H, Ph), 5.42 (d, J = 24.0 Hz, 1H, P-CH=), 3.88 (s, 2H, NH$_2$). IR (KBr): ν(Re=O) = 987 cm^{-1}. Calcd for $C_{26}H_{22}ONCl_3ReP$, C, 45.39; H, 3.22; N, 2.04. Found: C, 45.09; H, 3.12; N, 1.97.

Synthesis of complex 1b. A mixture of $ReOCl_3(PPh_3)_2$ (300 mg, 0.36 mmol) and 2-ethynyl-5-methylaniline (70 mg, 0.54 mmol) in acetone (20 ml) was stirred for 5 hours at room temperature. The solvent was removed under vacuum to give an oily residue. The residue was treated with tetrahydrofuran (3 mL) and ether (15 mL) to give a brown precipitate, which was collected by filtration and washed with isopropanol (5 mL), methanol (2 mL) and ether (5 mL × 2) to give a green solid. Then it was dried under vacuum. Yield: 111 mg, 45%. $^{31}P\{^1H\}$ NMR (162.0 MHz, CDCl$_3$): δ = 9.9. ^1H NMR (400.1 MHz, CDCl$_3$): δ = 7.82-7.73 (m, 7H, Ph), 7.64 (t, J = 4.0 Hz, 3H, Ph), 7.53-7.51 (m , 6H, Ph), 7.05 (d, J = 12.0 Hz, 1H, Ph), 6.68 (s, 1H, Ph), 5.36 (d, J = 24.0 Hz, 1H, P-CH=), 3.82 (s, 2H, NH$_2$), 2.26 (s, 3H, CH$_3$). $^{13}C\{^1H\}$ NMR (125.0 MHz, CDCl$_3$): δ = 197.4 (d, ^2J(PC)= 16.3 Hz, Re-C), 143.1-121.9(multiple ^{13}C signals of Ar),

100.3 (d, ^1J(PC) = 111.2 Hz), 21.2 (s, CH$_3$). IR (KBr): ν(Re=O) = 992 cm^{-1}. Calcd for C$_{27}$H$_{24}$ONCl$_3$ReP, C, 46.19; H, 3.45; N, 2.00. Found: C, 45.71; H, 3.79; N, 1.83.

Synthesis of complex 2a. Hydrogen peroxide (1wt%, 8.9 mL) was added to the solution of complex **1a** (98 mg, 0.14 mmol) in dichloromethane (10 mL), and the mixture was stirred at room temperature in air for 5 minutes. The organic phase turned red. The mixture was washed with water (15 mL) and the organic layer was collected. The solvent was removed under vacuum to give a reddish oil, which was purified by column chromatography (eluent: dichloromethane/ether = 10/1). The red band was collected and concentrated to ca. 4 ml, and then *n*-hexane (15 ml) was added to give a red solid. The solid was filtered and washed with ether (5 ml x 2). Then it was dried under vacuum. Yield: 50 mg, 58%. ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ = 16.5. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 7.75-7.65 (m, 9H, Ph), 7.58-7.53 (m , 6H, Ph), 7.39 (d, *J* = 8.0 Hz ,1H , Ph), 7.16 (t, *J* = 4.0 Hz, 1H, Ph) 7.15 (d, *J* = 24.0Hz, 1H, P-CH=), 7.05 (br, 1H, NH), 6.62-6.57 (m, 2H, Ph). ^{13}C{^{1}H} NMR (125.0 MHz, CDCl$_3$): δ = 212.3 (br s, Re-C), 160.4-115.8 (multiple ^{13}C signals of Ar), 107.3 (d, ^1J(PC) = 108.7 Hz, P-C). IR (KBr): ν(Re=O) = 911, 938 cm^{-1}. HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{26}$H$_{22}$O$_3$ReP, 614.0896; Found, 614.0890.

Synthesis of complex 2b. Hydrogen peroxide (1wt%, 9 mL) was added to the solution of complex **1b** (100 mg, 0.16 mmol) in dichloromethane (10 mL), and the mixture was stirred at room temperature in air for 5 minutes. The organic phase turned red. The mixture was washed with water (15 mL) and the organic layer was collected. The solvent was removed under vacuum to give a reddish oil, which was purified by column chromatography (eluent: dichloromethane/ether = 10/1). The red band was collected and concentrated to ca. 2 ml, then *n*-hexane (10 ml) was added to give a red solid. The solid was filtered and washed with ether (5 ml x 2). Then it was dried under vacuum. Yield: 58 mg, 64%. ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ = 16.4. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 7.75-7.64 (m, 9H, Ph), 7.57-7.52 (m , 6H, Ph), 7.28 (d, *J* = 8.0 Hz ,1H , Ph), 7.06 (d, *J* = 28.0 Hz, 1H, P-CH=), 7.03 (br, 1H, NH), 6.46-6.40 (m, 2H, Ph), 2.25 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (125.0 MHz, CDCl$_3$): δ = 212.3 (d, ^2J(PC) = 16.2 Hz, Re-C), 160.7-116.0 (multiple ^{13}C signals of Ar), 105.4 (d, ^1J(PC) = 110.0

Hz, P-C), 21.8 (s, CH$_3$). IR (KBr): ν(Re=O) = 903, 936 cm^{-1}. HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{27}$H$_{24}$O$_3$ReP, 628.1052; found, 628.1046.

Synthesis of complex 2c. A mixture of ReOCl$_3$(PPh$_3$)$_2$ (300 mg, 0.36 mmol) and 4-amino-3-ethynylbenzonitrile (62 mg, 0.43 mmol) in acetone (15 ml) was stirred at 60 °C for 2 hours. The solvent was removed vacuum to give an oily residue. The residue was treated with tetrahydrofuran (3 mL) and ether (15 mL) to give a brown precipitate, which was collected by filtration and washed with ether (5 mL × 2). Then it was dried under vacuum to give a brown solid. The brown solid (157 mg) was dissolved in dichloromethane (10 mL), and hydrogen peroxide (1wt%, 4.5 mL) was added and the mixture was stirred at room temperature in air for 5 minutes. The organic phase turned red. The mixture was washed with water (15 mL) and the organic layer was collected. The solvent was removed under vacuum to give a reddish oil, which was purified by column chromatography (eluent: dichloromethane/ether = 10/1). The red band was collected and concentrated to ca. 2 ml, then n-hexane (10 ml) was added to give a red solid. The solid was filtered and washed with ether (5 ml x 2). Then it was dried under vacuum. Yield: 63 mg, 27%. ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ = 16.8. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 7.74-7.64 (m, 9H, Ph), 7.62-7.57 (m, 7H, Ph), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 4 Hz, 1H, Ph), 7.23 (d, J = 28.0 Hz, 1H, P-CH=), 7.08 (br, 1H, NH), 6.60 (d, J = 8.0 Hz, Ph). IR (KBr): ν(Re=O) = 904, 949 cm^{-1}. HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{27}$H$_{21}$O$_3$ReP, 639.0848; found, 639.0845.

