Supplementary Information

Direct Amidation of Metallaaromatics: Access to N-functionalized Osmapentalynes *via* a 1,5-Bromoamidated Intermediate

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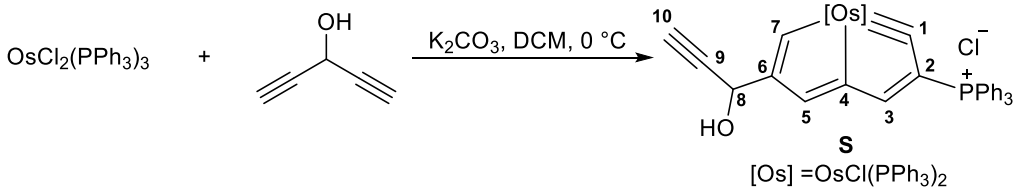
1. General Information

Unless stated otherwise, all syntheses and manipulations were carried out under an atmosphere of high purity argon using Schlenk line techniques or a glove box. All solvents were dried over sodium/benzophenone (*n*-hexane and diethyl ether) or calcium hydride (dichloromethane) and distilled under N_2 prior to use. Column chromatography was performed using silica gel (200–300 mesh) or aluminum oxide (200-300 mesh) in air. NMR spectra was recorded at 298K using a Bruker Advance III 500 spectrometer (^{31}P, 202.5 MHz; ^{1}H, 500.2 MHz; ^{13}C, 125.8 MHz;) or a Bruker Ascend III 600 spectrometer (^{31}P, 242.9 MHz; ^{1}H, 600.1 MHz; ^{13}C, 150.9 MHz;). The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) were measured relative to tetramethylsilane, and the ^{31}P{^{1}H} NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in hertz (Hz). Assignments of signals in ^{1}H and ^{13}C NMR spectra was done by reference to heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), and distortionless enhancement by polarization transfer (DEPT) NMR spectra. Multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Elemental analyses were performed on a Vario EL III elemental analyzer. High-resolution mass spectrometry (HRMS) was conducted using a Bruker En Apex-Ultra 7.0 T FT-MS instrument (**S**, **1**, **2a-2g**, **3a**, **3b**, **C**, **5**) and Agilent 1290-6545XT (**4a**, **6**). The theoretical molecular ion peak of **S**, **1**, **2a-2g**, **3a**, **3b**, **C** and **5** was accurately calculated from the Compass Isotope Pattern software supplied by Bruker company. The theoretical molecular ion peak of **4a** and **6** was acquired with Mass Hunter Qualitative Analysis software from Agilent. Absorption spectra were recorded on a Shimadzu UV2550 UV–Vis spectrophotometer.

2. Synthesis and characterization

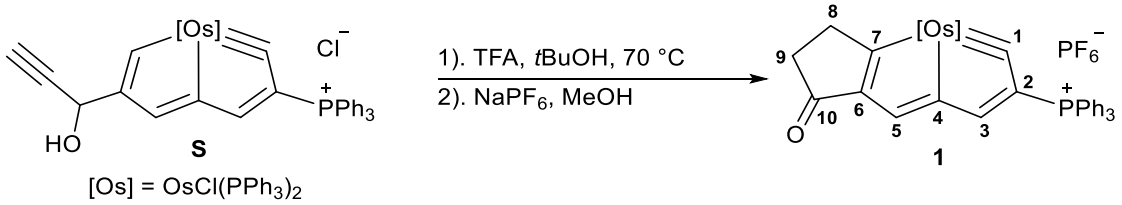
Preparation of complex S:



A mixture of $OsCl_2(PPh_3)_3$ (209.6 mg, 0.20 mmol) and K_2CO_3 (137.9 mg, 1.0 mmol) was dissolved in dichloromethane (10.0 mL) and cooled to 0 °C. Then the dichloromethane (2.0 mL) solution of penta-1,4-diyn-3-ol (32.0 mg 0.40 mmol) was slowly added to the mixture over a period of 5 min by syringe. The reaction mixture was stirred for 4 hours at 0 °C to give a yellow solution. The solution was filtered, and filtrate was evaporated under vacuum to a volume of ca. 1.0 mL. The crude product was purified by column chromatography (neutral alumina, eluent: dichloromethane/ methanol = 20:1) to yield a bright yellow solid complex **S** (204.7 mg, 0.17 mmol, 86%).

^{1}H NMR plus ^{1}H-^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ (ppm) = 13.73 (s, 1H, H7), 9.26 (d, *J*(P-H) = 1.7 Hz, 1H, H5), 7.91 (s, 1H, H3), 5.31 (s, 1H, H8), 4.87 (br, 1H, O*H*), 2.29 (d, *J*(H-H) = 2.1 Hz, 1H, H10), 7.85–7.00 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 5.80 (t, *J*(P-P) = 5.1 Hz, C*P*Ph_3), 3.02 (dd, *J*(P-P) = 282.3, *J*(P-P) =4.5 Hz, Os*P*Ph_3), 1.61 (dd, *J*(P-P) = 282.4, *J*(P-P) = 5.4 Hz, Os*P*Ph_3). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm)= 320.7 (q, *J*(P-C) = 13.5 Hz, C1), 221.3 (q, *J*(P-C) = 10.8 Hz, C7), 182.2 (d, *J*(P-C) = 23.4 Hz, C4), 166.7 (s, C6), 155.8 (s, C5), 152.1 (d, *J*(P-C) = 16.2 Hz, C3), 129.8 (d, *J*(P-C) = 9.1 Hz, C2), 83.9 (s, C9), 71.7 (s, C10), 60.4 (s, C8), 134.5–126.5, 119.2 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{64}H_{51}ClOOsP_3]^+$ requires 1155.2445, Found 1155.2476. Anal. Calcd (%) for $C_{64}H_{51}Cl_2OOsP_3$: C 64.59, H 4.32; Found: C 64.51, H 4.47.

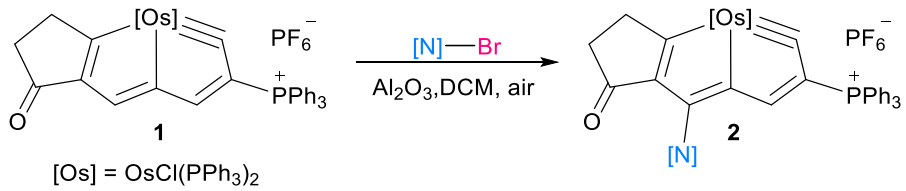
Preparation of complex 1:



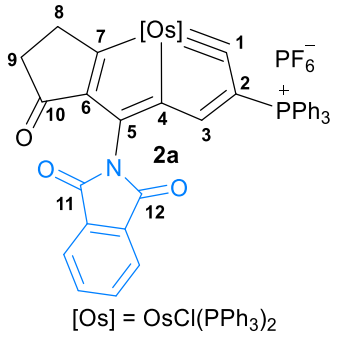
Trifluoroacetic acid (148.5 μL, 2.0 mmol) was added to a solution of **S** (238.0 mg, 0.20 mmol) in 10.0 mL of *t*-butyl alcohol. The reaction mixture was stirred for 6 hours at 75 °C to give a brown solution. Then, the mixture was concentrated to approximately 2.0 mL under vacuum and washed with Et_2O (3×10.0 mL) to afford a brown solid. The solid was redissolved in methanol (5.0 mL) and treated with sodium hexafluorophosphate (671.8 mg, 4.0 mmol), which was vigorously stirred at room temperature for 1 day. The reaction mixture was evaporated under vacuum to give as a yellow solid, which was washed with dichloromethane (3×10.0 mL) and the filtrate was dried under vacuum. The solid was purified by column chromatography (silica gel, eluent: dichloromethane/acetone = 30:1) to yield the corresponding complex **1** (218.4 mg, 0.17 mmol, 84%) as a yellow solid.

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 9.46 (s, 1H, H5), 8.11 (s, 1H, H3), {1.80 (t, 2H), 0.99 (s, 2H), H8, H9}, 7.83–6.93 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 6.26 (s, C*P*Ph_3), -2.44 (s, Os*P*Ph_3), -144.50 (hept, *J*(F-P) = 709.5 Hz, *P*F_6). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 324.4 (q, *J*(P-C) = 14.8 Hz, C1), 262.7 (t, *J*(P-C) = 9.9 Hz, C7), 204.3 (s, C10), 180.7 (dt, *J*(P-C) = 23.0 Hz, *J*(P-C) = 3.6 Hz, C4), 166.0 (s, C6), 162.0 (dt, *J*(P-C) = 15.9 Hz, *J*(P-C) = 3.3 Hz, C3), 161.1 (q, *J*(P-C) = 33.6 Hz, C2), 147.0 (s, C5), {42.9 (s), 40.1 (s), C8, C9}, 134.5–126.5, 119.5 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{64}H_{51}ClOOsP_3]^+$ requires 1155.2445, Found 1155.2457. Anal. Calcd (%) for $C_{64}H_{51}ClF_6OOsP_4$: C 59.15, H 3.96; Found: C 58.84, H 4.27.

General Preparation Procedure of complexes 2a-g:



A mixture of **1** (260.0 mg, 0.20 mmol) and N-bromocarboxamides or N-bromocarboximides (0.60 mmol) in dichloromethane (10.0 mL) in the presence of Al_2O_3 (509.8 mg, 5.0 mmol) was stirred at room temperature under open air for 12 hours to give a brown solution. Then the solution was filtered, and the filtrate was concentrated under vacuum. The resulting residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone = 10:1) to yield complex **2** as a bright orange solid.

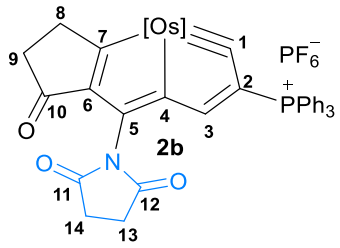


Method 1: According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2a** was obtained as a bright orange solid (266.0 mg, 0.18 mmol, 92%).

Method 2: A mixture of **1** (260.0 mg, 0.20 mmol) and NBP (0.60 mmol) in dichloromethane (10.0 mL) in the presence of CH_3COONa (82.0 mg, 1.0 mmol) was stirred at 40°C under air for 24 hours to give a brown solution. The solution was filtered, and the filtrate was concentrated under vacuum. The resulting residue was purified by column chromatography (silica gel, eluent: dichloromethane/acetone = 10:1) to yield complex **2a** (234.1 mg, 0.16 mmol, 81%) as a bright orange solid.

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 8.30 (d, *J*(P-H) = 1.8 Hz, 1H, H3), {1.65 (s, 2H), 0.67 (s, 2H), H8, H9}, 8.15–6.85 (m, other aromatic protons).^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 6.30 (s, C*P*Ph$_3$), -0.18 (s, Os*P*Ph$_3$), -144.50 (hept, *J*(F-P) = 710.8 Hz, *P*F$_6$). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.1 (q, *J*(P-C) = 14.6

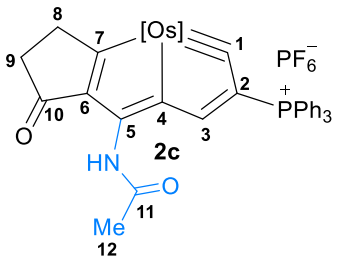
Hz, C1), 260.4 (t, *J*(P-C) = 8.0 Hz, C7), 202.4 (s, C10), 169.9 (dt, *J*(P-C) = 22.8 Hz, *J*(P-C) = 2.6 Hz, C4), 166.8 (s, C11, C12), 159.0 (d, *J*(P-C) = 18.7 Hz, C3), 159.0 (s, C6), 140.3 (s, C5), 132.2 (dt, *J*(P-C) = 95.7 Hz, *J*(P-C) = 2.9 Hz, C2), {42.1 (s), 40.2 (s), C8, C9}, 136.5–127.5, 119.4 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{72}H_{54}ClNO_3OsP_3]^+$ requires 1300.2611, Found 1300.2659. Anal. Calcd (%) for $C_{72}H_{54}ClF_6NO_3OsP_4$: C 59.86, H 3.77, N 1.00; Found: C 59.67, H 4.06, N 1.25.



[Os] = $OsCl(PPh_3)_2$

According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2b** was obtained as bright orange solid (251.8 mg, 0.18 mmol, 90%).

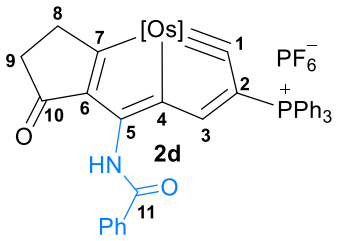
^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 8.51 (s, 1H, H3), 3.00-3.20 (m, 4H, H13, H14), {1.60 (s, 2H), 0.61 (s, 2H), H8, H9}, 7.85–6.85 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 6.31 (s, C*P*Ph_3), -0.01 (s, Os*P*Ph_3), -144.52 (p, *J*(F-P) = 709.5 Hz, *P*F_6). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.2 (s, C1), 259.8 (s, C7), 202.3 (s, C10), 176.1 (s, C11, C12), 169.3 (d, *J*(P-C) = 24.4 Hz, C4), 159.4 (t, *J*(P-C) = 15.7 Hz, C3), 157.9 (s, C6), 140.6 (s, C5), 132.3 (d, *J*(P-C) = 94.5 Hz, C2), {41.6 (s), 39.7 (s), C8, C9}, 29.2 (s, C13, C14), 135.5–127.5, 119.1 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{68}H_{54}ClNO_3OsP_3]^+$ requires 1252.2610, Found 1252.2648. Anal. Calcd (%) for $C_{68}H_{54}ClF_6NO_3OsP_4$: C 58.47, H 3.90, N 1.00; Found: C 58.40, H 3.61, N 0.60.



[Os] = $OsCl(PPh_3)_2$

According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2c** was obtained as bright orange solid (252.5 mg, 0.19 mmol, 93%).

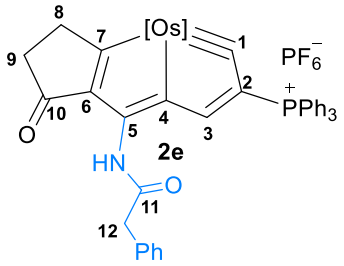
^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 11.21 (s, 1H, N*H*), 9.38 (s, 1H, H3), 2.44 (s, 3H, H12), {1.88 (s, 2H), 1.11 (s, 2H), H8, H9}, 7.82–6.95 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 5.31 (s, C*P*Ph_3), -1.58 (s, Os*P*Ph_3), -144.49 (hept, *J*(F-P) = 710.1 Hz, *P*F_6). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.9 (q, *J*(P-C) = 14.0 Hz, C1), 256.9 (t, *J*(P-C) = 8.4 Hz, C7), 207.0 (s, C10), 167.6 (s, C11), 165.2 (d, *J*(P-C) = 17.2 Hz, C3), 157.4 (dt, *J*(P-C) = 23.5 Hz, *J*(P-C) = 3.6 Hz, C4), 153.5 (s, C6), 152.1 (s, C5), 123.3 (dt, *J*(P-C) = 99.2 Hz, *J*(P-C) = 2.7 Hz, C2), {41.4 (s), 40.6 (s), C8, C9}, 25.1 (s, C12), 135.8–127.5, 120.2 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{66}H_{54}ClNO_2OsP_3]^+$ requires 1212.2660, Found 1212.2652. Anal. Calcd (%) for $C_{66}H_{54}ClF_6NO_2OsP_4$: C 58.43, H 4.01, N 1.03; Found: C 58.17, H 4.21, N 1.36.



[Os] = $OsCl(PPh_3)_2$

According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2d** was obtained as bright orange solid (227.0 mg, 0.16 mmol, 80%).

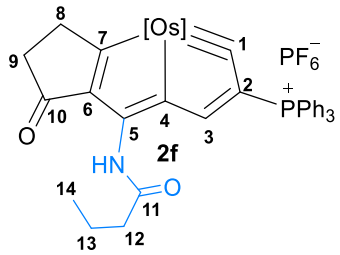
^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 12.16 (s, 1H, N*H*), 9.59 (s, 1H, H3), {1.95 (s, 2H), 1.18 (s, 2H), H8, H9}, 8.26–6.97 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 5.43 (s, C*P*Ph_3), -1.69 (s, Os*P*Ph_3), -144.52 (p, *J*(F-P) = 709.5 Hz, *P*F_6).^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.9 (q, *J*(P-C) = 13.9 Hz, C1), 256.7 (t, *J*(P-C) = 8.5 Hz, C7), 207.5 (s, C10), 165.8 (d, *J*(P-C) = 17.3 Hz, C3), 164.0 (s, C11), 157.7 (dt, *J*(P-C) = 23.5 Hz, *J*(P-C) = 3.5 Hz, C4), 154.1 (s, C6), 152.1 (s, C5), 123.6 (dt, *J*(P-C) = 99.2 Hz, *J*(P-C) = 2.7 Hz, C2), {41.6 (s), 40.6 (s), C8, C9}, 135.7–127.8, 120.2 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{71}H_{56}ClNO_2OsP_3]^+$ requires 1274.2818, Found 1274.2838. Anal. Calcd (%) for $C_{71}H_{56}ClF_6NO_2OsP_4$: C 60.11, H 3.98, N 0.99; Found: C 59.87, H 4.36, N 1.30.



[Os] = $OsCl(PPh_3)_2$

According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2e** was obtained as bright orange solid (243.7 mg, 0.17 mmol, 85%).

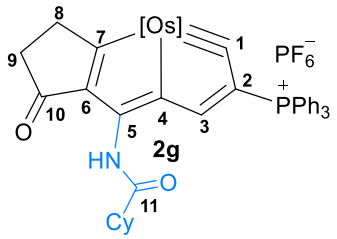
^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 11.22 (s, 1H, N*H*), 9.25 (s, 1H, H3), 3.93 (s, 2H, H12), {1.88 (s, 2H), 1.14 (s, 2H), H8, H9}, 7.94–6.85 (m, other aromatic protons). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ (ppm) = 5.34 (s, C*P*Ph_3), -1.80 (s, Os*P*Ph_3), -144.61 (p, *J*(F-P) = 706.8 Hz, *P*F_6). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.6 (q, *J*(P-C) = 13.8 Hz, C1), 256.7 (t, *J*(P-C) = 8.7 Hz, C7), 206.9 (s, C10), 168.7 (s, C11), 165.2 (d, *J*(P-C) = 17.2 Hz, C3), 157.7 (dt, *J*(P-C) = 23.4 Hz, *J*(P-C) = 3.6 Hz, C4), 153.8 (s, C6), 151.7 (s, C5), 123.5 (d, *J*(P-C) = 99.2 Hz, C2), 45.6 (s, C12), {41.5 (s), 40.5 (s), C8, C9}, 135.5–127.9, 120.1 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{72}H_{58}ClNO_2OsP_3]^+$ requires 1288.2974, Found 1288.3001. Anal. Calcd (%) for $C_{72}H_{58}ClF_6NO_2OsP_4$: C 60.36, H 4.08, N 0.98; Found: C 60.56, H 4.07, N 1.08.



[Os] = $OsCl(PPh_3)_2$

According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2f** was obtained as bright orange solid (210.5 mg, 0.15 mmol, 76%).

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 11.21 (s, 1H, N*H*), 9.38 (s, 1H, H3), 1.00-2.70 (m, 11H, H8, H9, C_3H_7), 7.94–6.85 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 5.34 (s, C*P*Ph_3), -1.57 (s, Os*P*Ph_3), -144.51 (p, *J*(F-P) = 709.7 Hz, *P*F_6).^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.9 (q, *J*(P-C) = 13.9 Hz, C1), 257.0 (t, *J*(P-C) = 8.1 Hz, C7), 207.0 (s, C10), 170.6 (s, C11), 165.3 (d, *J*(P-C) = 17.3 Hz, C3), 157.3 (dt, *J*(P-C) = 23.4, *J*(P-C) = 3.5 Hz, C4), 153.5 (s, C6), 152.3 (s, C5), 123.1 (dt, *J*(P-C) = 99.1 Hz, *J*(P-C) = 2.7 Hz, C2), {41.4 (s), 40.6 (s), 40.1 (s), 19.5 (s), 13.9 (s), C8, C9, *C*$_3$H$_7$}, 135.5–127.5, 120.2 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{68}H_{58}ClNO_2OsP_3]^+$ requires 1240.2974, Found 1240.3001. Anal. Calcd (%) for $C_{68}H_{58}ClF_6NO_2OsP_4$: C 58.98, H 4.22, N 1.01; Found: C 59.20, H 4.60, N 1.05.

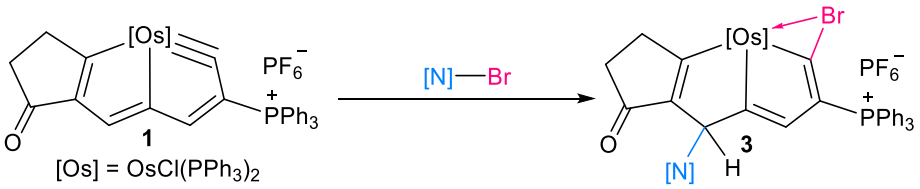


[Os] = $OsCl(PPh_3)_2$

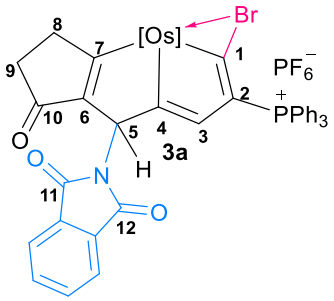
According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol), the product **2g** was obtained as bright orange solid (201.1 mg, 0.14 mmol, 71%).

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 11.26 (s, 1H, N*H*), 9.39 (s, 1H, H3), 1.19-2.65 (m, 15H, H8, H9, C_6H_{11}), 7.93–6.90 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 5.29 (s, C*P*Ph_3), -1.68(s, Os*P*Ph_3), -144.51 (hept, *J*(F-P) = 710.5 Hz, *P*F_6).^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 327.9 (q, *J*(P-C) = 13.9 Hz, C1), 256.8 (t, *J*(P-C) = 8.4 Hz, C7), 207.0 (s, C10), 173.7 (s, C11), 165.3 (d, *J*(P-C) = 17.3 Hz, C3), 157.4 (dt, *J*(P-C) = 23.5 Hz, *J*(P-C) = 3.6 Hz, C4), 153.7 (s, C6), 152.7 (s, C5), 122.8 (dt, *J*(P-C) = 99.6 Hz, *J*(P-C) = 2.7 Hz, C2), {47.1 (s), 41.4 (s), 40.6 (s), 30.3 (s), 26.1 (s), 26.0 (s), C8, C9, C_6H_{11}}, 135.5–127.7, 120.3 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{71}H_{62}ClNO_2OsP_3]^+$ requires 1280.3287, Found 1280.3307. Anal. Calcd (%) for $C_{71}H_{62}ClF_6NO_2OsP_4$: C 59.85, H 4.39, N 0.98; Found: C 59.65, H 4.58, N 1.30.

General Preparation Procedure of complex 3a-b:

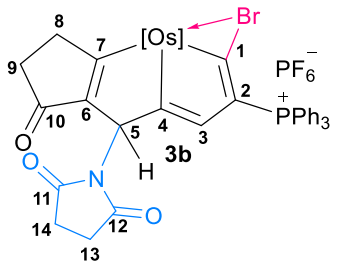


A mixture of **1** (260.0 mg, 0.20 mmol) and N-bromocarboximides (NBS or NBP) (1.5 eq) in dichloromethane (10.0 mL) was stirred at room temperature for 15 minutes to give a brown solution. Removal of the dichloromethane under vacuum gave a brown solid residue mixture of **3** and N-bromocarboximides (about 0.5 eq indicated by *in-situ* NMR), which was used without purification. Many attempts were made to remove the excess N-bromocarboximides from samples but failed. (NBS: N-bromosuccinimide, NBP: N-bromophthalimide)



According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol) the product **3a** was obtained as bright orange solid (282.2 mg, 0.185 mmol, 92.5%).

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 6.22 (s, 1H, H3), 6.12 (s, 1H, H5), 0.98-2.30 (m, 4H, H8, H9), 7.95–7.00 (m, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 10.73 (s, C*P*Ph$_3$), -21.90 (dd, *J*(P-P) = 381.2 Hz, *J*(P-P) = 287.3 Hz, Os*P*Ph$_3$), -144.49 (hept, *J*(F-P) = 710.7 Hz, *P*F$_6$). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 201.6 (br, C7), 198.3 (br, C1), 197.8 (s, C10), 173.0 (dt, *J*(P-C) = 19.3 Hz, *J*(P-C) = 4.5 Hz, C4), 168.3 (s, NBP), {169.7 (s), 166.2 (s), C11, C12}, 152.9 (s, C6), 134.3 (d, *J*(P-C) = 26.2 Hz, C3), 120.3 (d, *J*(P-C) = 94.5 Hz, C2), 57.5 (s, C5), {46.7 (s), 41.8 (s), C8, C9}, 136.5–122.8, 117.9 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{72}H_{55}BrClNO_3OsP_3]^+$ requires 1380.1855, Found 1380.1864.

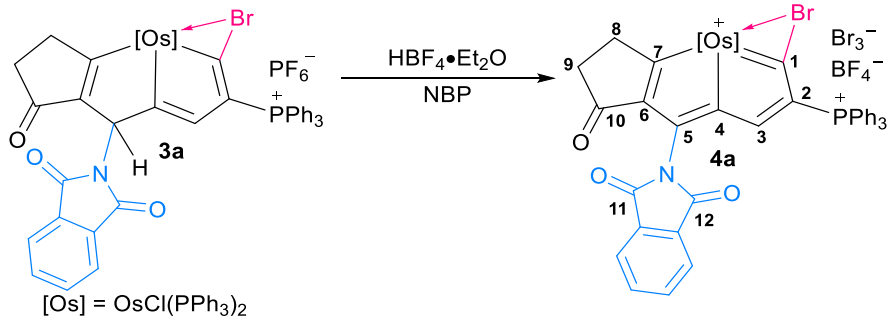


[Os] = $OsCl(PPh_3)_2$

According to general procedure starting from metallapentalyne **1** (260.0 mg, 0.20 mmol) the product **3b** was obtained as bright orange solid (265.9 mg, 0.18 mmol, 90%).

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 6.20 (s, 1H, H3), 5.91 (s, 1H, H5), 0.80-2.70 (m, 8H, H8, H9, H13, H14), 7.90–7.00 (m, other aromatic protons).^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 10.78 (s, C*P*Ph_3), -22.13 (dd, *J*(P-P) = 498.4, *J*(P-P) = 289.0 Hz, Os*P*Ph_3), -144.45 (hept, *J*(F-P) = 710.6 Hz, *P*F_6). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 201.5 (br, C7), 198.2 (br, C1), 197.8 (s, C10), 177.7 (s, NBS), {178.6 (s), 175.2 (s), C11, C12}, 172.2 (ddd, *J*(P-C) = 19.8, *J*(P-C) = 6.0, *J*(P-C) = 4.1 Hz, C4), 152.6 (s, C6), 134.2 (d, *J*(P-C) = 14.1 Hz, C3) 120.3 (d, *J*(P-C) = 94.4 Hz, C2), 58.1 (s, C5), {46.6 (s), 41.6 (s), 28.2 (s), 28.2 (s), C8, C9, C13, C14}, 136.5–126.5, 117.9 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{68}H_{55}BrClNO_3OsP_3]^+$ requires 1332.1854, Found 1332.1888.

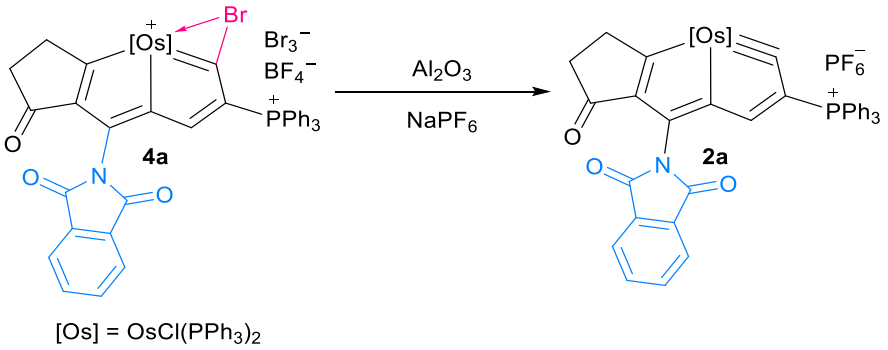
Preparation of complex 4a:



A solution of $HBF_4{\cdot}Et_2O$ (50-55%, w/w, 1.0 mL) and NBP (90.0 mg, 0.40 mmol) was added to a dichloromethane (10.0 mL) solution of *in-situ* generated **3a** (ca. 305.0 mg 0.20 mmol). The mixture was stirred at room temperature for 1 h to give a brown solution of complex **4a**. The solution was filtered, and the filtrate was concentrated under vacuum to yield complex **4a** (272.5 mg, 0.16 mmol, 80%) as a brown solid.

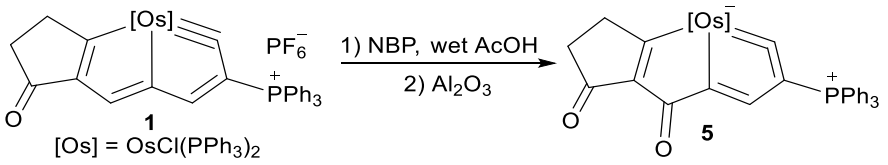
^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ (ppm) = 8.13 (s, H3), 1.70-1.90 (m, 4H, H8, H9), 8.10–6.80 (m, other aromatic protons).^{31}P NMR (242.9 MHz, CD_2Cl_2): δ (ppm) = 13.99 (s, C*P*Ph$_3$), -5.11 (s, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ (ppm) = 270.7 (br, C1), 220.2 (br, C7), 195.3 (s, C10), 174.1 (d, *J*(P-C) = 19.8 Hz, C4), 165.8 (s, C11, C12), 164.3 (d, *J*(P-C) = 10.7 Hz, C6), 159.8 (d, *J*(P-C) = 93.4 Hz, C2), 151.0 (s, C5), 125.4 (s, C3), {55.1 (s), 42.1 (s), C8, C9}, 137.5–126.5, 115.2 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{72}H_{54}BrClNO_3OsP_3]^{2+}$ requires 690.5946 [**4a**+2H]$^{2+}$, Found 690.5911 [**4a**+2H]$^{2+}$.

Preparation of complex 2a from 4a:



A mixture of sodium hexafluorophosphate (335.9 mg, 2.0 mmol) and Al_2O_3 (509.8 mg, 5.0 mmol) was added to a dichloromethane (5.0 mL) solution of *in-situ* generated **4a** (340.6 mg, 0.20 mmol). The mixture was stirred at room temperature for 1 h to give a brown solution of complex **2a**. Then the solution was filtered, and the filtrate was concentrated under vacuum. The resulting residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone = 10:1) to yield complex **2a** as a bright orange solid (216.8 mg, 0.15 mmol, 75%).

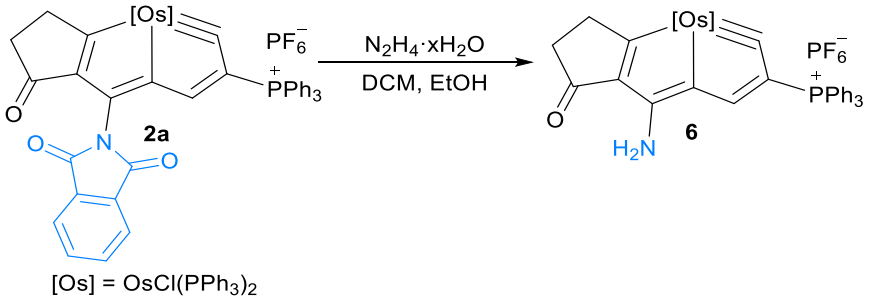
Preparation of complex 5:



NBP (136.0 mg, 0.60 mmol) was added to a mixture of wet acetic acid (49.2 mg, 0.60 mmol) and **1** (260.0 mg, 0.20 mmol) in dichloromethane (5.0 mL) solution. The mixture was stirred at room temperature for 15 minutes to give a brown solution of complex **C**. Then the solution was treated with Al_2O_3 (509.8 mg, 5.0 mmol) for 1 h, and the mixture was filtered and concentrated under vacuum. The resulting residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 10:1) to yield complex **5** (159.1 mg, 0.14 mmol, 68%) and phthalylimide (about 1.2 eq) as a mixture. Many attempts were made to remove the excess phthalylimide from samples but failed.

^{1}H NMR plus HSQC (600.1 MHz, $CDCl_3$): δ (ppm) = 6.89 (s, H3), {1.60 (s, 2H), 0.88 (s, 2H), H8, H9}, 6.90–7.90 (m, other aromatic protons).^{31}P NMR (242.9 MHz, $CDCl_3$): δ (ppm) = 4.40 (s, C*P*Ph$_3$), 1.68 (t, *J*(P-P) = 83.7 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, $CDCl_3$): δ (ppm) = 334.52(q, *J*(P-C) = 14.9 Hz, C1), 254.02(s, C7), 203.36(s, C10), 193.94(s, C5), 164.05(d, *J*(P-C) = 22.4 Hz, C4), 152.62(s, C6), 132.70(s, C3), 101.32(d, *J*(P-C) = 112.2 Hz, C2), {41.10(s), 38.64(s), C8, C9}, 135.5–122.5 (m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{64}H_{50}ClO_2OsP_3+H]^+$ requires 1171.2394, Found 1171.2406.

Preparation of complex 6:



85%-Hydrazine hydrate (130.0 μL, 2.27 mmol) was added to a mixed (dichloromethane+ethanol, 5.0 mL+5.0 mL) solution of **2a** (289.0 mg, 0.20 mmol). The mixture was stirred at room temperature for 1 h to give a yellow solution. Then dichloromethane (20.0 ml) was added to the solution, and the mixture was washed with distilled water (5×10.0 mL). The mixture was dried over Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone = 10:1) to yield complex **6** (236.8 mg, 0.18 mmol, 90 %) as a yellow solid.

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2+MeOD): δ (ppm) = 7.35 (s, 1H, H3), {1.82 (s, 2H), 1.15 (s, 2H), H8, H9}, 6.84–7.90 (m, other aromatic protons).^{31}P NMR (242.9 MHz, CD_2Cl_2+MeOD): δ (ppm) = 5.79 (s, C*P*Ph$_3$), 2.57 (s, Os*P*Ph$_3$), -142.53 (hept, *J*(F-P) = 709.5 Hz, *P*F$_6$). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2+MeOD): δ (ppm) = 333.49 (q, *J*(P-C) = 14.0 Hz, C1), 262.03 (t, *J*(P-C) = 7.9 Hz, C7), 205.71(s, C10), 167.80(s, C5), 152.44 (dt, *J*(P-C) = 22.7, *J*(P-C) = 4.5 Hz, C4), 150.77(s, C6), 142.34(d, *J*(P-C) = 16.2 Hz, C3), 112.40(dt, *J*(P-C) = 103.8, *J*(P-C) = 2.2 Hz, C2), {41.58(s), 41.07(s), C8, C9}, 135.5-128.0, 121.6(m, other aromatic carbons). HRMS (ESI): (*m/z*) Calcd for $[C_{64}H_{52}ClNOOsP_3]^+$ requires 1170.2554, Found 1170.2484.

3. Proposed Mechanism for the formation of complex 5

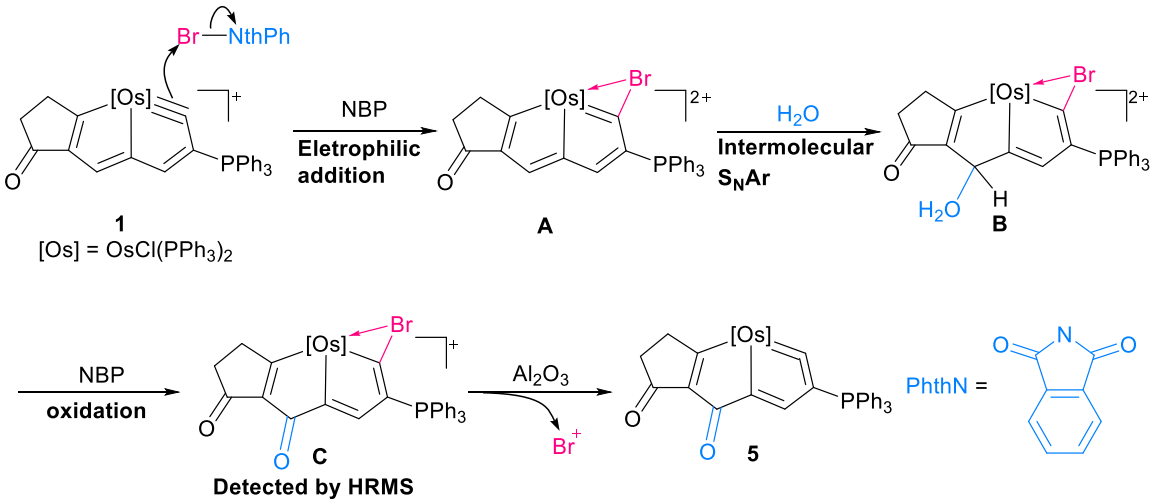


Figure S1. Proposed mechanism for the formation of complex **5**.

Initially, the addition of bromine cation derived from N-bromophthalimide to metal-carbon triple bond produced extremely electron-deficient cationic metallabromirenium **A**. Subsequently, nucleophilic attack of H_2O afforded the intermediate **B**, which would be easily oxidized into intermediate **C**. The readily elimination of the bromine cation would afford the final product **5**.

4 Thermal Stability Tests

Table S1. Thermal stability tests for complexes **1**, **2a-2g** in the solid state under air condition.[a]

Temperature (℃) / Complexes No.	80 (5 h)	100 (5 h)	120 (5 h)	140 (5 h)	160 (5 h)	180 (5 h)
1	●	●	▲	▲	▲	■
2a	●	●	▲	▲	■	-
2b	●	●	▲	▲	■	-
2c	●	●	▲	▲	■	-
2d	●	●	▲	▲	■	-
2e	●	●	▲	▲	■	-
2f	●	●	▲	▲	■	-
2g	●	●	▲	▲	■	-

[a] ● = stable; ▲ = Partly decomposed; ■ = Completely decomposed.

5. X-ray Crystallographic Analysis

Single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex, Rigaku XtaLAB Synergy-S diffractometer coupled to a RigakuHypix detector with Cu Kα radiation (λ = 1.54184 Å) or Mo Kα radiation (λ = 0.71073 Å). All data except **2d** were corrected for absorption effects using the multi-scan technique. Complex **2d** was corrected for absorption effects using the gaussian technique. Single crystals suitable for X-ray diffraction were obtained by recrystallization from a solution of CH_2Cl_2 layered with *n*-hexane. The crystal was kept at a steady T = 100 K during the data collection. The structures were solved with the SHELXT solution program by using **Olex 2** (Dolomanov *et al.*, 2009) as the graphical interface. The model was refined using Least Squares minimisation with the 2018/3 version of the program SHELXL[1] . Non-H atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. The disordered solvents were removed from the dataset using the SOLVENT MASK routine of Olex 2 which was reported in the CIF. CCDC 2053993 (**S**), 2054261 (**1**), 2054330 (**2a**), 2054286 (**2b**), 2054272 (**2c**), 2054274 (**2d**), 2054285 (**2e**), 2054269 (**4a**) and 2069503 (**5**) contain the supplementary crystallographic data for this paper. Further details on the crystal data, data collection, and refinements are provided in Supplementary Table S11, S12 and S13. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/?access=referee

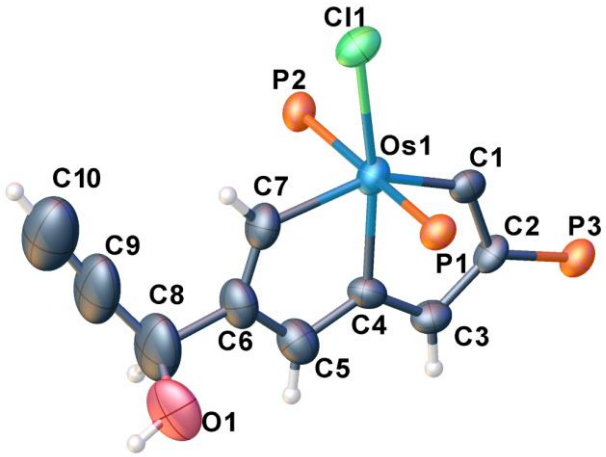


Figure S2. X-ray molecular structure of **S**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S2. Selected bond distances and angles for complex **S**.

Bond Distances(Å)					
Os1–Cl1	2.4365(15)	C4–C3	1.396(8)	C6–C8	1.535(11)
Os1–C1	1.850(6)	C4–C5	1.387(9)	C8–C9	1.421(13)
Os1–C4	2.083(6)	C2–C3	1.404(9)	C8–O1	1.387(19)
Os1–C7	2.043(6)	C7–C6	1.355(10)	C9–C10	1.216(13)
C1–C2	1.428(8)	C6–C5	1.390(10)		

Bond Angles(°)			
C1–Os1–C4	73.5(2)	C6–C7–Os1	121.6(5)
C7–Os1–C4	74.0(3)	C7–C6–C5	112.4(6)
C2–C1–Os1	128.2(4)	C7–C6–C8	125.4(8)
C5–C4–C3	123.9(6)	C5–C6–C8	122.2(8)
C3–C2–C1	108.1(5)	C4–C5–C6	114.6(7)
C4–C3–C2	111.5(5)		

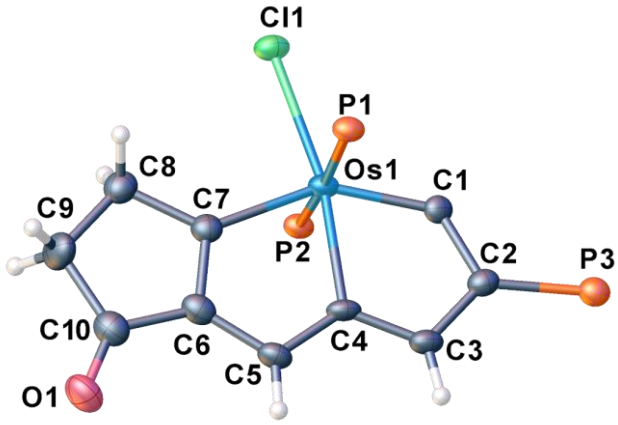


Figure S3. X-ray molecular structure of **1**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S3. Selected bond distances and angles for complex **1**.