2. Computational details

The optimizations were performed with the Gaussian 16 software package.[3] The structures evaluated were optimized at the B3LYP level of density functional theory (DFT).[4] The def2-TZVP basis set had been used for Re atom,[5] while 6-311G(2d,p) basis set had been used for the rest of the atoms.[6] Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO//6-311G(2d,p)/def2-TZVP level.[7] The anisotropy of the current density was calculated with the AICD 2.0 program computing the NMR properties using the CSGT method with the Gaussian16 with the geometry previously obtained.[8] GIMIC analysis was finished by GIMIC code [9] based on the formatted checkpoint file of Gaussian.
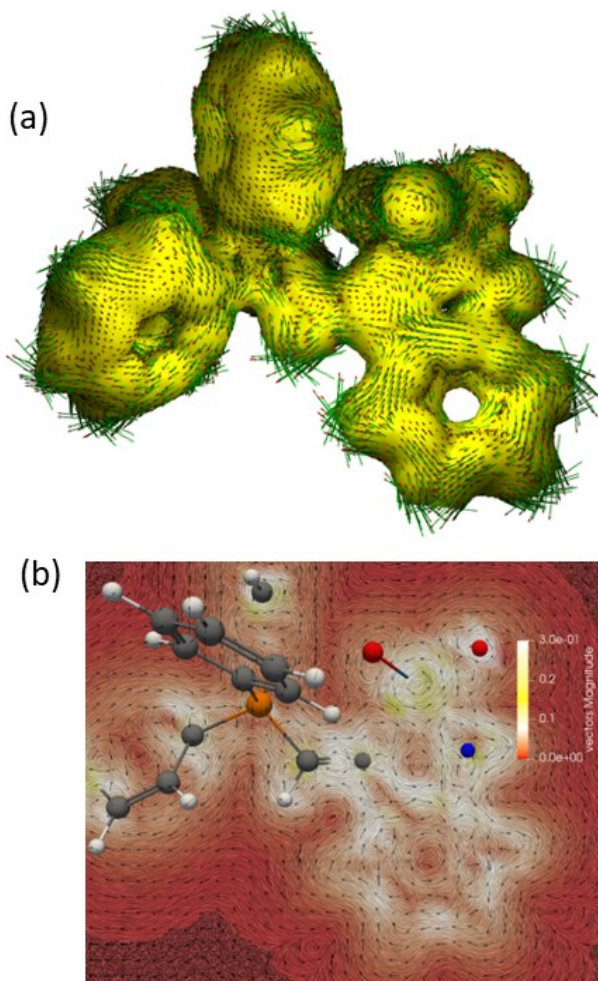
Figure S1. (a) AICD surface of all orbital contributions of **2a** with isovalue of 0.012 a.u. The GIMIC map of **2a**, plotted at the five-membered rhenacycle plane. The magnetic field vector is orthogonal with respect to the ring plane and points upward.

3. X-ray crystallographic study

Single crystals of **1b** (CCDC No. 2348545), and **2a** (CCDC No. 2348544) suitable for X-ray diffraction were grown from CH_2Cl_2 solution layered with ether. Intensity data were collected on a Bruker Smart APEXII diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Diffraction data were processed using the CrysAlisPro software (version 1.171.35.19). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all compounds were performed using the Olex2 software package (which embedded SHELXL).[10,11] All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except noted separately.

Table S1. Crystallographic data and refinement details for complexes **1b**, **2a**.

	1b	2a
Empirical formula	$C_{27}Cl_3H_{24}NOPRe \cdot 1.5CH_2Cl_2$	$C_{26}H_{21}NO_3PRe$
Color & habit	green, block	red, block
Crystal size (mm³)	0.15 x 0.12 x 0.10	0.12 x 0.09 x 0.08
Temperature (K)	150 K	296 K
Crystal system	monoclinic	triclinic
Space group	*P2₁/n*	*P-1*
a(Å)	10.4425(6)	9.3616(11)
b(Å)	22.9633(12)	10.5556(12)
c(Å)	14.0700(8)	12.6536(15)
α	90	105.445(2)
β	109.990(2)	95.230(2)
γ	90	103.571(2)
V(Å³), Z	3170.6(3), 4	1155.7(2), 2
D_{cal} (Mg/m³)	1.737	1.760
Abs. coeff. (mm⁻¹)	4.412	5.354
2θ range for data collection (°)	4.514 to 50.046	3.386 to 54.866
Reflections collected	54895	7635
Indep. Reflection, R(int)	5588, 0.0978	5125, 0.0227
Data/ restraints / parameters	5588/93/308	5125/0/289
Goodness-of-fit on F^2	1.125	1.014
R1 [I>2sigma(I)], wR2	0.0448, 0.0923	0.0222, 0.0586
R1 (all data), wR2	0.0595, 0.0993	0.0245, 0.0601
Largest diff. peak and hole (e·Å⁻³)	0.64, -1.88	1.09, -1.01

*$R1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |Fc|^2)/\Sigma|w(F_o^2)^2|^{1/2}$, $[F_o > \sigma(F_o)]$