Bond Distances(Å)					
Os1–Cl1	2.4403(7)	C1–C2	1.398(4)	C6–C7	1.396(5)
Os1–C1	1.858(3)	C2–C3	1.398(5)	C6–C10	1.464(5)
Os1–C4	2.106(3)	C3–C4	1.398(5)	C7–C8	1.511(5)
Os1–C7	2.045(3)	C4–C5	1.397(5)	C8–C9	1.536(5)
O1–C10	1.225(4)	C5–C6	1.410(5)	C9–C10	1.517(5)

Bond Angles(°)			
C1–Os1–C4	72.31(13)	C7–C6–C5	114.9(3)
C7–Os1–C4	75.01(13)	C7–C6–C10	112.1(3)
C2–C1–Os1	130.1(3)	C6–C7–Os1	119.3(2)
C1–C2–C3	107.9(3)	C6–C7–C8	109.1(3)
C2–C3–C4	111.8(3)	C7–C8–C9	105.7(3)
C5–C4–C3	123.6(3)	C10–C9–C8	106.3(3)
C4–C5–C6	112.3(3)	C6–C10–C9	106.7(3)

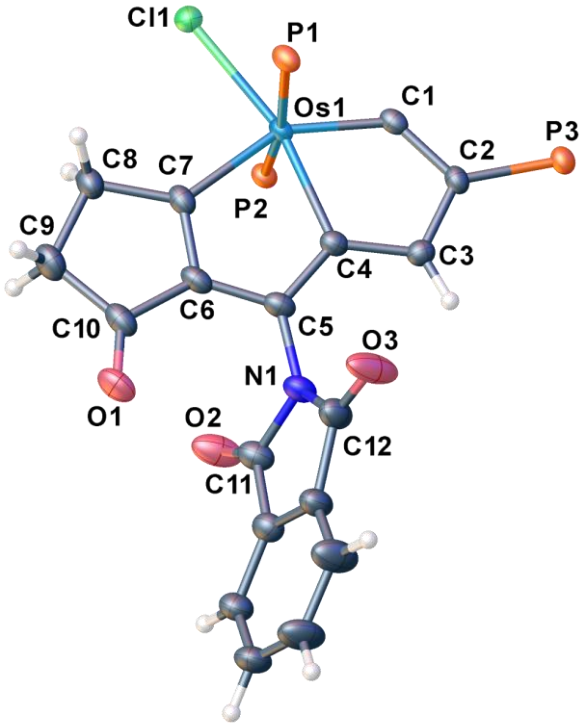


Figure S4. X-ray molecular structure of **2a**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S4. Selected bond distances and angles for complex **2a**.

Bond Distances(Å)					
Os1–Cl1	2.4098(5)	N1–C5	1.430(3)	C6–C7	1.388(3)
Os1–C1	1.842(2)	O3–C12	1.201(3)	C6–C10	1.468(3)
Os1–C7	2.044(2)	C2–C1	1.404(3)	C7–C8	1.508(3)
Os1–C4	2.111(2)	C2–C3	1.404(3)	C4–C3	1.414(3)
O1–C10	1.223(3)	C5–C6	1.397(3)	C9–C10	1.511(4)
O2–C11	1.207(3)	C5–C4	1.397(3)	C9–C8	1.543(4)
Bond Angles( )					
C1–Os1–C4	72.32(9)		C4–C5–C6	113.5(2)	
C7–Os1–C4	75.89(9)		C7–C6–C5	115.6(2)	
C11–N1–C5	120.8(2)		C6–C7–C8	109.2(2)	
C12–N1–C5	123.7(2)		C5–C4–C3	125.0(2)	
C1–C2–C3	108.44(19)		C2–C3–C4	110.4(2)	
C2–C1–Os1	130.53(17)		C7–C8–C9	105.7(2)	

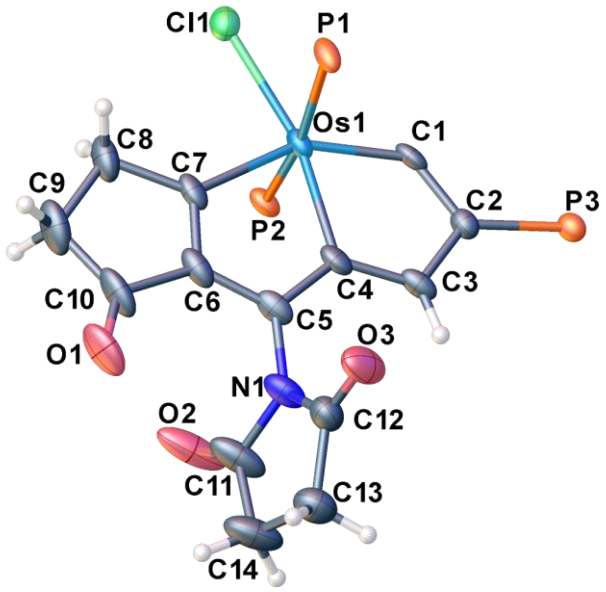


Figure S5. X-ray molecular structure of **2b**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S5. Selected bond distances and angles for complex **2b**.

Bond Distances(Å)					
Os1–Cl1	2.4140(11)	O3–C12	1.199(6)	O1–C10	1.208(6)
Os1–C1	1.845(4)	C2–C1	1.395(6)	O2–C11	1.210(7)
Os1–C7	2.055(4)	C2–C3	1.400(5)	C3–C4	1.396(6)
Os1–C4	2.114(4)	C5–C6	1.393(6)	C7–C8	1.506(6)
N1–C5	1.426(6)	C5–C4	1.398(5)	C12–C13	1.504(6)
N1–C12	1.397(6)	C6–C7	1.373(6)	C9–C10	1.519(8)
N1–C11	1.416(6)	C6–C10	1.476(5)	C9–C8	1.539(7)
Bond Angles(°)					
C1–Os1–C4	72.25(15)		C2–C1–Os1	130.8(3)	
C7–Os1–C4	75.45(16)		C4–C3–C2	112.1(4)	
C12–N1–C11	112.3(4)		C6–C7–Os1	118.3(3)	
C1–C2–C3	107.4(3)		C6–C7–C8	110.0(3)	
C6–C5–C4	113.2(4)		C3–C4–C5	125.8(4)	
C7–C6–C5	116.2(3)		C6–C10–C9	105.7(4)	

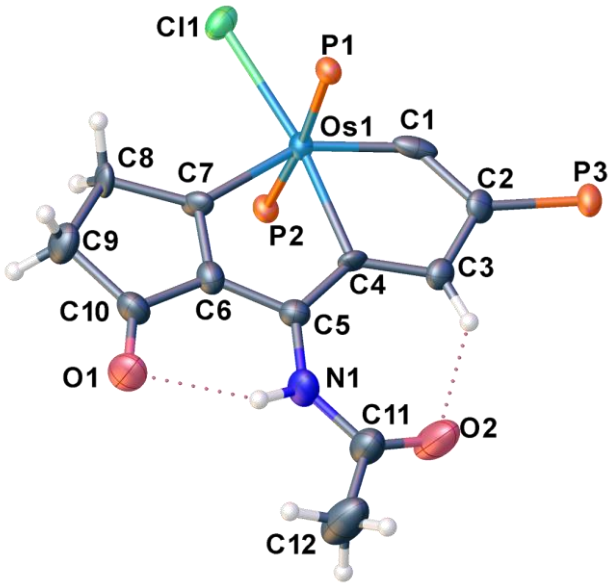


Figure S6. X-ray molecular structure of **2c**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S6. Selected bond distances and angles for complex **2c**.

Bond Distances(Å)					
Os1–Cl1	2.4116(19)	C7–C6	1.356(11)	O2–C11	1.220(12)
Os1–C7	2.057(8)	C7–C8	1.504(10)	C1–C2	1.411(12)
Os1–C4	2.146(7)	C6–C10	1.462(11)	C10–C9	1.518(12)
Os1–C1	1.818(10)	C6–C5	1.427(11)	C8–C9	1.543(12)
O1–C10	1.225(11)	C4–C3	1.394(10)	C11–C12	1.497(15)
N1–C5	1.387(11)	C4–C5	1.411(11)		
N1–C11	1.362(12)	C3–C2	1.415(11)		
Bond Angles(°)					
C7–Os1–C4	75.7(3)		C4–C3–C2	112.3(7)	
C1–Os1–C4	72.6(3)		C2–C1–Os1	131.5(6)	
C11–N1–C5	133.7(8)		C1–C2–C3	107.2(7)	
C6–C7–C8	109.6(7)		C4–C5–C6	111.6(7)	
C7–C6–C5	117.7(7)		C7–C8–C9	105.5(7)	
C3–C4–C5	127.1(7)		C10–C9–C8	105.2(7)	

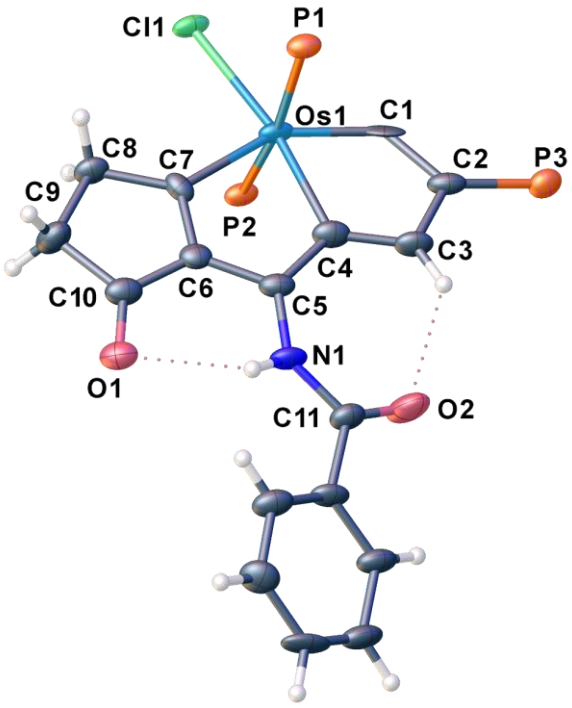


Figure S7. X-ray molecular structure of **2d**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S7. Selected bond distances and angles for complex **2d**.

Bond Distances(Å)					
Os1–Cl1	2.411(2)	N1–C5	1.387(12)	C5–C4	1.441(14)
Os1–C7	2.059(9)	N1–C11	1.381(13)	C8–C9	1.557(14)
Os1–C1	1.839(8)	C7–C6	1.386(13)	C4–C3	1.379(15)
Os1–C4	2.143(9)	C7–C8	1.483(13)	C2–C3	1.418(14)
O1–C10	1.242(12)	C1–C2	1.425(13)	C10–C9	1.512(14)
O2–C11	1.206(13)	C6–C5	1.428(14)		

Bond Angles( )			
C7–Os1–C4	77.5(4)	C6–C5–C4	112.3(8)
C1–Os1–C4	72.7(4)	C7–C8–C9	105.7(8)
C11–N1–C5	131.2(9)	C3–C4–C5	126.5(9)
C6–C7–C8	109.7(8)	C3–C2–C1	109.3(9)
C2–C1–Os1	128.9(7)	C4–C3–C2	110.5(9)
C7–C6–C5	118.1(9)	C10–C9–C8	104.8(8)

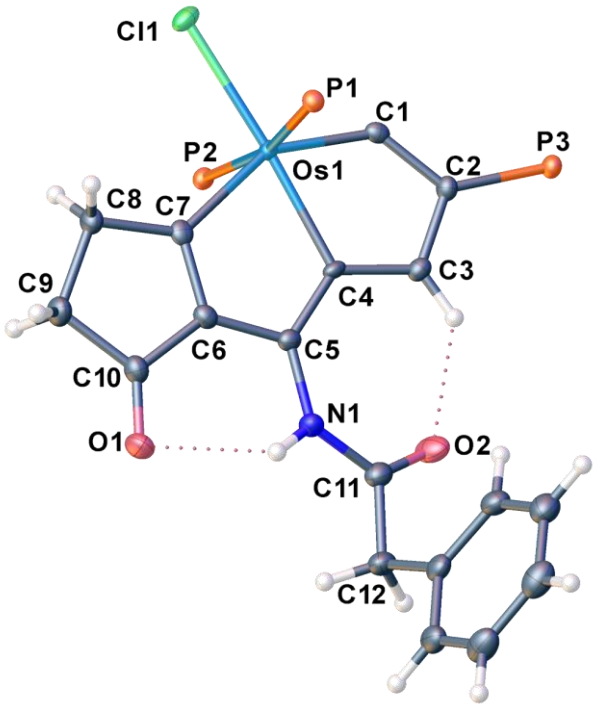


Figure S8. X-ray molecular structure of **2e**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S8. Selected bond distances and angles for complex **2e**.

Bond Distances(Å)					
Os1–C7	2.061(2)	N1–C5	1.392(3)	C2–C3	1.405(3)
Os1–C4	2.141(2)	C6–C7	1.378(3)	C2–C1	1.397(3)
Os1–C1	1.839(2)	C6–C5	1.418(3)	C10–C9	1.514(3)
O2–C11	1.207(3)	C7–C8	1.511(3)	C11–C12	1.511(3)
O1–C10	1.226(3)	C4–C3	1.395(3)	C8–C9	1.544(3)
N1–C11	1.387(3)	C4–C5	1.408(3)		

Bond Angles( )			
C7–Os1–C4	75.29(8)	C3–C4–C5	126.41(19)
C1–Os1–C4	72.69(9)	C1–C2–C3	107.76(19)
C11–N1–C5	132.0(2)	C4–C3–C2	112.75(19)
C7–C6–C10	112.8(2)	C4–C5–C6	111.45(19)
C7–C6–C5	117.4(2)	C2–C1–Os1	130.67(16)
C6–C7–Os1	118.35(16)	C7–C8–C9	105.49(18)

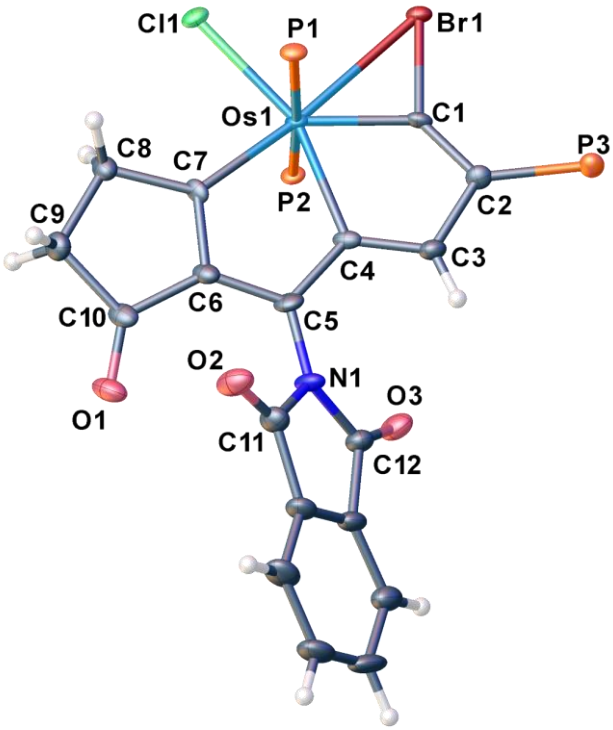


Figure S9. X-ray molecular structure of **4a**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S9. Selected bond distances and angles for complex **4a**.

Bond Distances(Å)					
Os1–Br1	2.7241(5)	C4–C3	1.377(7)	C9–C8	1.538(7)
Os1–C7	2.023(5)	N1–C5	1.379(7)	C7–C8	1.514(7)
Os1–C1	1.949(5)	C6–C7	1.389(7)	C2–C1	1.366(7)
Os1–C4	2.146(5)	C5–C6	1.393(7)	C2–C3	1.425(7)
Br1–C1	1.896(5)	C5–C4	1.414(7)		

Bond Angles(°)			
C7–Os1–C4	74.12(19)	Br1–Os1–C1	44.10(13)
C1–Os1–C4	68.38(19)	C1–Br1–Os1	45.67(15)
C6–C5–C4	112.8(4)	C2–C1–Os1	133.9(4)
C6–C7–C8	109.4(4)	Os1–C1–Br1	90.2(2)
C7–C6–C5	114.4(4)	C4–C3–C2	113.0(4)
C1–C2–C3	104.6(4)	C3–C4–C5	122.8(5)
C10–C9–C8	105.6(4)	C7–C8–C9	105.9(4)

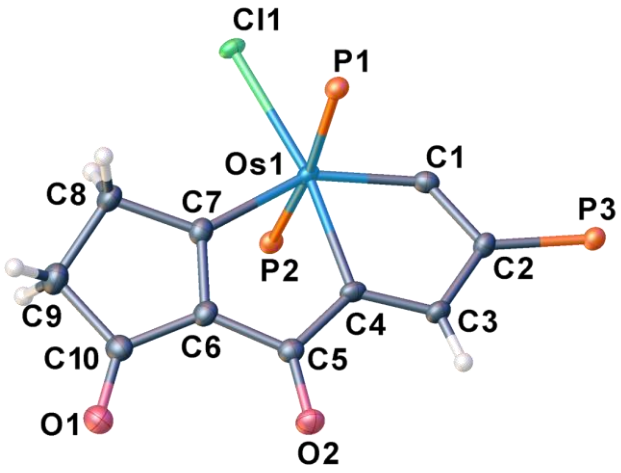


Figure S10. X-ray molecular structure of **5**. (ellipsoids set at 50% probability). The phenyl groups in the PPh_3 moieties are omitted for clarity.

Table S10. Selected bond distances and angles for complex **5**.

Bond Distances(Å)					
Os1-C4	2.111(3)	C1-C2	1.374(4)	C6-C7	1.382(4)
Os1-C1	1.870(3)	C3-C2	1.450(4)	C7-C8	1.512(4)
Os1-C7	2.059(3)	C4-C3	1.366(4)	C8-C9	1.530(4)
O2-C5	1.250(3)	C4-C5	1.465(4)	C10-C9	1.519(4)
O1-C10	1.223(4)	C6-C5	1.449(4)	C6-C10	1.464(4)
Bond Angles(°)					
C1-Os1-C4	72.69(11)		C7-C6-C5	115.4(3)	
C7-Os1-C4	75.01(11)		C6-C7-C8	109.5(2)	
C2-C1-Os1	130.0(2)		C6-C7-Os1	120.7(2)	
C1-C2-C3	107.3(2)		O2-C5-C4	124.3(3)	
C4-C3-C2	111.8(2)		O2-C5-C6	126.1(3)	
C3-C4-Os1	118.2(2)		O1-C10-C6	129.1(3)	
C5-C4-Os1	118.88(19)		O1-C10-C9	123.9(3)	
C6-C5-C4	109.6(2)		C7-C6-C5	115.4(3)	
C1-Os1-C4	72.69(11)				

Table S11. Crystal data and structure refinement for **S**, **1** and **2a**.

Compound	**S** $2CH_2Cl_2$	**1**	**2a** $3CH_2Cl_2$
Formula	$C_{64}H_{51}Cl_2OOsP_3$ $2CH_2Cl_2$	$C_{64}H_{51}ClF_6OOsP_4$	$C_{72}H_{54}ClF_6NO_3OsP_4$ $3CH_2Cl_2$
$D_{calc.}$/ g cm^{-3}	1.328	1.614	1.444
μ/mm^{-1}	5.929	6.644	5.852
Formula Weight	1190.21	1300.21	1445.23
Colour	clear light yellow	clear light yellow	clear light brown
Shape	cube	block	block
Size/mm^3	0.10×0.10×0.10	0.10×0.10×0.10	0.20×0.10×0.10
T/K	100.01(10)	100.0(3)	100.00(10)
Crystal System	monoclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$P2_1/c$	P-1
a/Å	12.9793(3)	13.1516(3)	13.98058(8)
b/Å	32.8708(5)	17.1534(3)	14.27702(8)
c/Å	14.4140(3)	23.7077(4)	19.13965(8)
α/°	90	90.1	73.8520(4)
β/°	104.590(2)	90	83.3208(4)
γ/°	90	90	73.5796(5)
V/Å^3	5951.3(2)	5348.31(17)	3516.95(3)
Z	4	4	2
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.442	3.180	2.405
Θ_{max}/°	78.019	76.162	75.175
Measured Refl's.	40288	68618	103664
Indep't Refl's	12157	10957	14243
Refl's I≥2 σ(I)	10261	9615	14182

R_{int}	0.0498	0.0583	0.0303
Parameters	681	694	820
Restraints	58	0	0
Largest Peak	1.921	1.729	1.429
Deepest Hole	-1.007	-1.666	-2.079
GooF	1.049	1.026	1.036
wR_2 (all data)	0.1591	0.0986	0.0653
wR_2	0.1469	0.0922	0.0653
R_1 (all data)	0.0690	0.0425	0.0258
R_1	0.0567	0.0361	0.0257

Table S12. Crystal data and structure refinement for **2b-2d**.

Compound	**2b** $3CH_2Cl_2$	**2c** $\cdot 1.6CH_2Cl_2 \cdot 1H_2O$	**2d** $0.5CH_2Cl_2 \cdot 1H_2O$
Formula	$C_{68}H_{54}ClF_6NO_3OsP_4 \cdot 3CH_2Cl_2$	$C_{66}H_{54}ClF_6NO_2OsP_4 \cdot 1.6CH_2Cl_2 \cdot 1H_2O$	$C_{71}H_{56}ClF_6NO_2OsP_4 \cdot 0.5CH_2Cl_2 \cdot 1H_2O$
$D_{calc.}$/ g cm^{-3}	1.316	1.418	1.529
μ/mm^{-1}	1.996	5.635	5.840
Formula Weight	1397.23	1357.23	1419.25
Colour	clear light brown	clear light brown	clear light yellow
Shape	cube	block	block
Size/mm^3	0.10×0.10×0.10	0.10×0.01×0.01	0.14×0.10×0.06
T/K	100.00(10)	99.99(10)	99.99(10)
Crystal System	triclinic	monoclinic	triclinic
Space Group	P-1	$P2_1/c$	P-1
a/Å	13.8668(2)	12.7923(4)	14.8347(4)
b/Å	14.0860(2)	11.9466(3)	15.0458(3)
c/Å	19.4128(3)	41.9680(11)	15.7073(2)
α/°	85.6910(10)	90	77.018(2)

β/°	73.941(2)	97.901(3)	88.368(2)
γ/°	75.2440(10)	90	64.742(2)
V/Å^3	3523.67(10)	6352.9(3)	3080.61(12)
Z	2	4	2
Z'	1	1	1
Wavelength/Å	0.71073	1.54184	1.54184
Radiation type	Mo Kα	Cu Kα	Cu Kα
Θ_{min}/°	1.956	3.488	2.896
Θ_{max}/°	27.500	75.167	64.989
Measured Refl's.	65977	36975	68766
Indep't Refl's	16167	12627	10409
Refl's I≥2 σ(I)	14494	12183	9739
R_{int}	0.0722	0.0357	0.0940
Parameters	757	731	800
Restraints	688	0	112
Largest Peak	3.188	1.833	6.547
Deepest Hole	-1.614	-4.038	-2.268
GooF	1.021	1.112	1.087
wR_2 (all data)	0.1042	0.1714	0.2139
wR_2	0.1023	0.1702	0.2108
R_1 (all data)	0.0492	0.0812	0.0926
R_1	0.0434	0.0781	0.0866

Table S13. Crystal data and structure refinement for **2e**, **4a and 5**.

Compound	**2e** $0.5CH_2Cl_2$ $0.2H_2O$	**4a** $4CH_2Cl_2$	**5** $3CH_2Cl_2$ H_2O
Formula	$C_{72}H_{58}ClF_6NO_2OsP_4$ $0.5CH_2Cl_2$ $0.2H_2O$	$C_{72}H_{54}BBr_4ClF_4NO_3OsP_3$ $4CH_2Cl_2$	$C_{64}H_{50}ClO_2OsP_3$ $3CH_2Cl_2$ H_2O
$D_{calc.}$/ g cm^{-3}	1.544	1.535	1.480
μ/mm^{-1}	5.842	7.500	7.071
Formula Weight	1433.26	1702.94	1357.46
Colour	clear light brown	clear light yellow	clear light brown
Shape	block	block	plank
Size/mm^3	0.20×0.20×0.05	0.20×0.20×0.10	0.10×0.10×0.05
T/K	100.0(2)	100.00(10)	99.99(10)
Crystal System	triclinic	triclinic	monoclinic
Space Group	P-1	P-1	$P2_1/n$
a/Å	11.89493(6)	14.5039(2)	12.60580(10)
b/Å	15.07972(8)	14.8044(2)	13.68200(10)
c/Å	17.48685(8)	19.0406(3)	35.3873(2)
α/°	91.6955(4)	88.2430(10)	90
β/°	95.1283(4)	79.3200(10)	93.2200(10)
γ/°	99.0034(4)	74.6840(10)	90
V/Å^3	3082.58(3)	3874.19(10)	6093.70(7)
Z	2	2	4
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu Kα	Cu Kα	Cu Kα
Θ_{min}/°	2.539	3.096	2.501
Θ_{max}/°	74.452	64.996	75.259
Measured Refl's.	86906	47107	78888
Indep't Refl's	12253	13183	12462

Refl's I≥2 σ(I)	12040	12784	11674
R_{int}	0.0392	0.0432	0.0402
Parameters	784	866	706
Restraints	0	63	0
Largest Peak	1.300	2.366	0.813
Deepest Hole	-1.042	-1.882	-0.960
GooF	1.032	1.085	1.035
wR_2 (all data)	0.0586	0.1175	0.0750
wR_2	0.0583	0.1170	0.0739
R_1 (all data)	0.0256	0.0455	0.0331
R_1	0.0246	0.0445	0.0303

6. HRMS and NMR Spectra

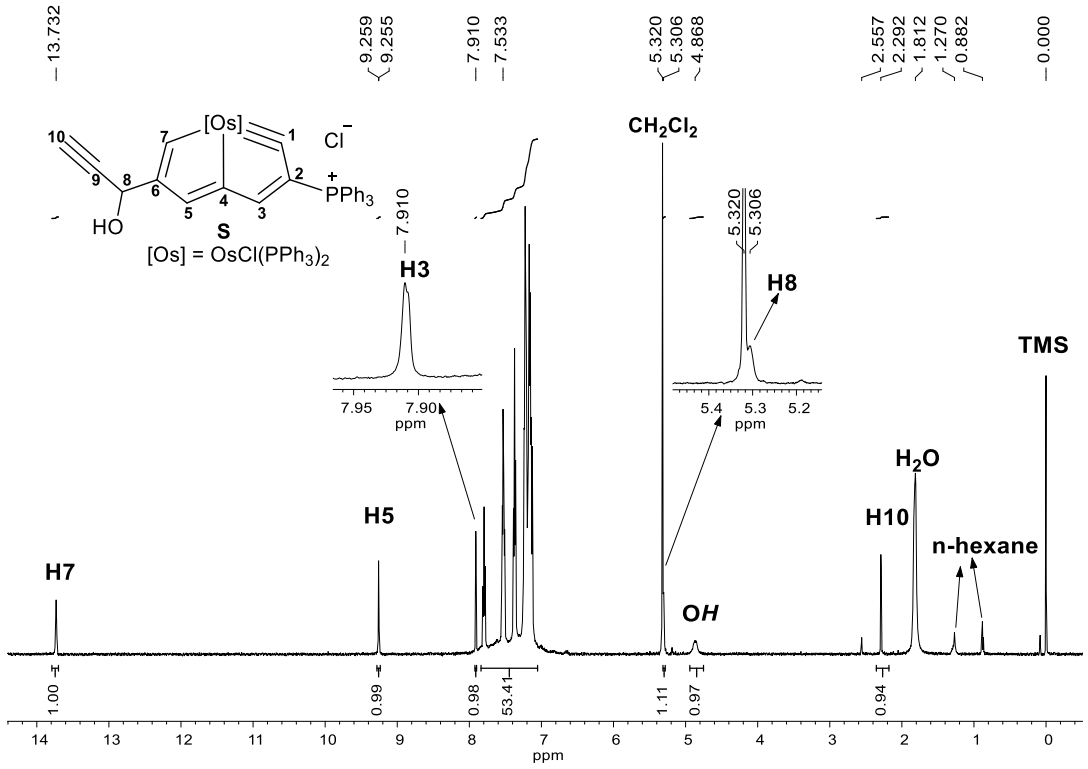


Figure S11. The ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for complex **S**.

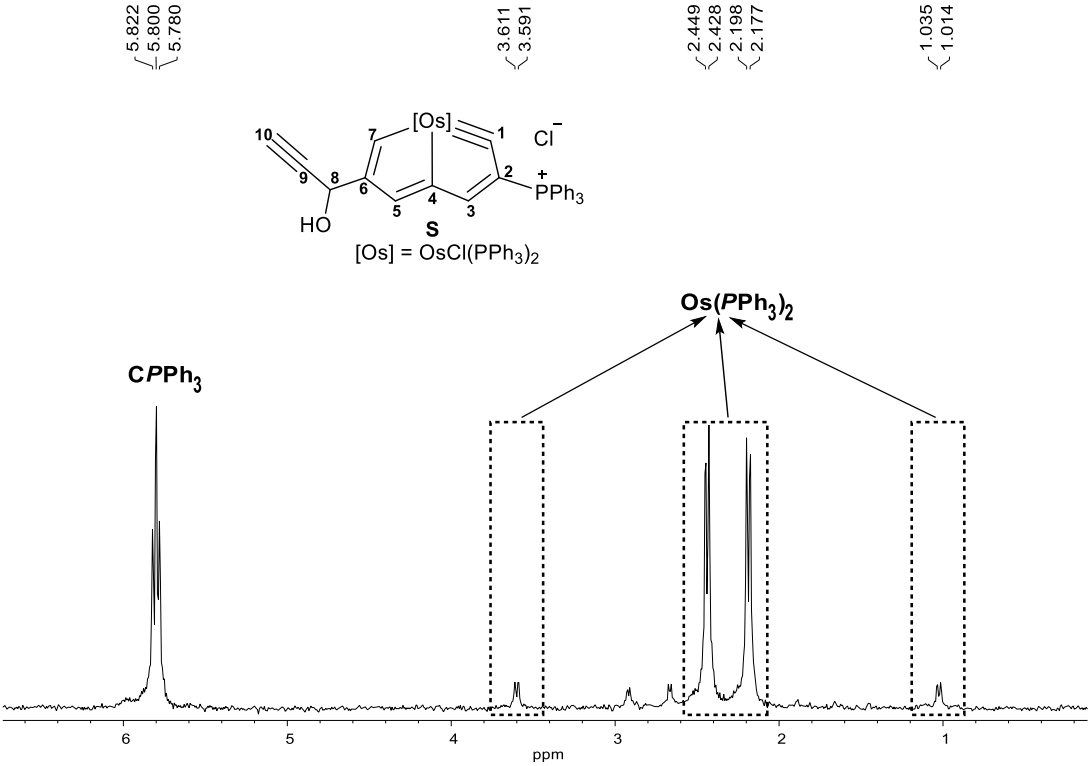


Figure S12. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **S**.

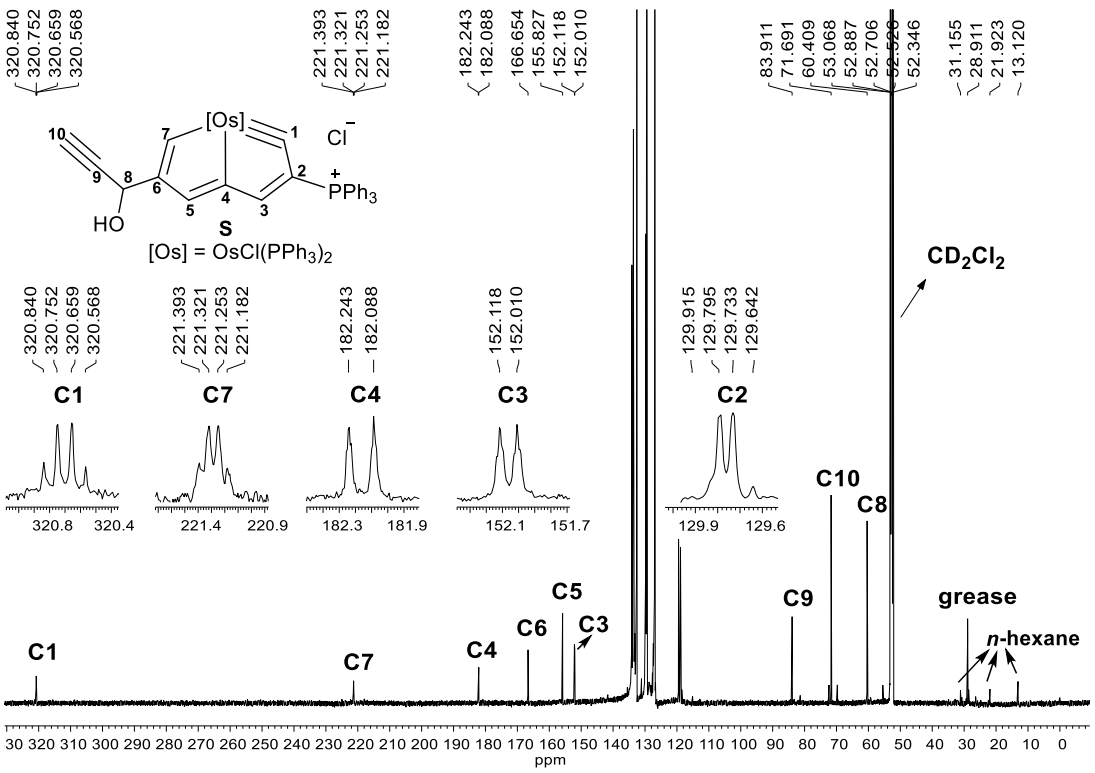


Figure S13. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **S**

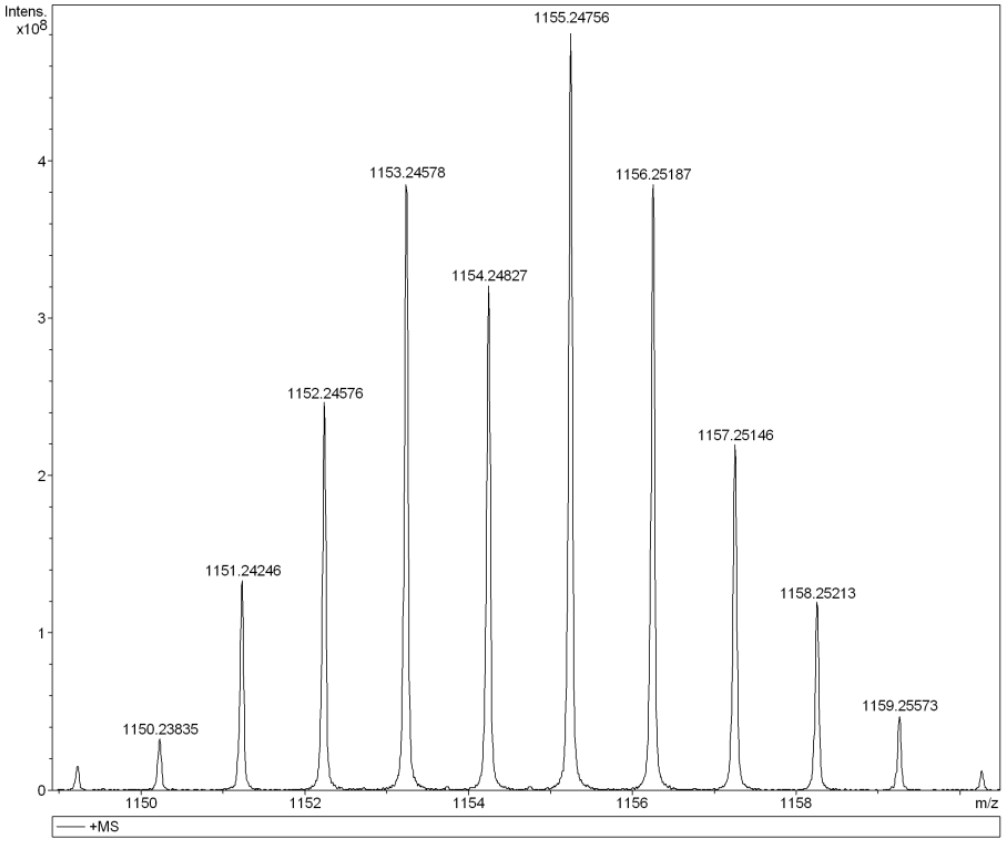


Figure S14. Positive-ion ESI-MS spectrum for complex $[\mathbf{S}]^+$ measured in methanol.

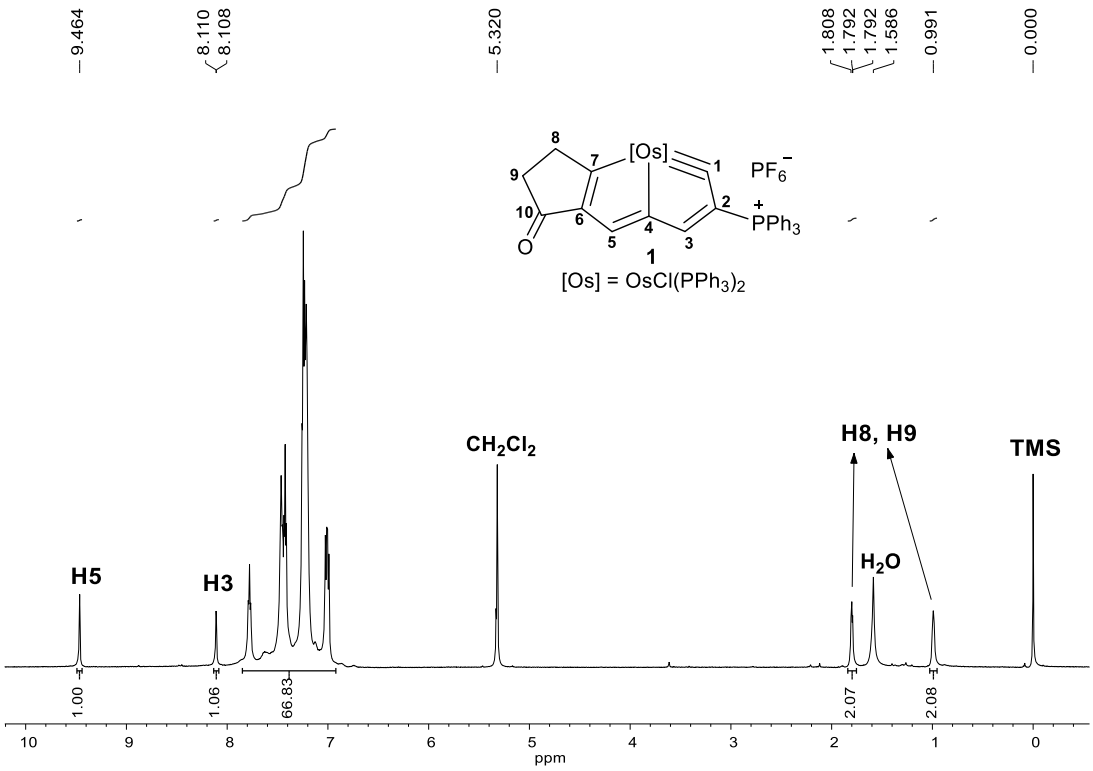


Figure S15. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **1**.

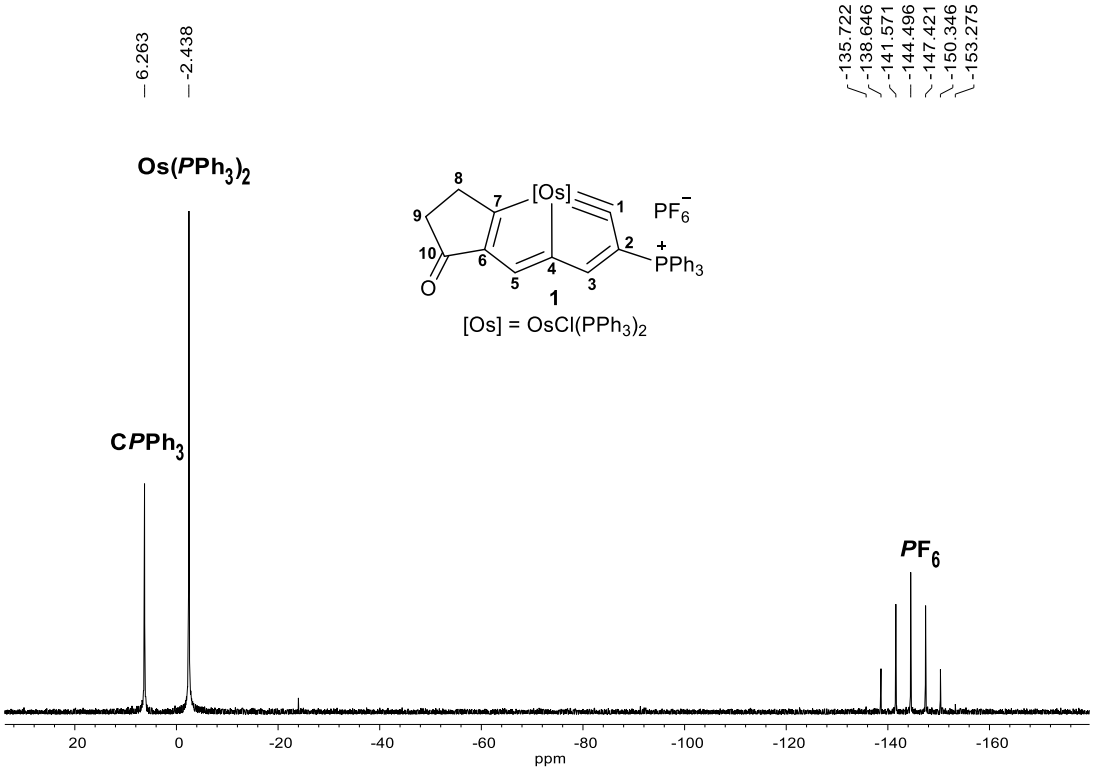


Figure S16. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **1**.