4. NMR spectra

CDCl₃

H₂O
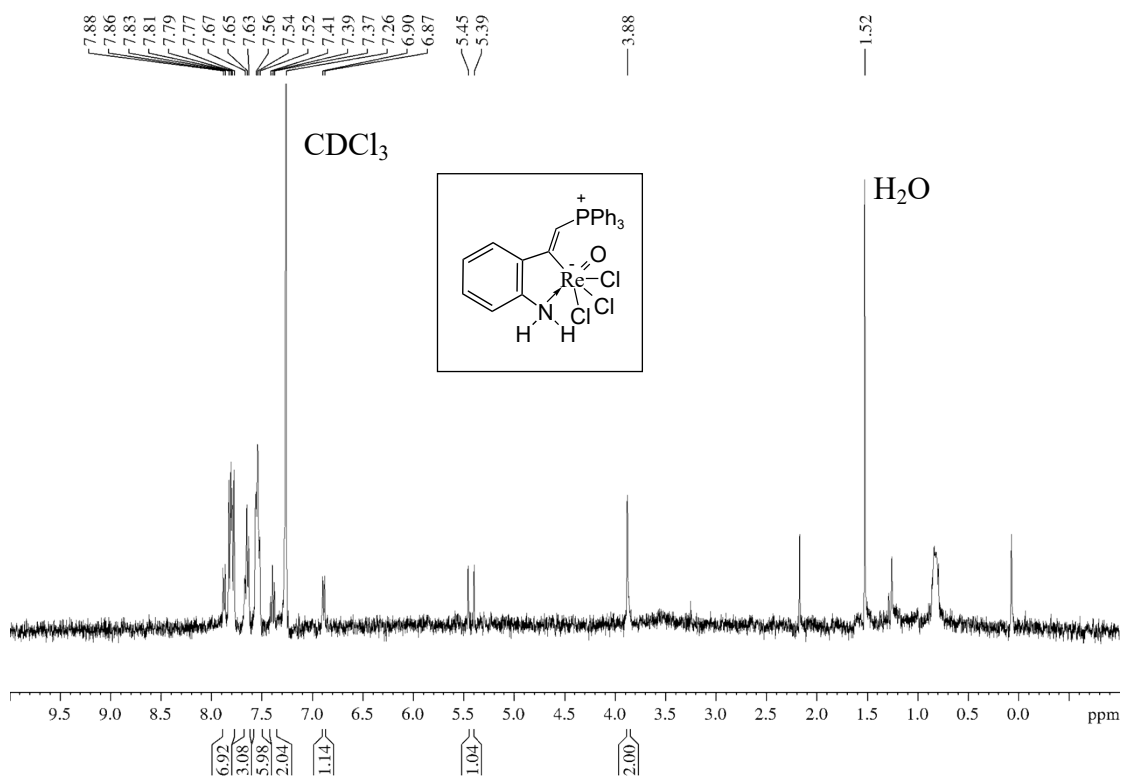
Figure S2. The ^{1}H NMR spectrum of complex **1a** in CDCl₃ at 400.1 MHz.
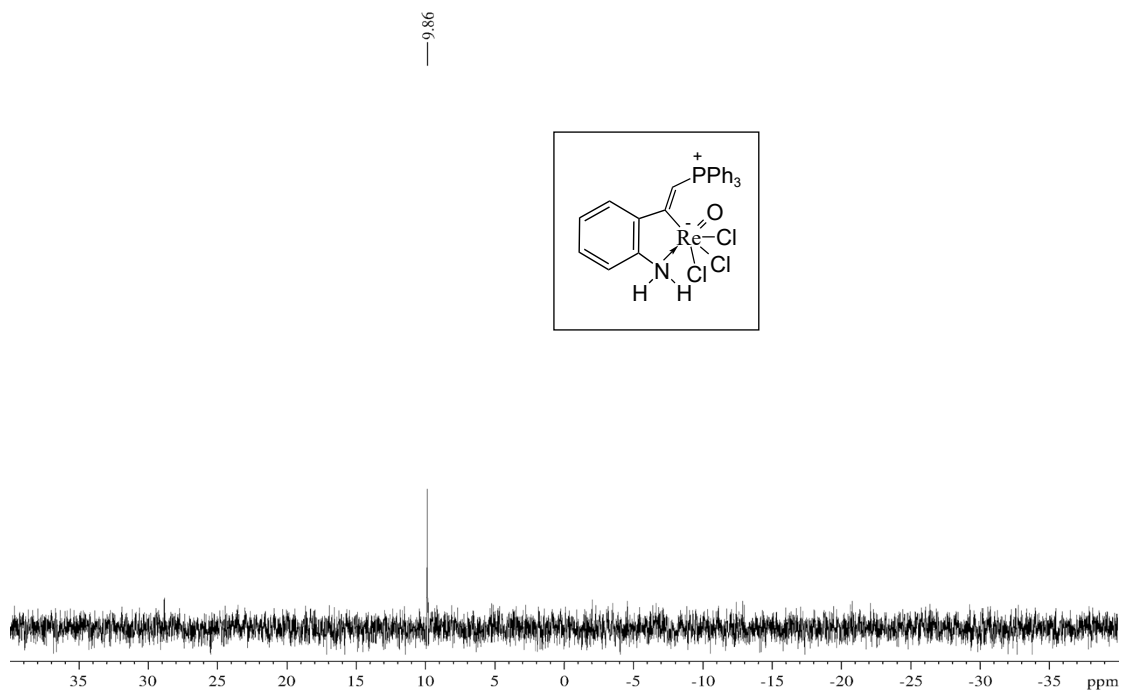
Figure S3. The ^{31}P{^{1}H} NMR spectrum of complex **1a** in CDCl₃ at at 162.0 MHz.
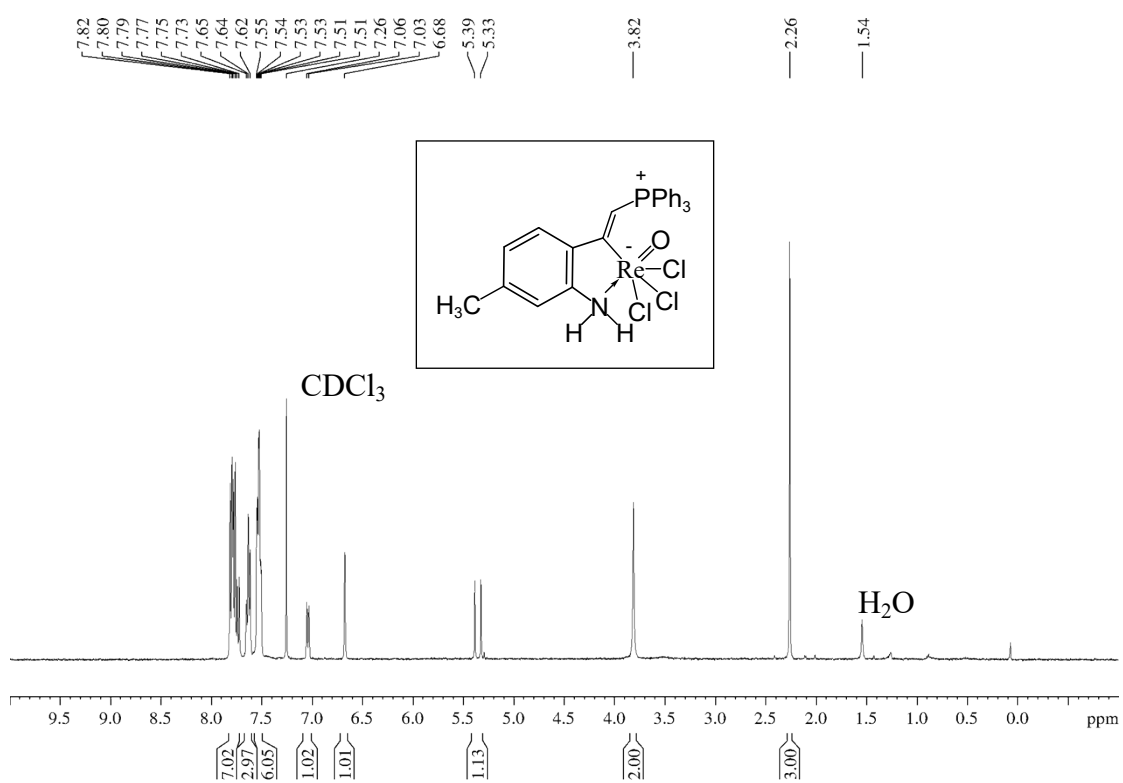
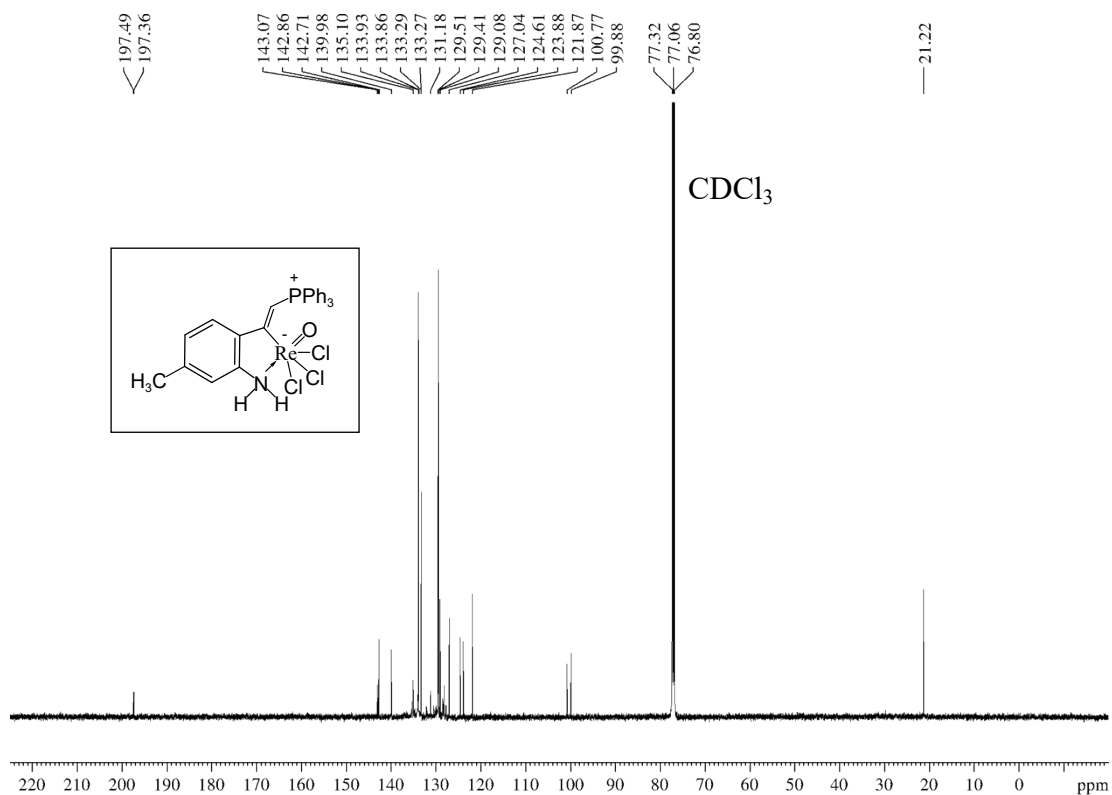***Figure S4.*** The ¹H NMR spectrum of complex **1b** in CDCl₃ at 400.1 MHz.
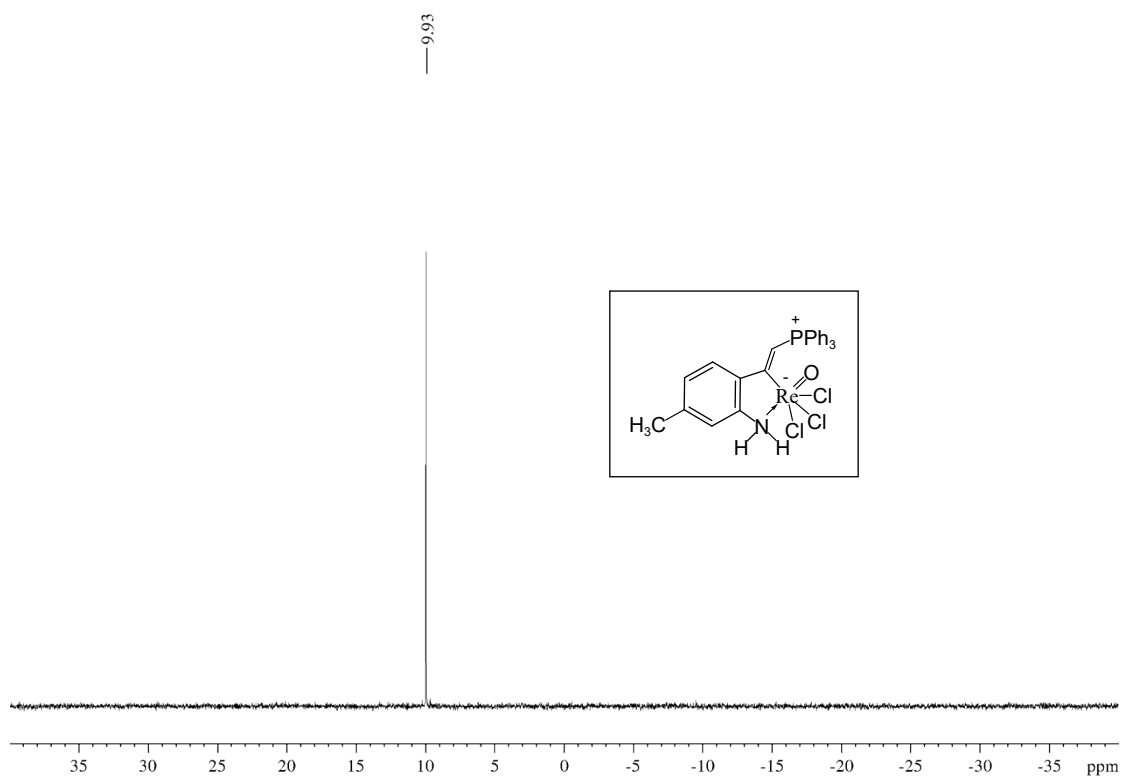