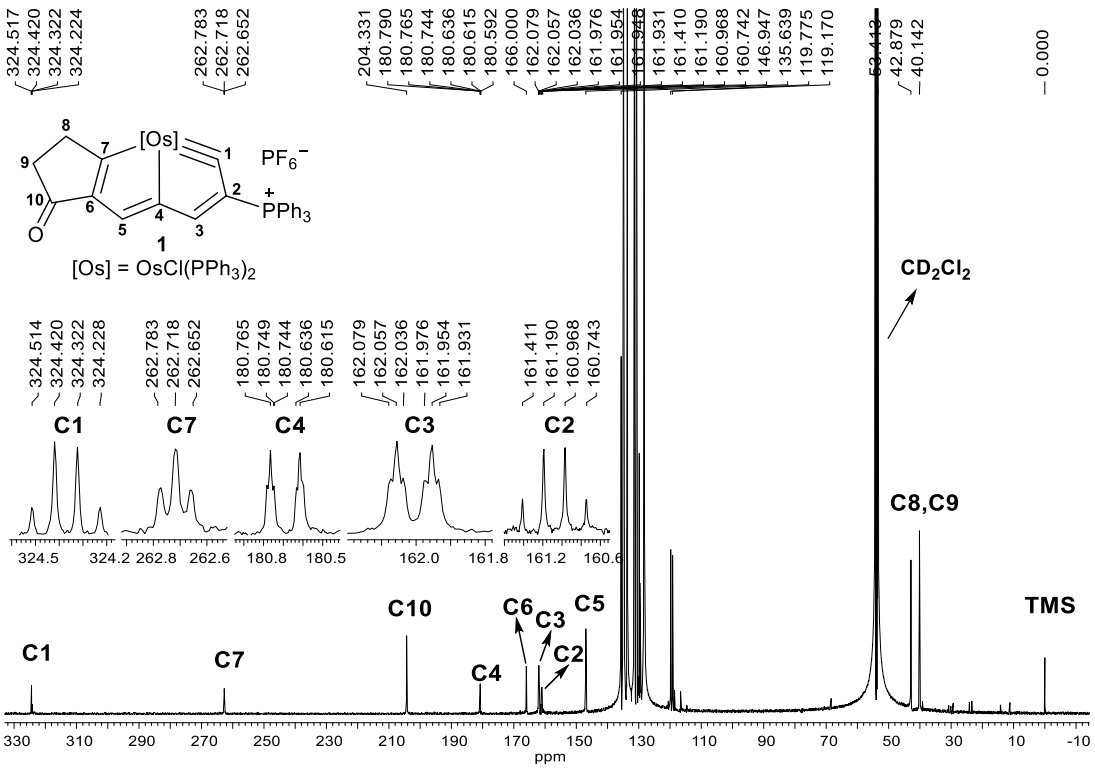


Figure S17. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **1**.

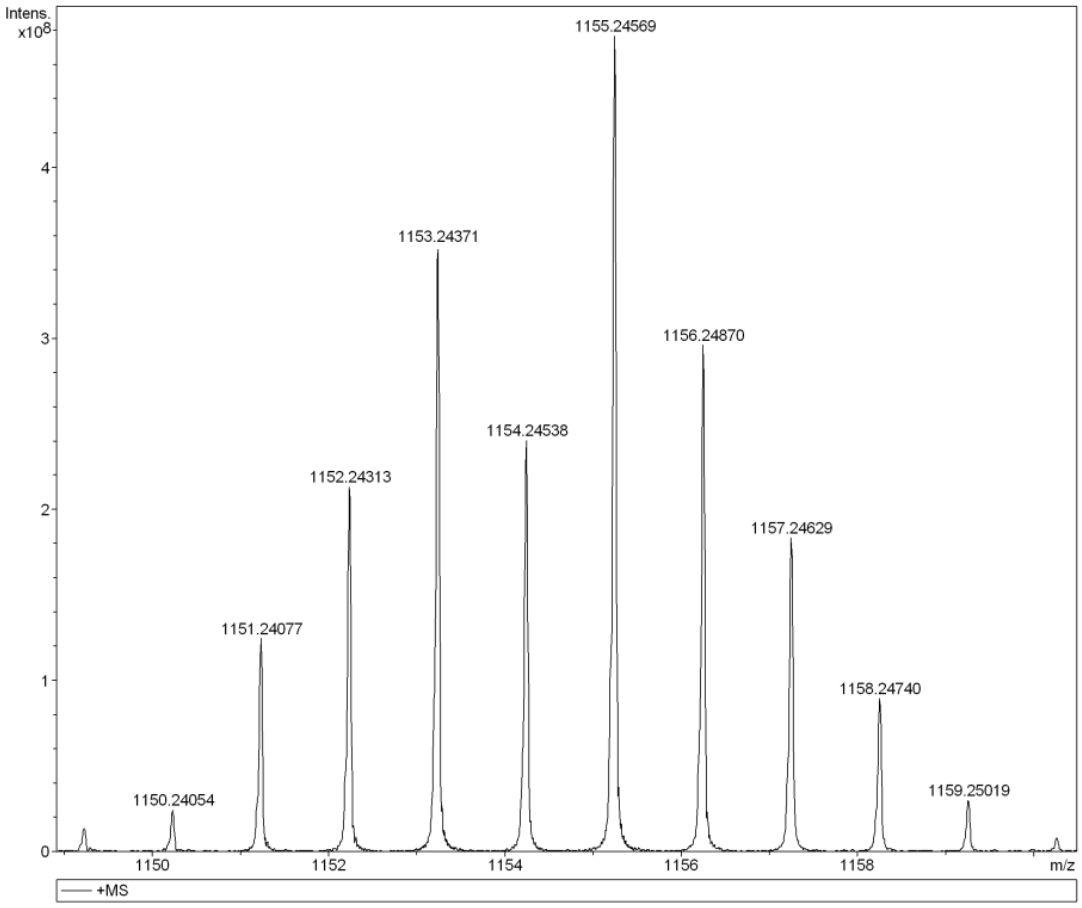


Figure S18. Positive-ion ESI-MS spectrum for complex $[\mathbf{1}]^{+}$measured in methanol.

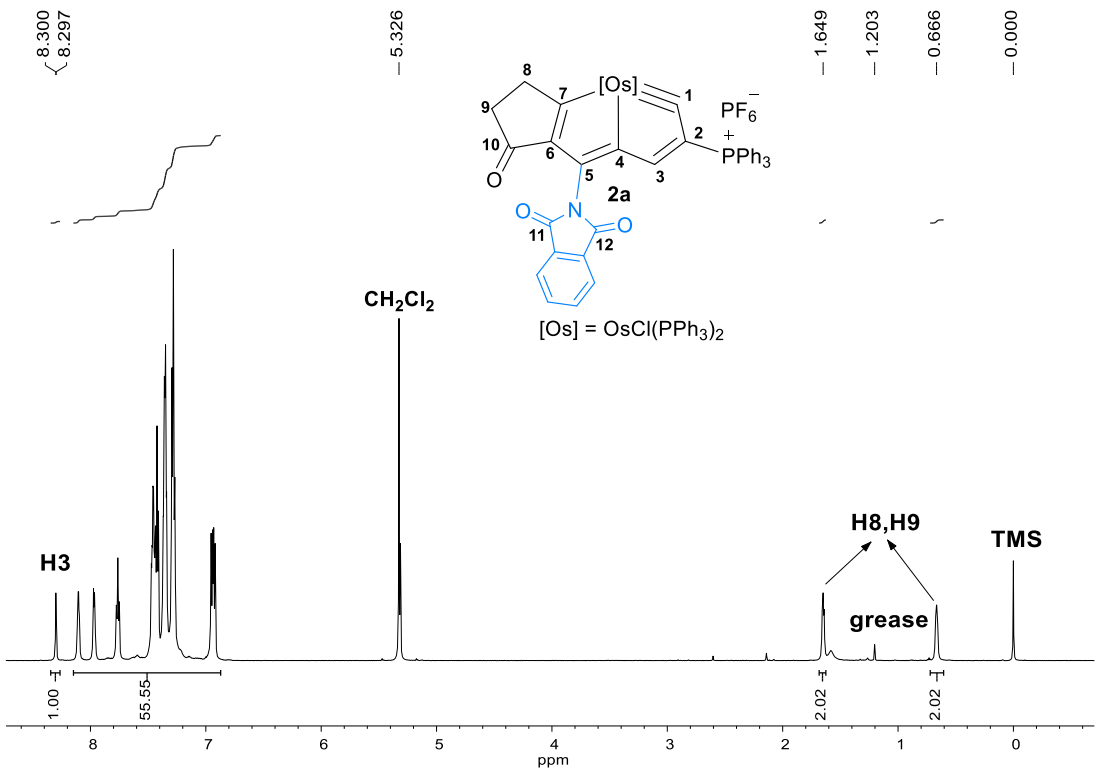


Figure S19. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2a**.

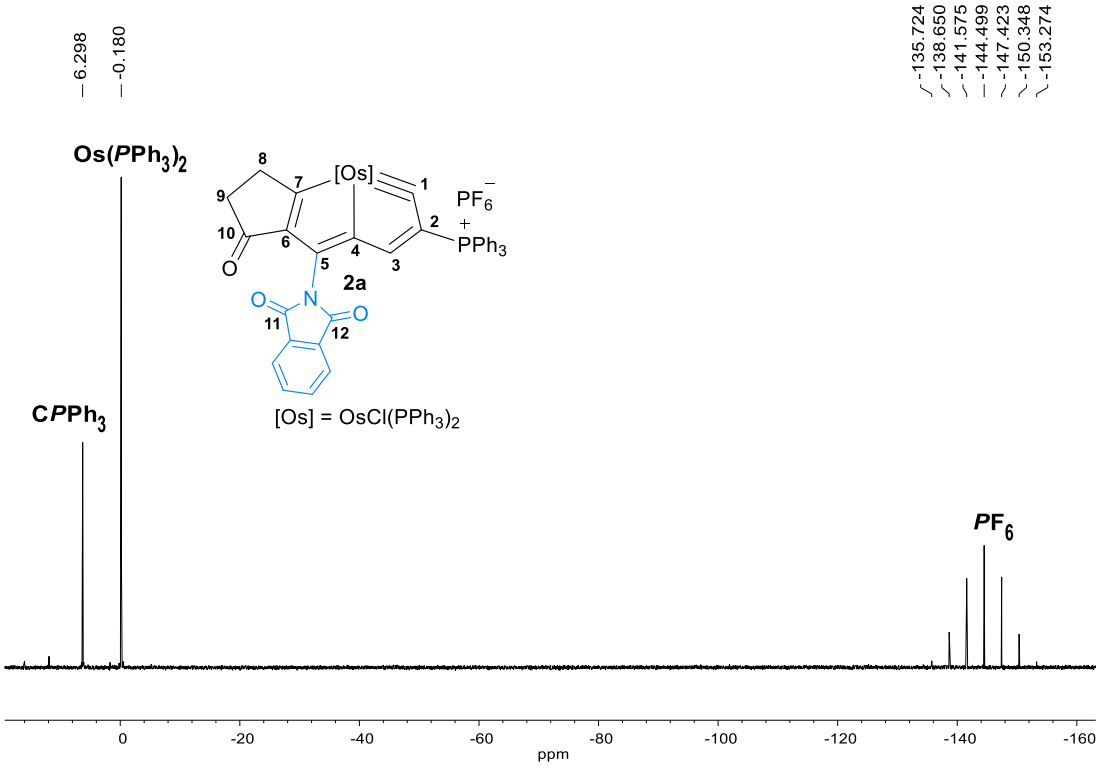


Figure S20. The ^{31}P{^{1}H} NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **2a**.

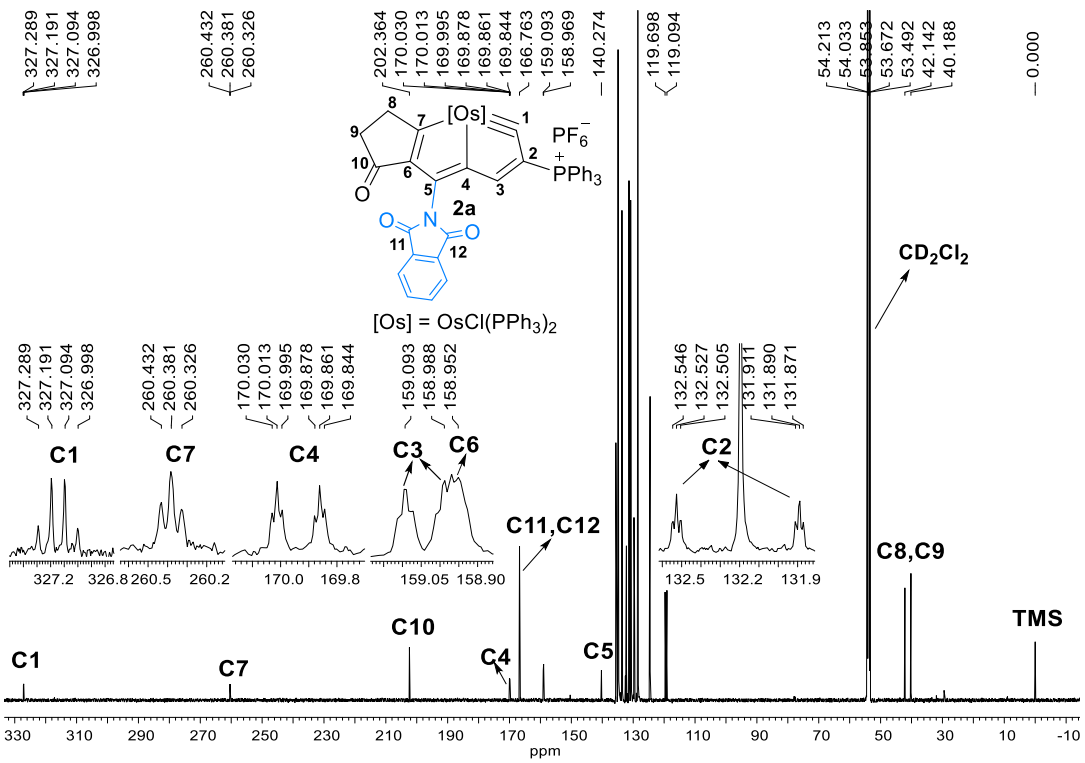


Figure S21. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2a**.

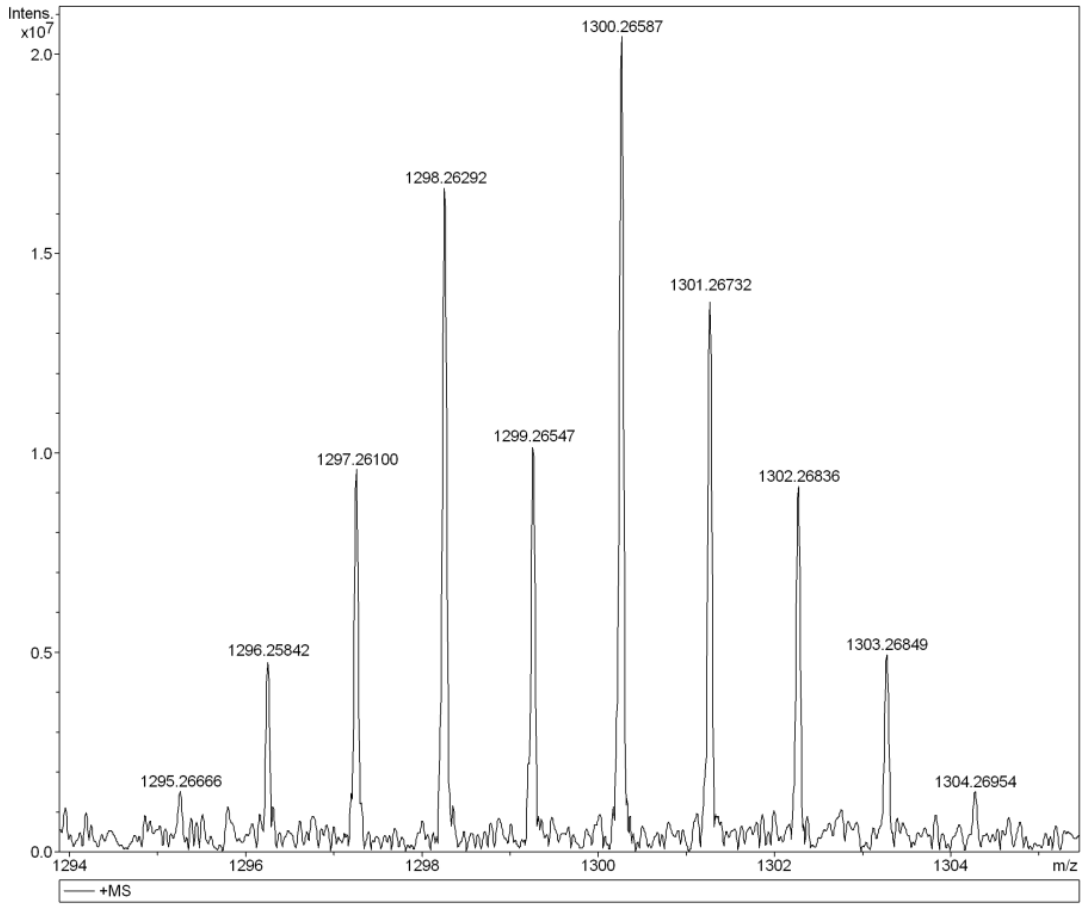


Figure S22. Positive-ion ESI-MS spectrum for complex $[\mathbf{2a}]^+$ measured in methanol.

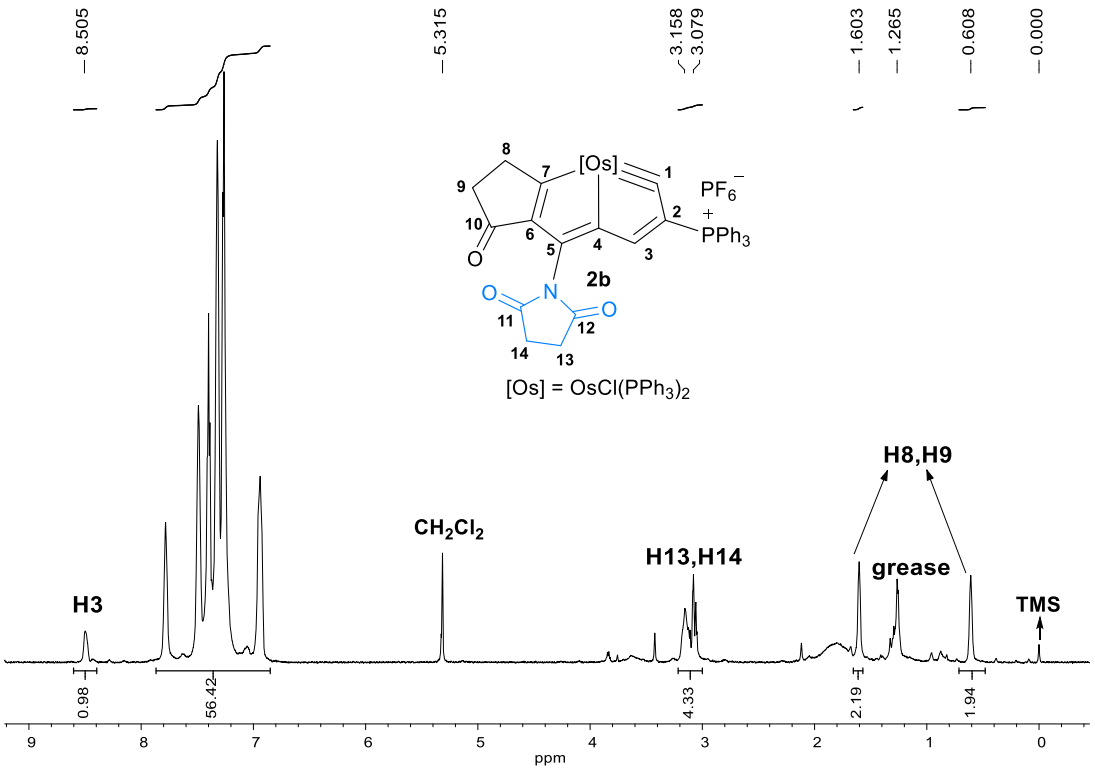


Figure S23. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2b**.