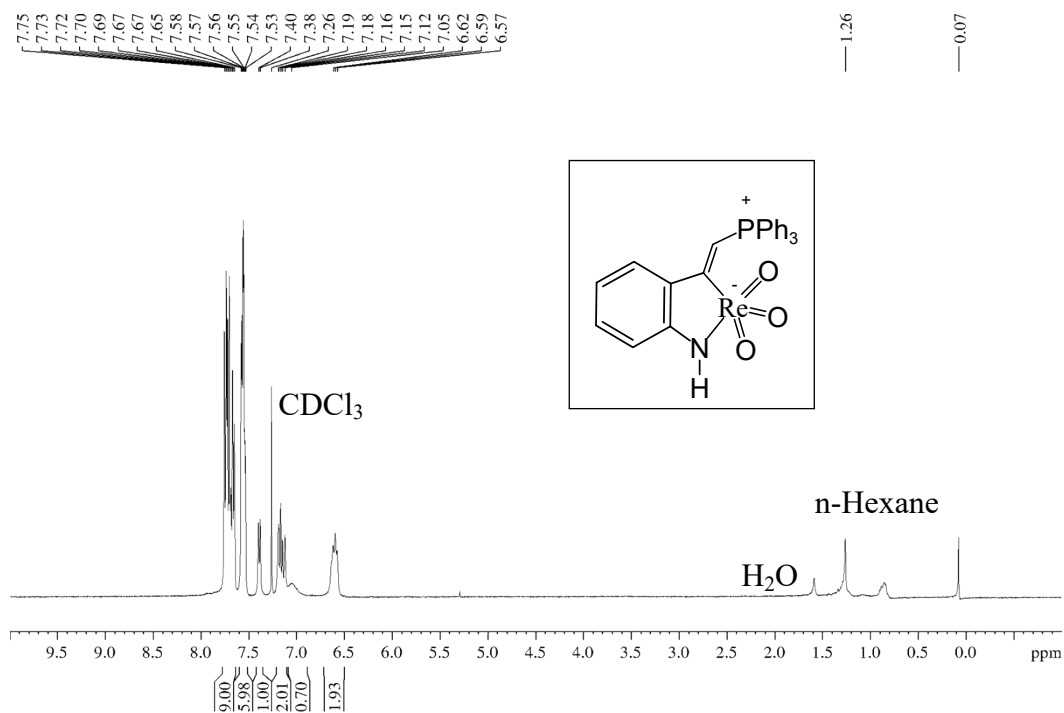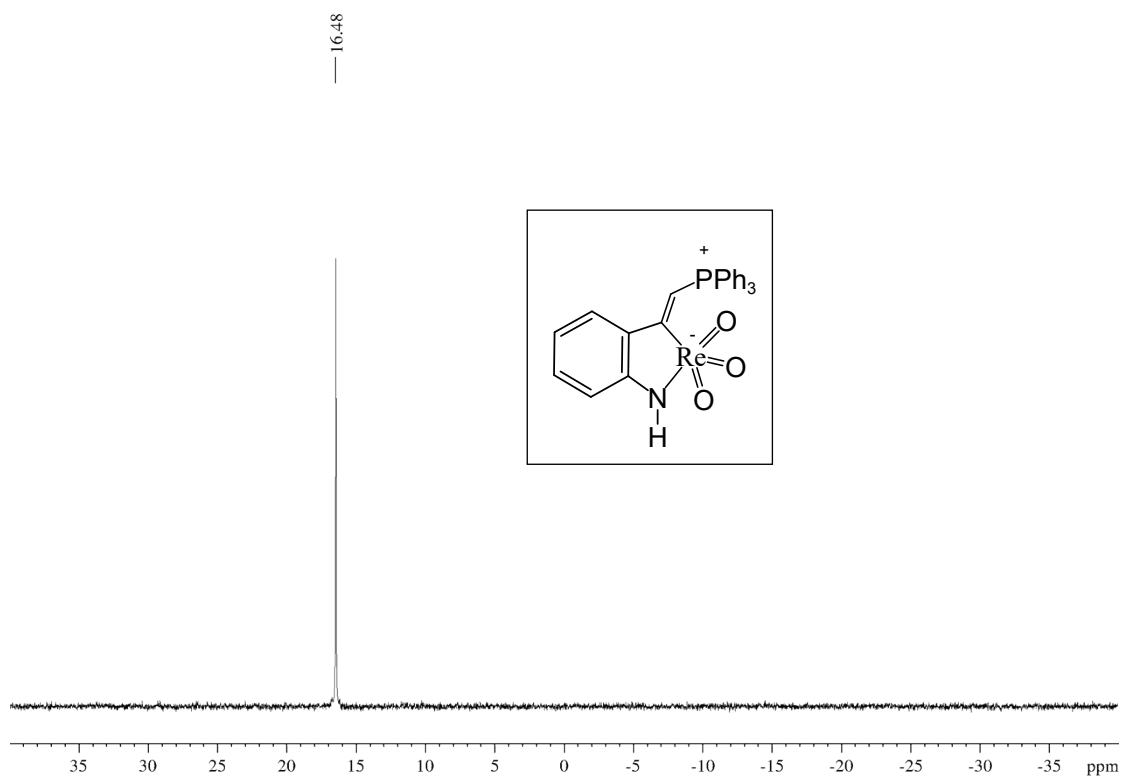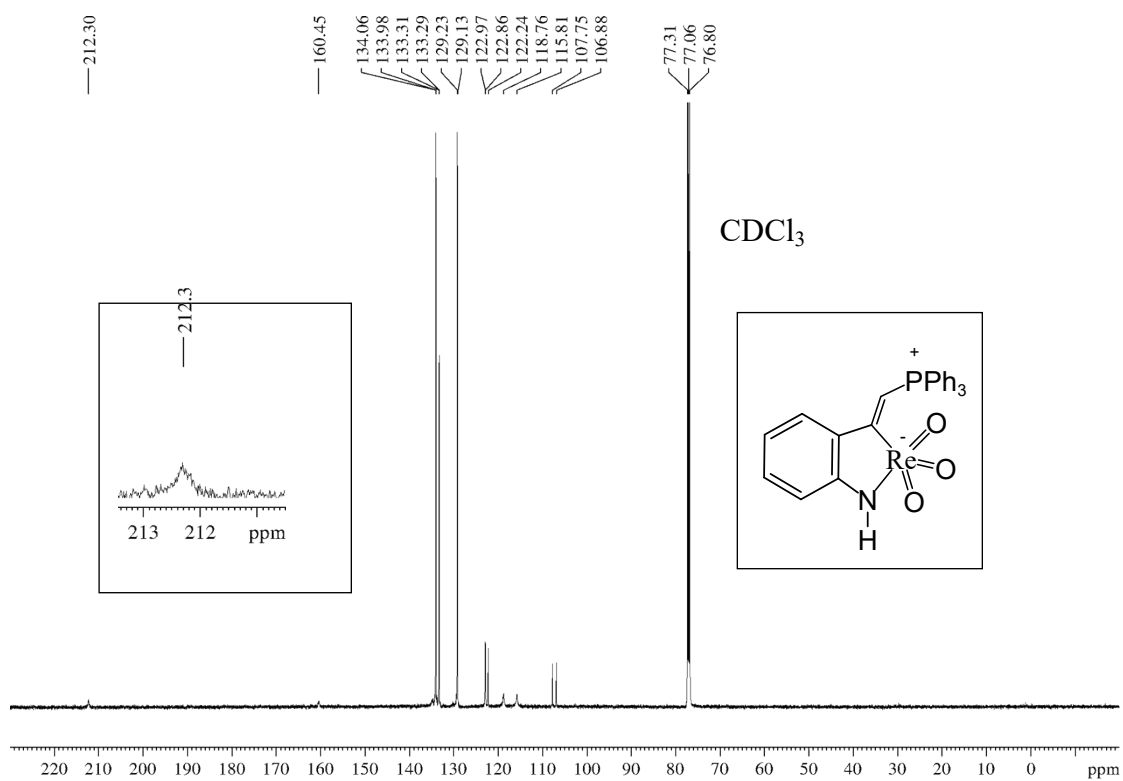***Figure S5.*** The ³¹P{¹H} NMR spectrum of complex **1b** in CDCl₃ at at 162.0 MHz.

Figure S6. The $^{13}C\{^1H\}$ NMR spectrum of complex **1b** in CDCl$_3$ at 125.0 MHz.

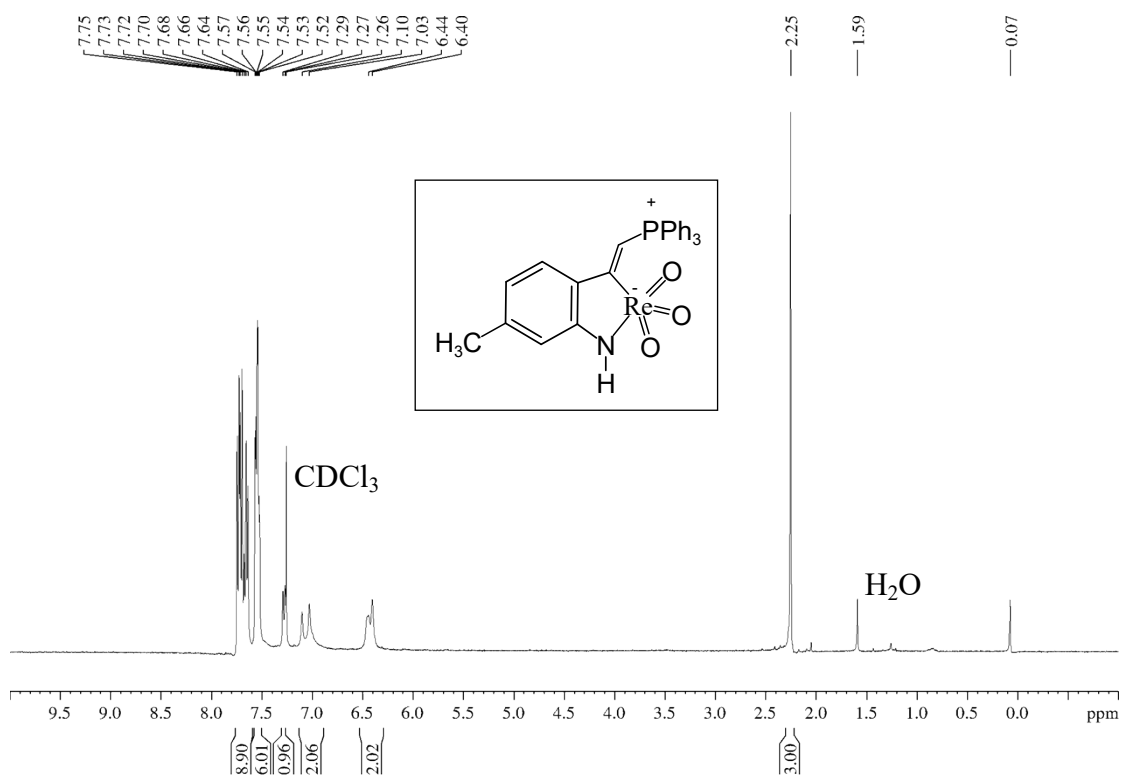***Figure S7.*** The ^1H NMR spectrum of complex **2a** in CDCl$_3$ at 400.1 MHz.