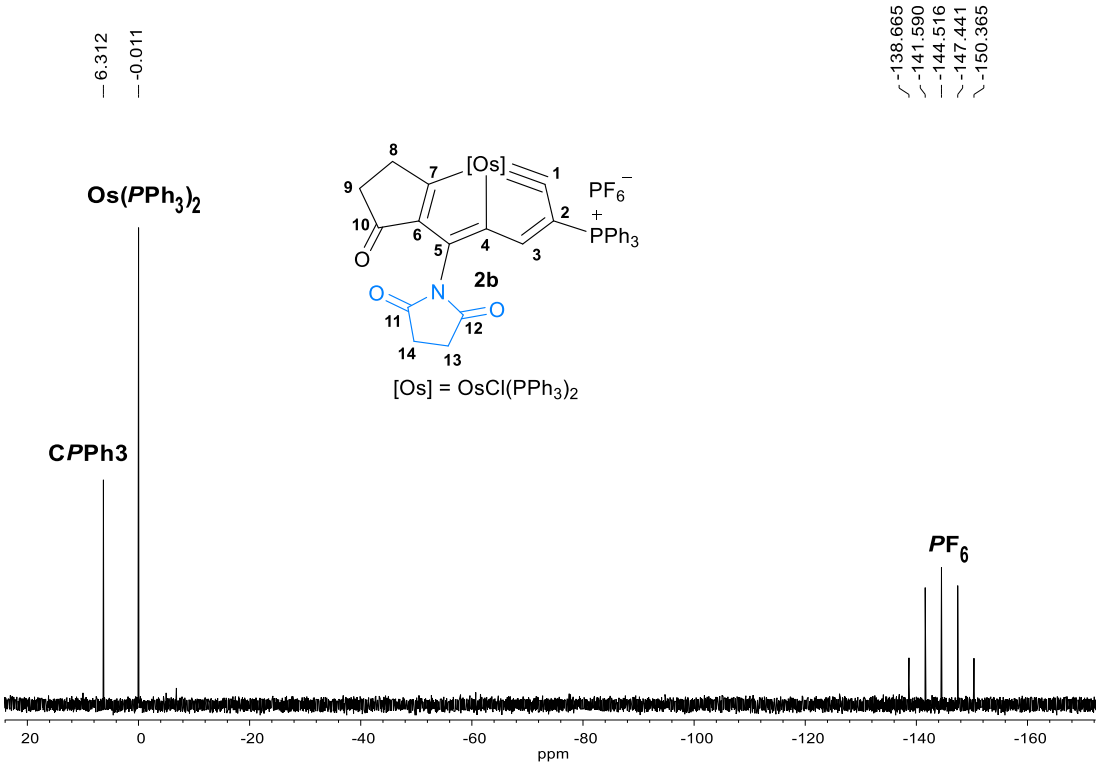


Figure S24. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **2b**.

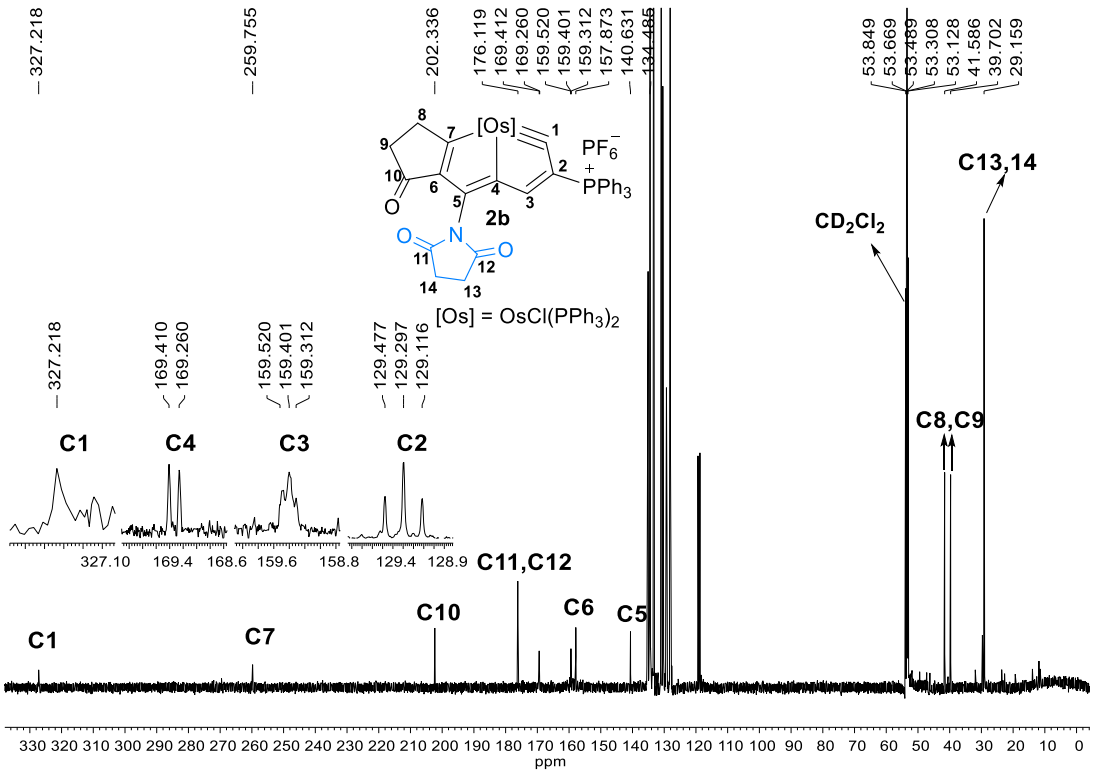


Figure S25. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2b**.

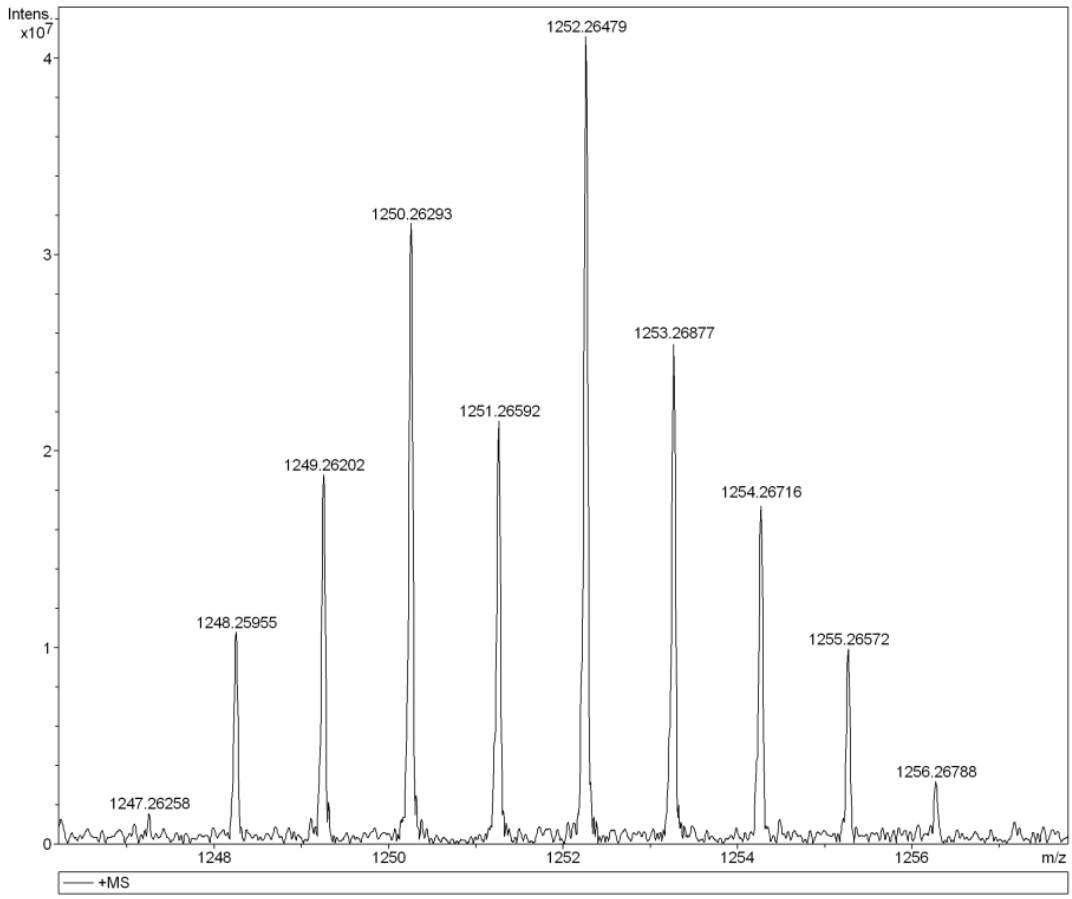


Figure S26. Positive-ion ESI-MS spectrum for complex $[\mathbf{2b}]^+$ measured in methanol.

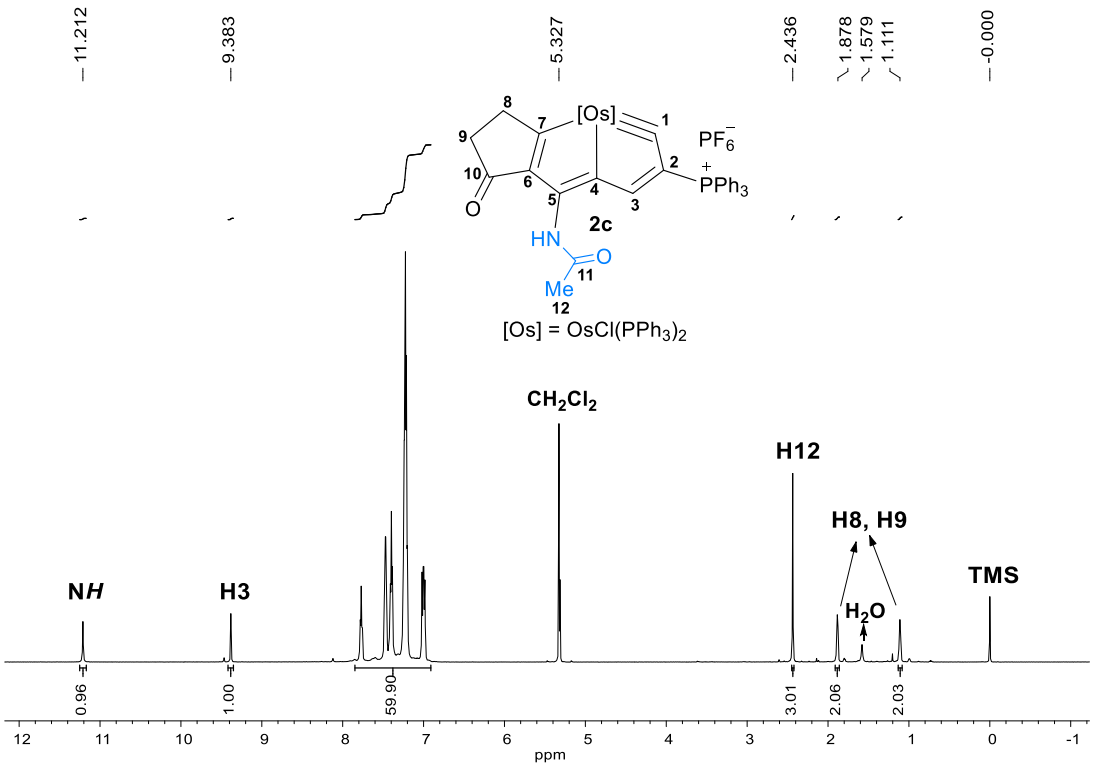


Figure S27. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2c**.

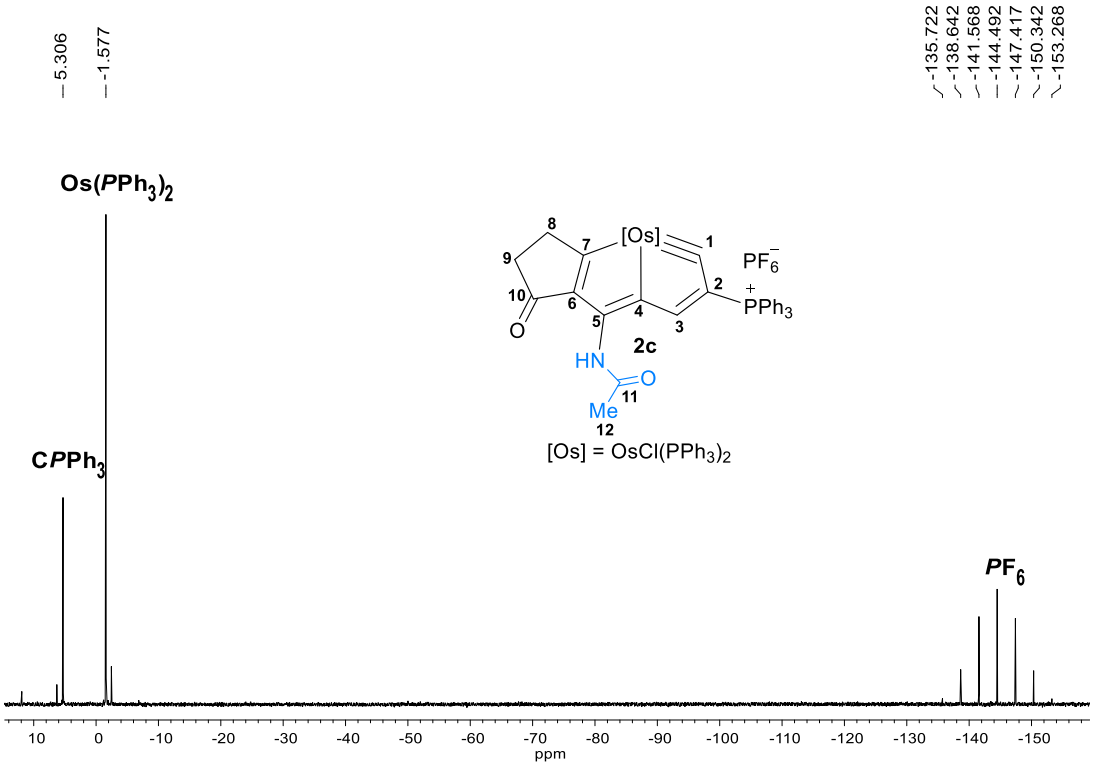


Figure S28. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **2c**.

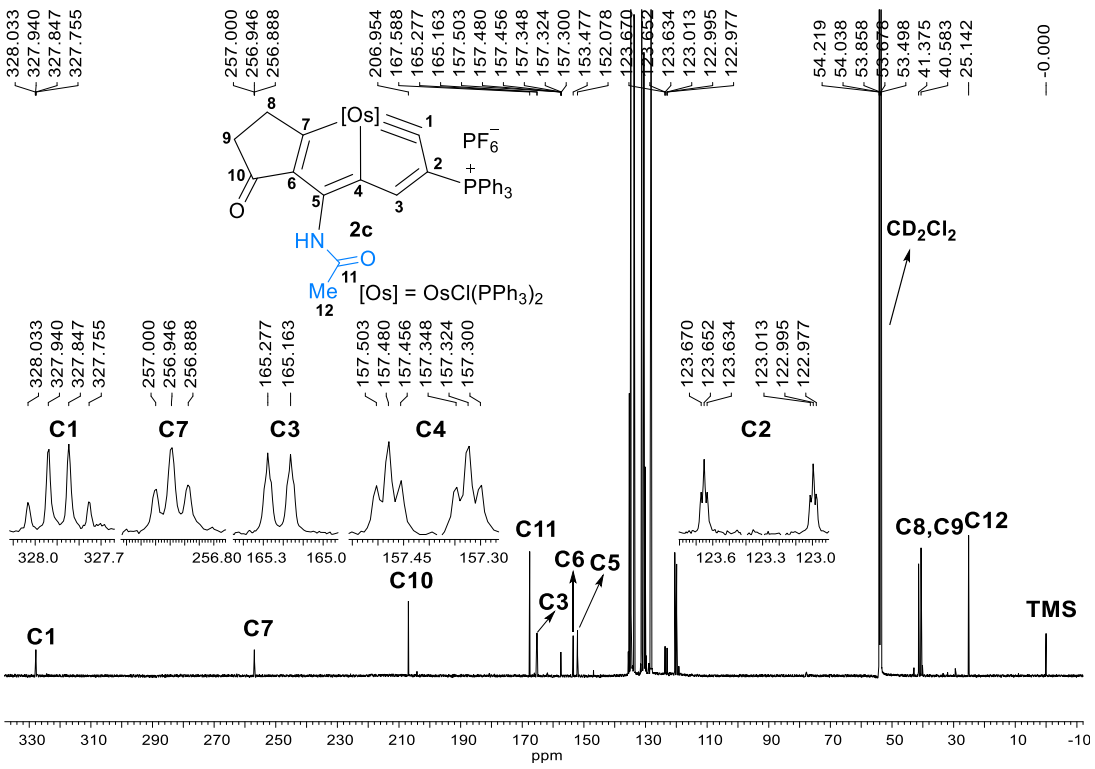


Figure S29. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2c**.

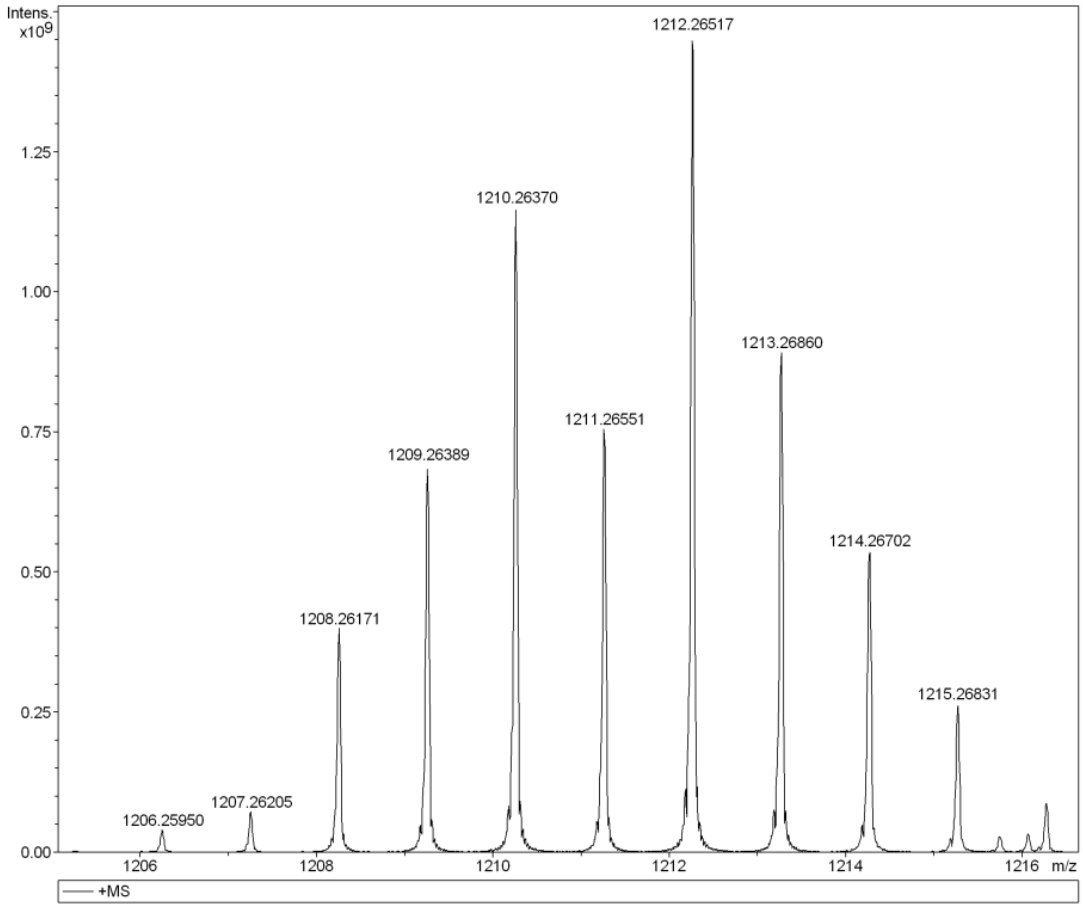


Figure S30. Positive-ion ESI-MS spectrum for complex $[\mathbf{2c}]^+$ measured in methanol.