16.48

Figure S8. The $^{31}P\{^1H\}$ NMR spectrum of complex **2a** in CDCl$_3$ at at 162.0 MHz.

212.30

160.45
134.06
133.98
133.31
133.29
129.23
129.13
122.97
122.86
122.24
118.76
115.81
107.75
106.88

77.31
77.06
76.80

CDCl$_3$

212.3

213 212 ppm

Figure S9. The $^{13}C\{^1H\}$ NMR spectrum of complex **2a** in CDCl$_3$ at 125.0 MHz.

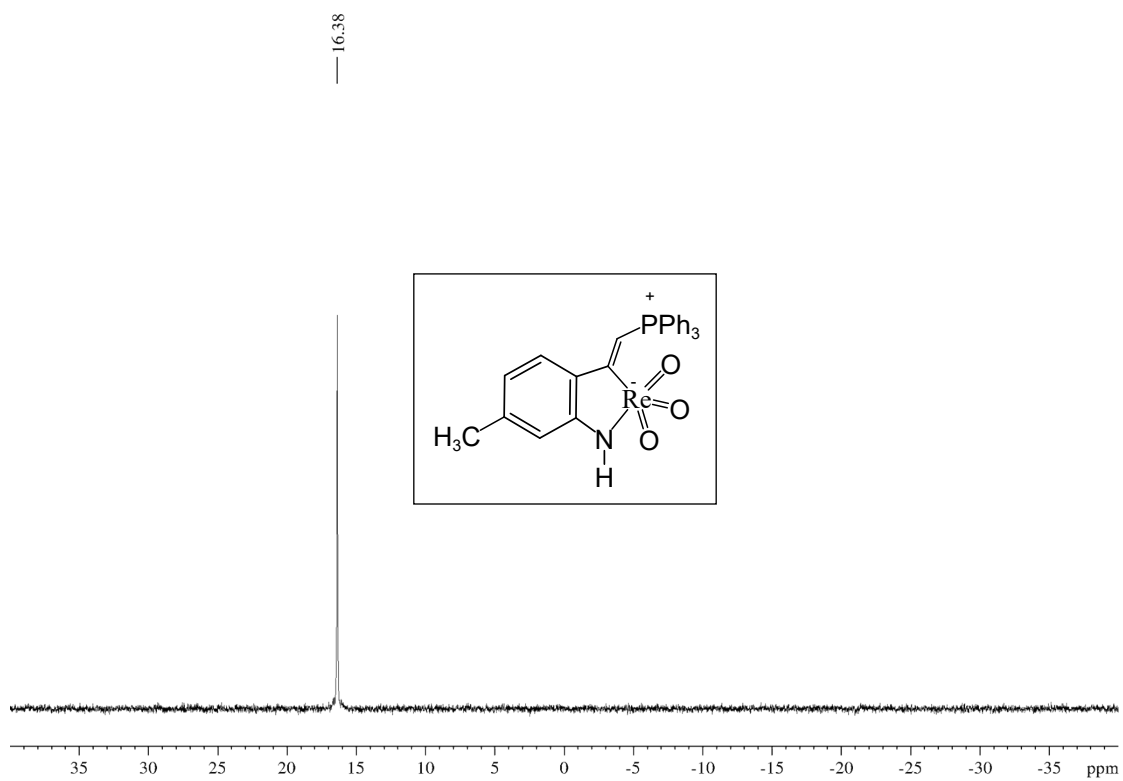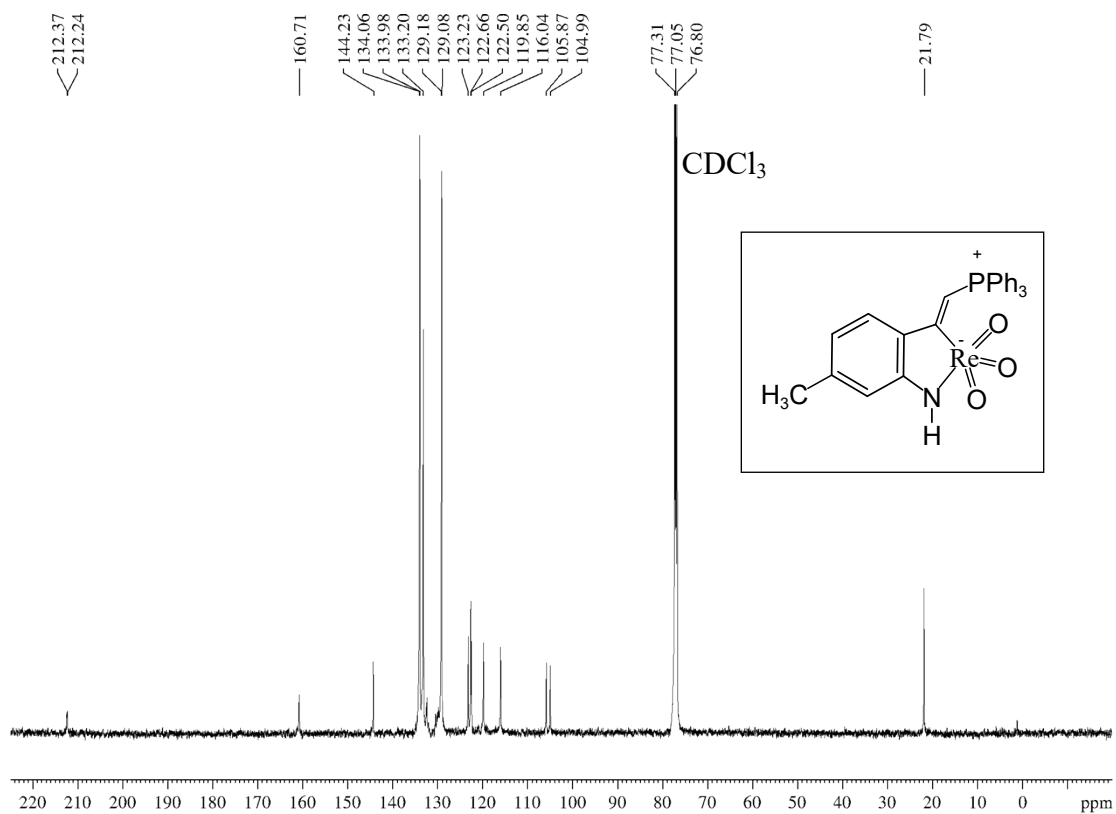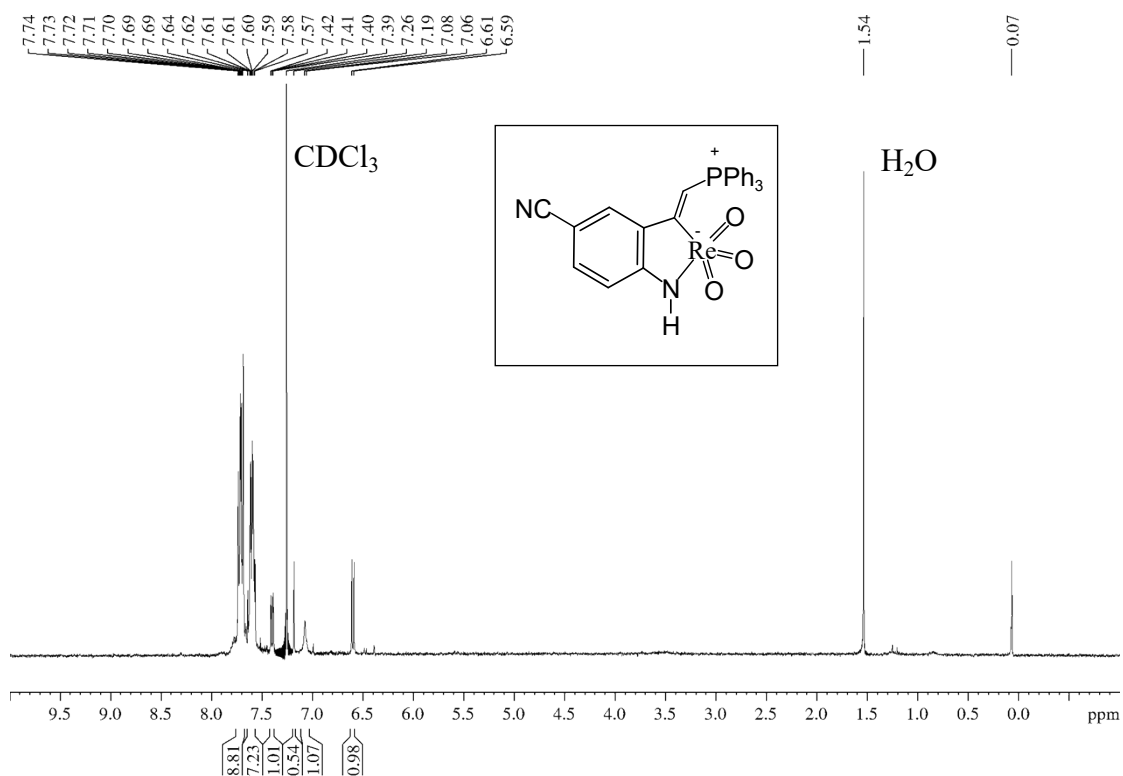*Figure S10.* The ^{1}H NMR spectrum of complex **2b** in CDCl$_3$ at 400.1 MHz.