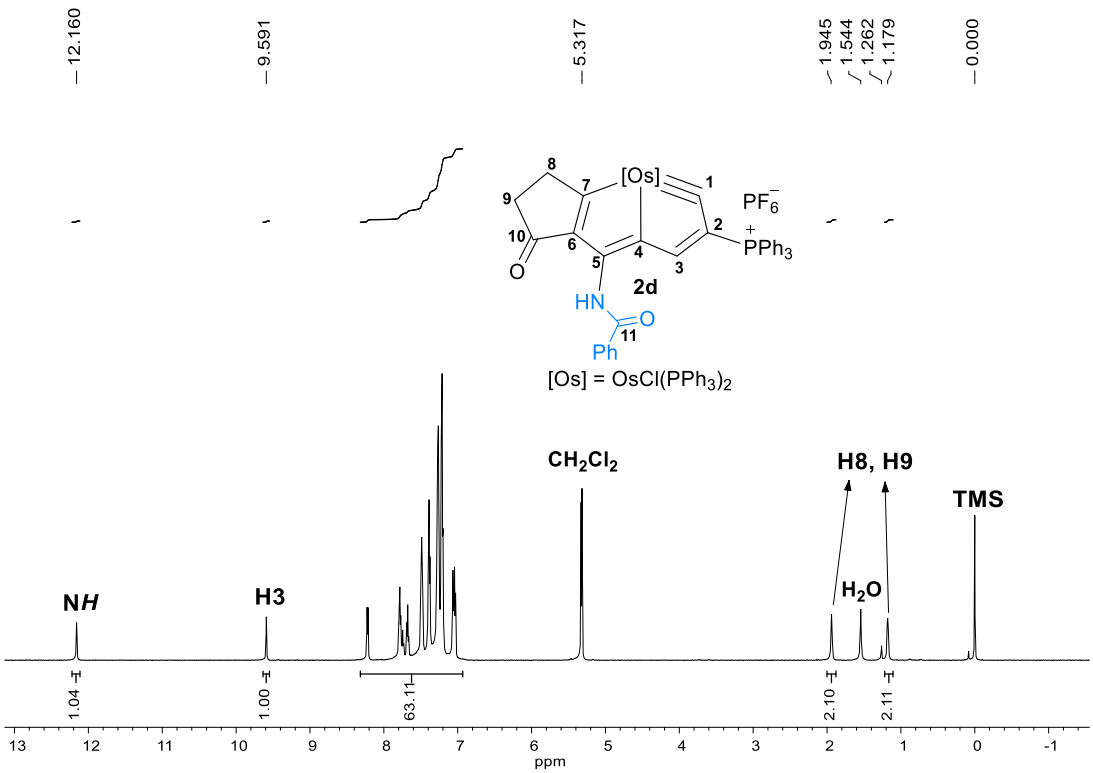


Figure S31. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2d**.

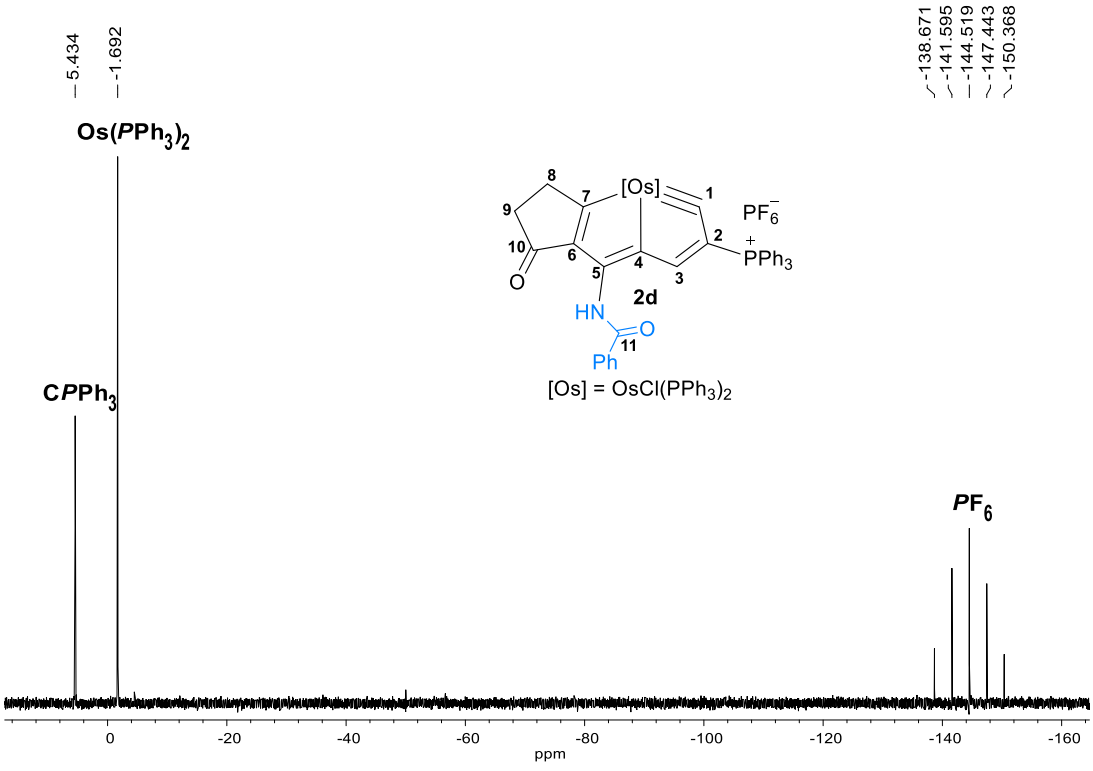


Figure S32. The ^{31}P{^{1}H} NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **2d**.

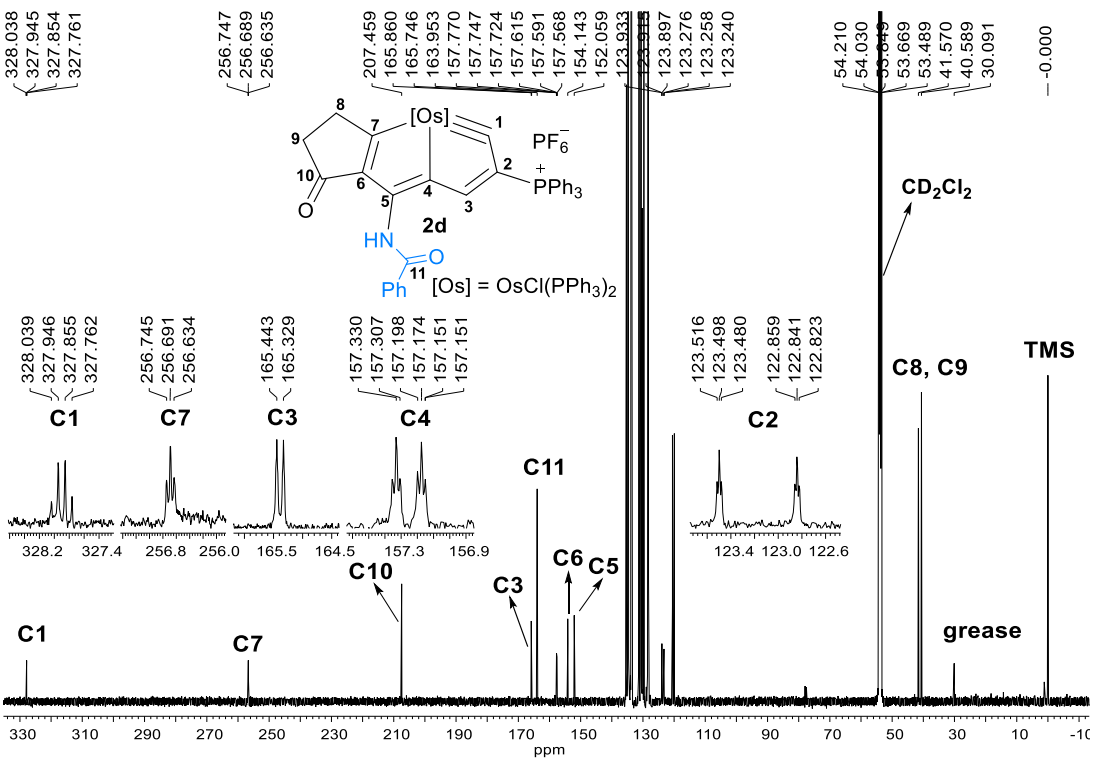


Figure S33. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2d**.

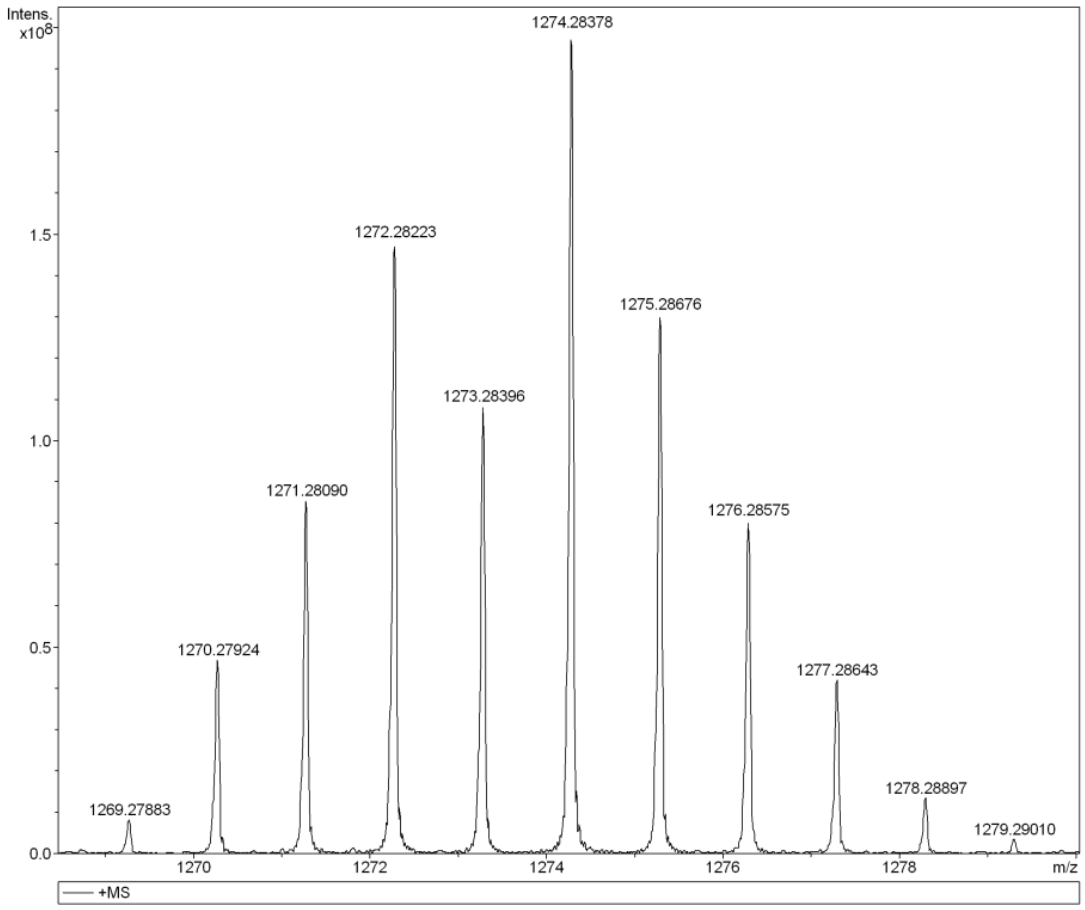


Figure S34. Positive-ion ESI-MS spectrum for complex $[\mathbf{2d}]^+$ measured in methanol.

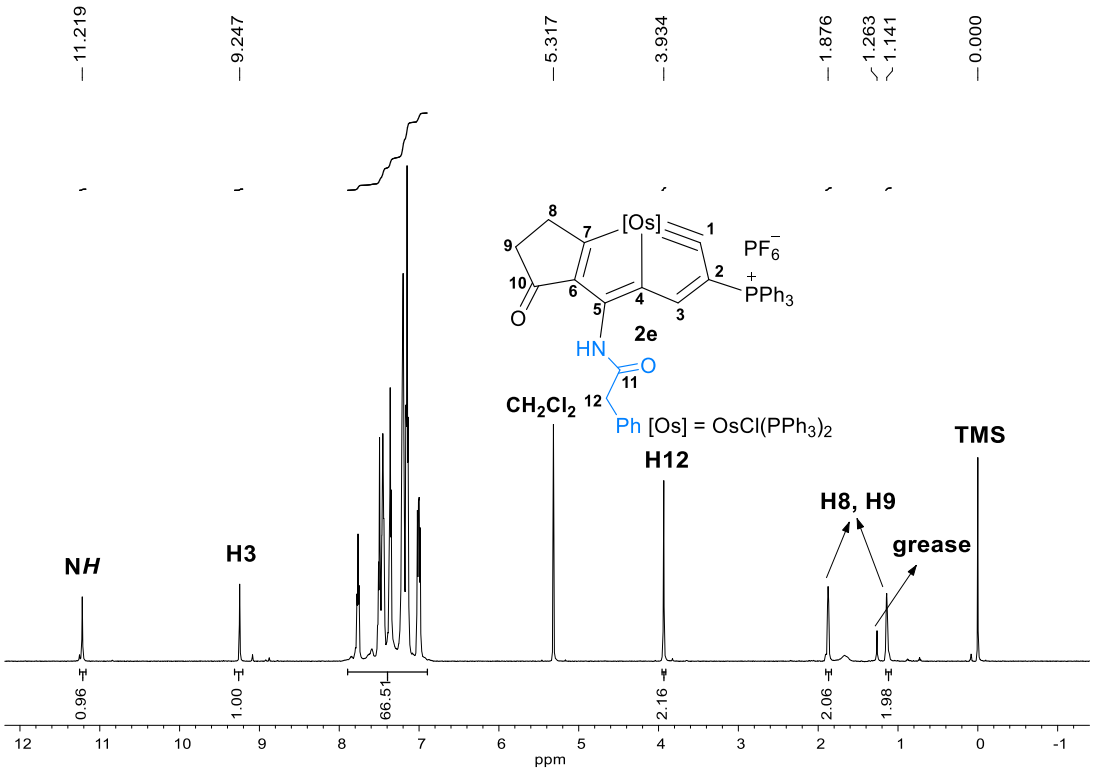


Figure S35. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2e**.

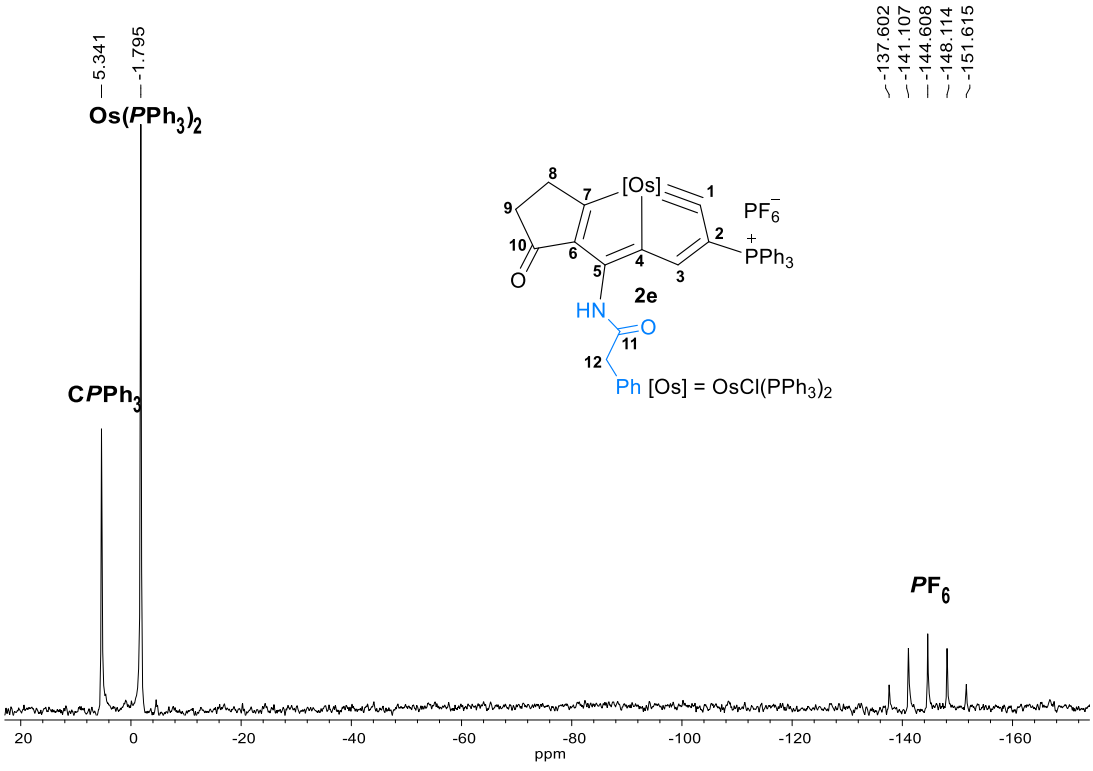


Figure S36. The ^{31}P{^{1}H} NMR spectrum (202.5 MHz, CD_2Cl_2) for complex **2e**.

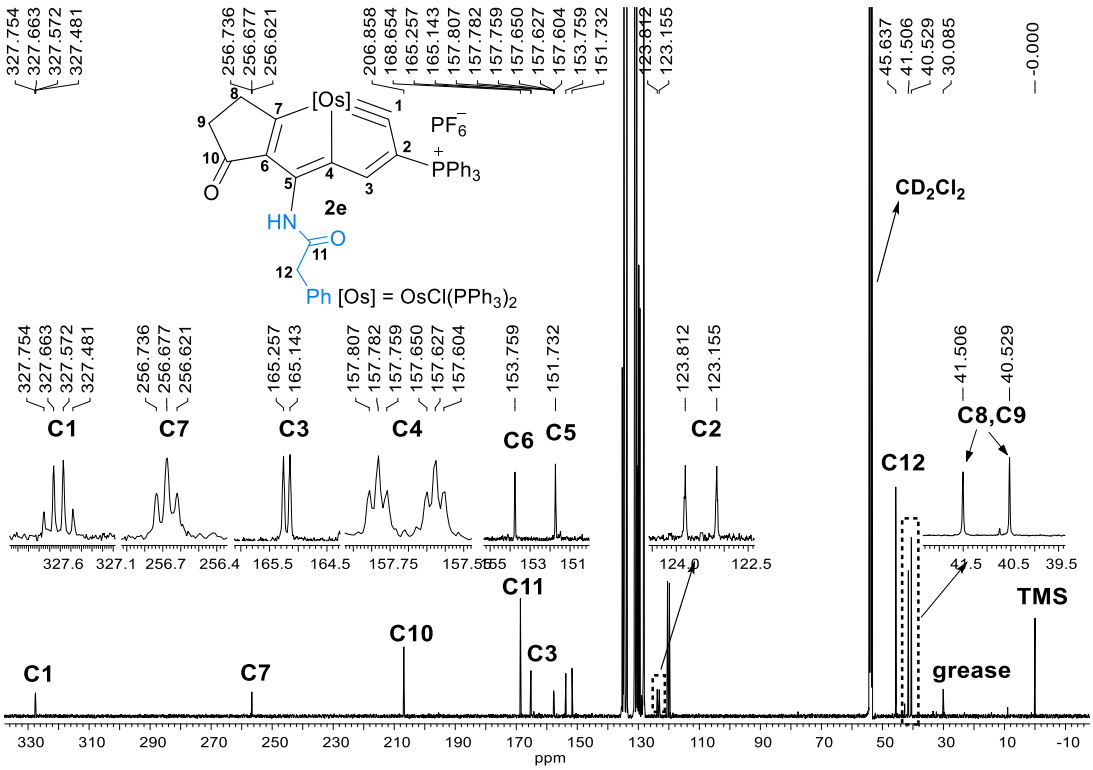


Figure S37. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2e**.

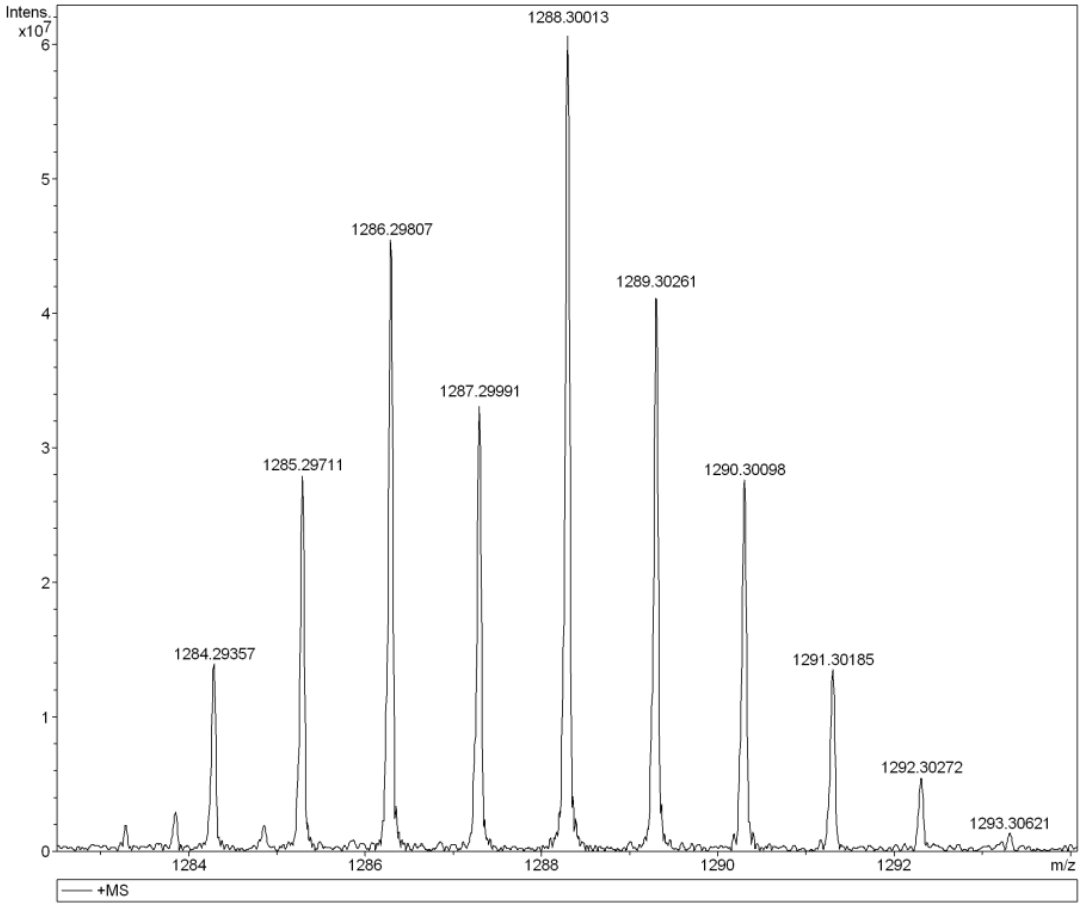


Figure S38. Positive-ion ESI-MS spectrum for complex $[\mathbf{2e}]^+$ measured in methanol.