Figure S11. The ^{31}P{^{1}H} NMR spectrum of complex **2b** in CDCl$_3$ at at 162.0 MHz.

Figure S12. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **2b** in CDCl$_3$ at 125.0 MHz.

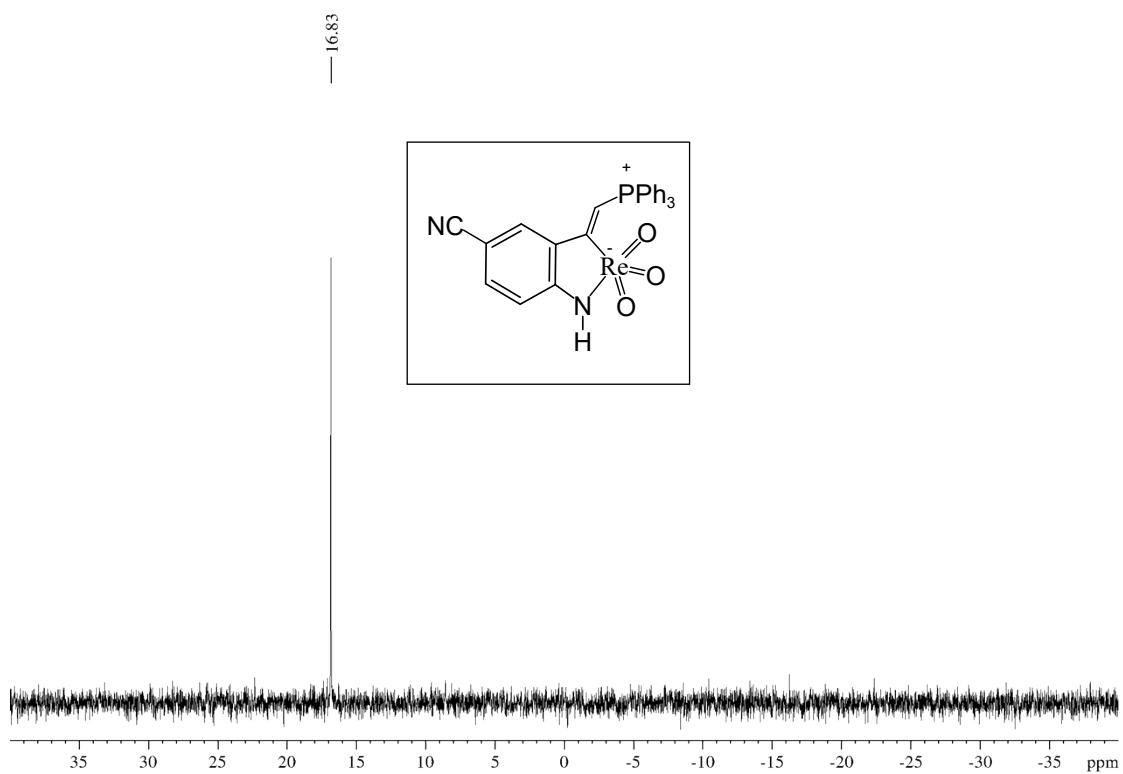*Figure S13.* The ^{1}H NMR spectrum of complex **2c** in CDCl$_3$ at 400.1 MHz.

16.83

Figure S14. The $^{31}P\{^1H\}$ NMR spectrum of complex **2c** in CDCl$_3$ at at 162.0 MHz.

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