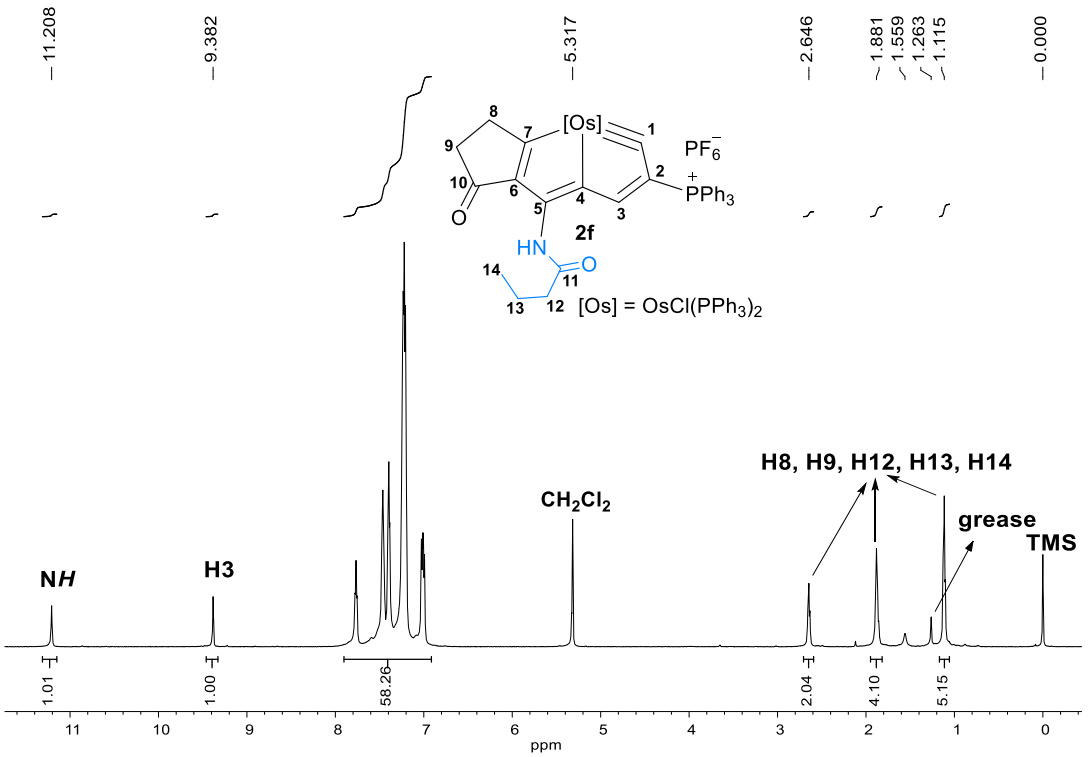


Figure S39. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2f**.

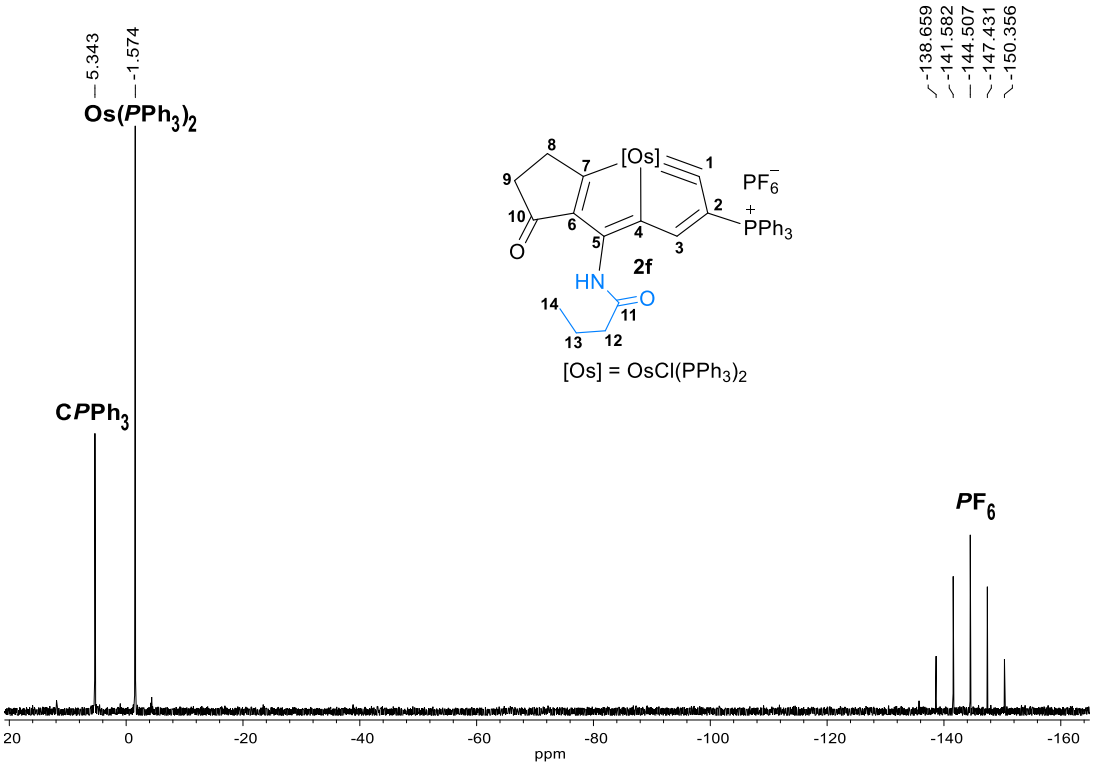


Figure S40. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **2f**.

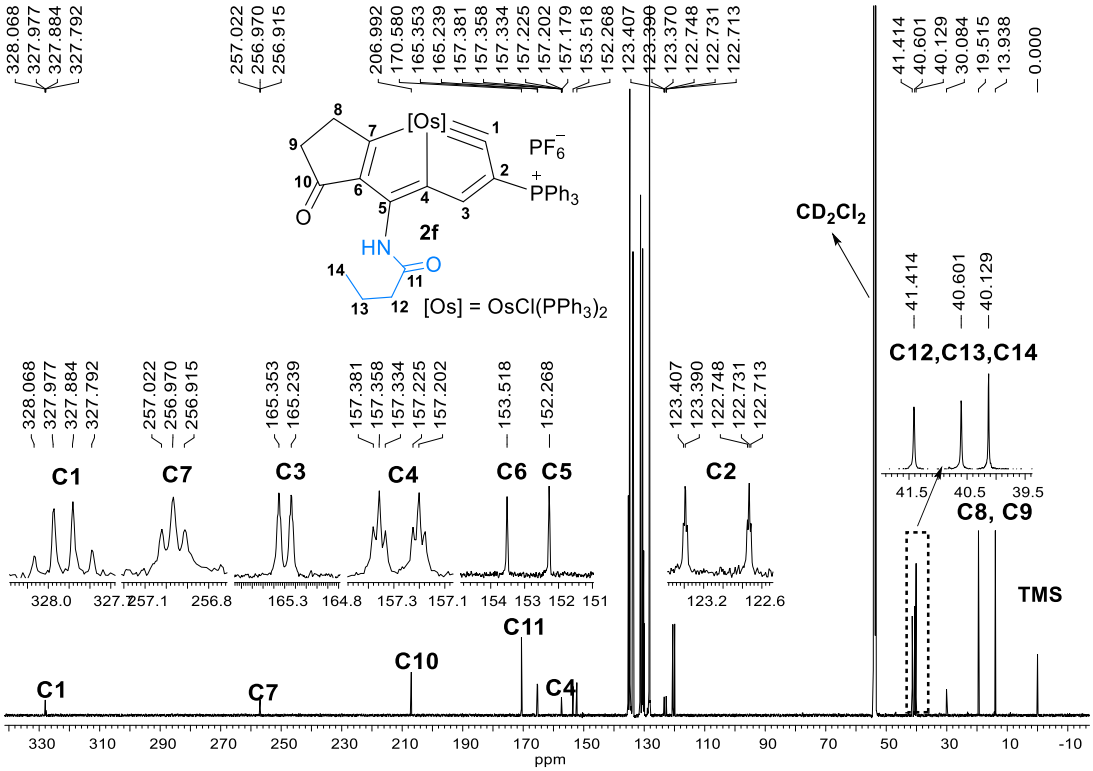


Figure S41. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2f**.

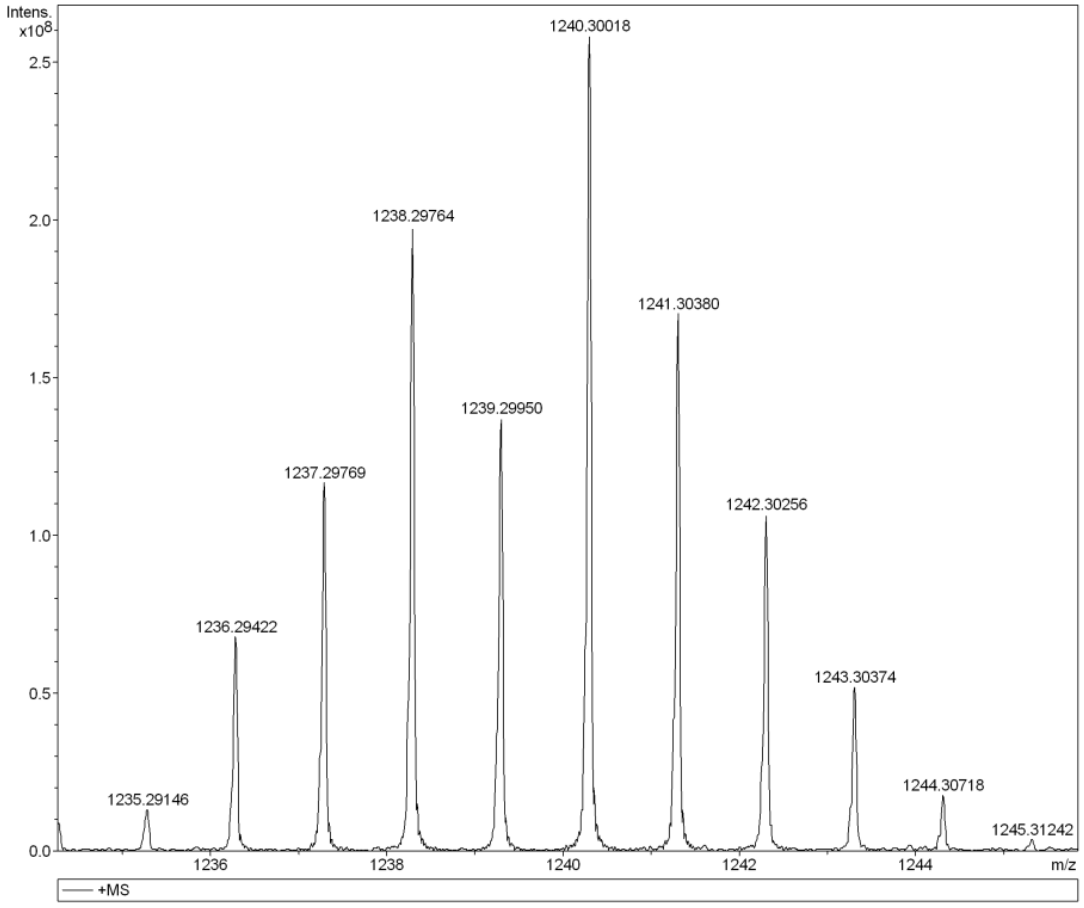


Figure S42. Positive-ion ESI-MS spectrum for complex $[\mathbf{2f}]^+$ measured in methanol.

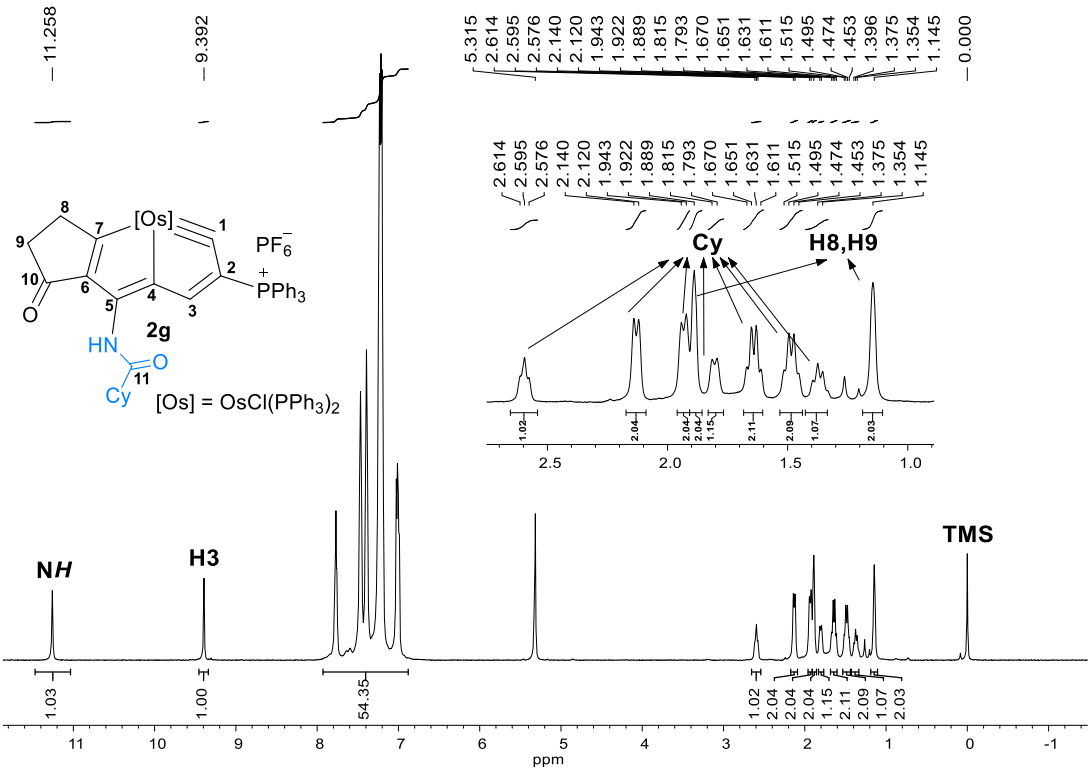


Figure S43. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2g**.

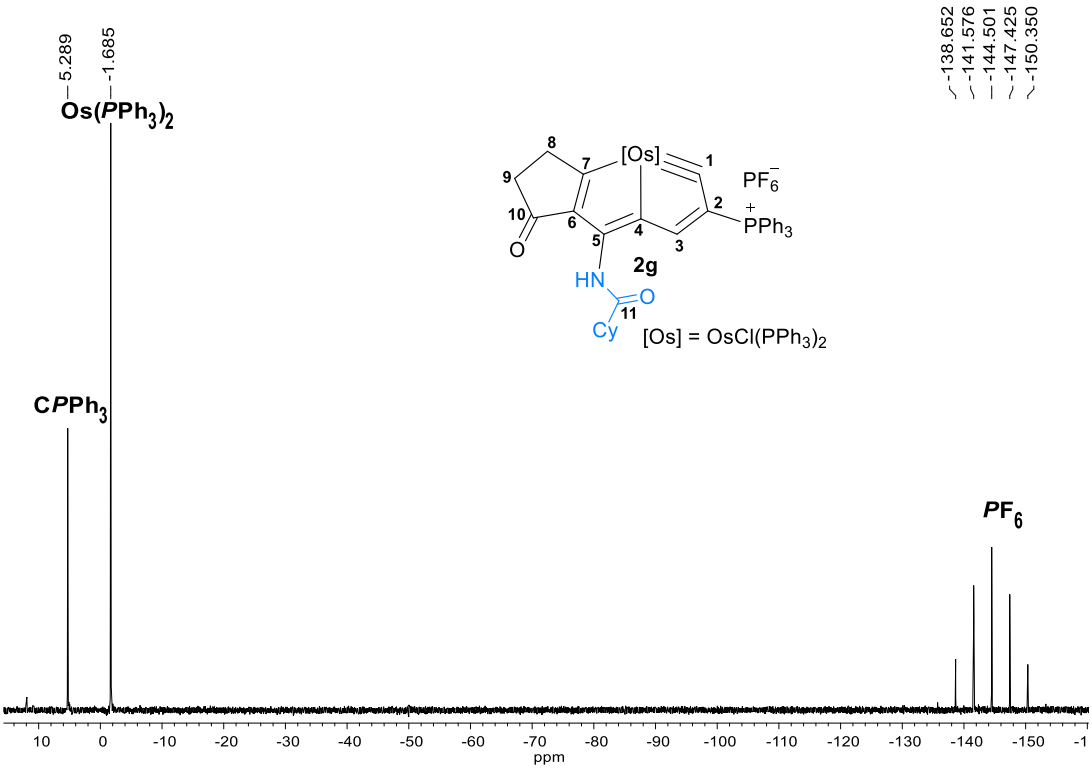


Figure S44. The ^{31}P{^{1}H} NMR spectrum (242.9 MHz, CD_2Cl_2) for complex **2g**.

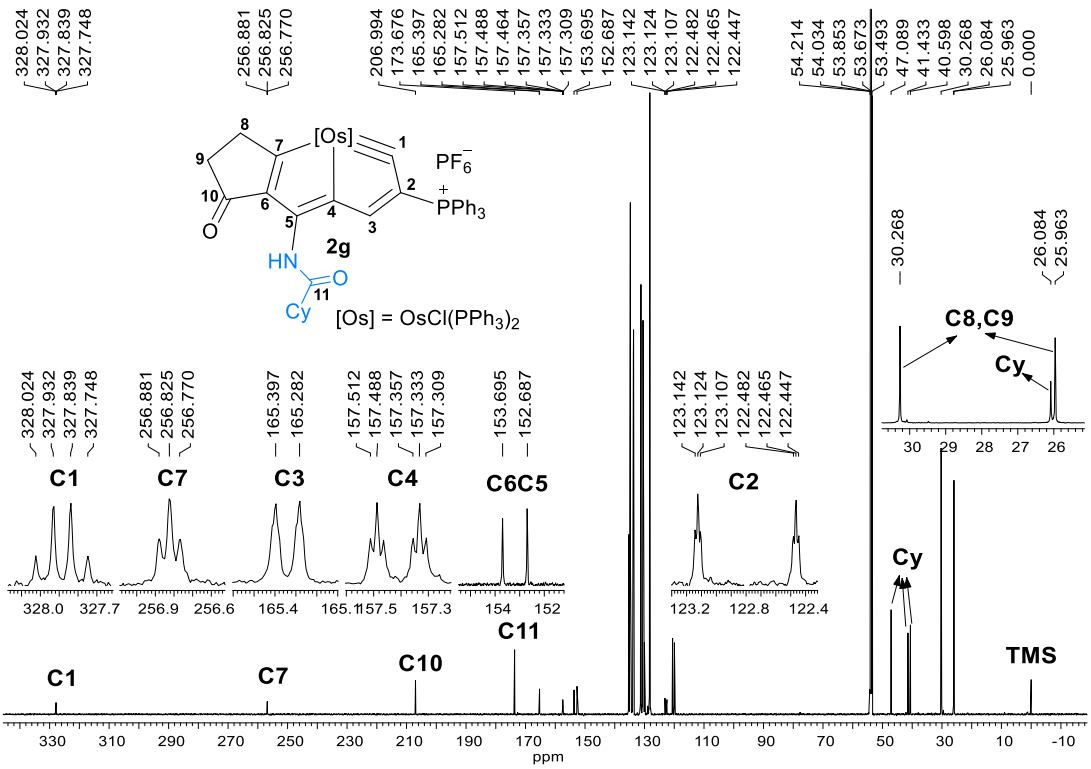


Figure S45. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2g**.

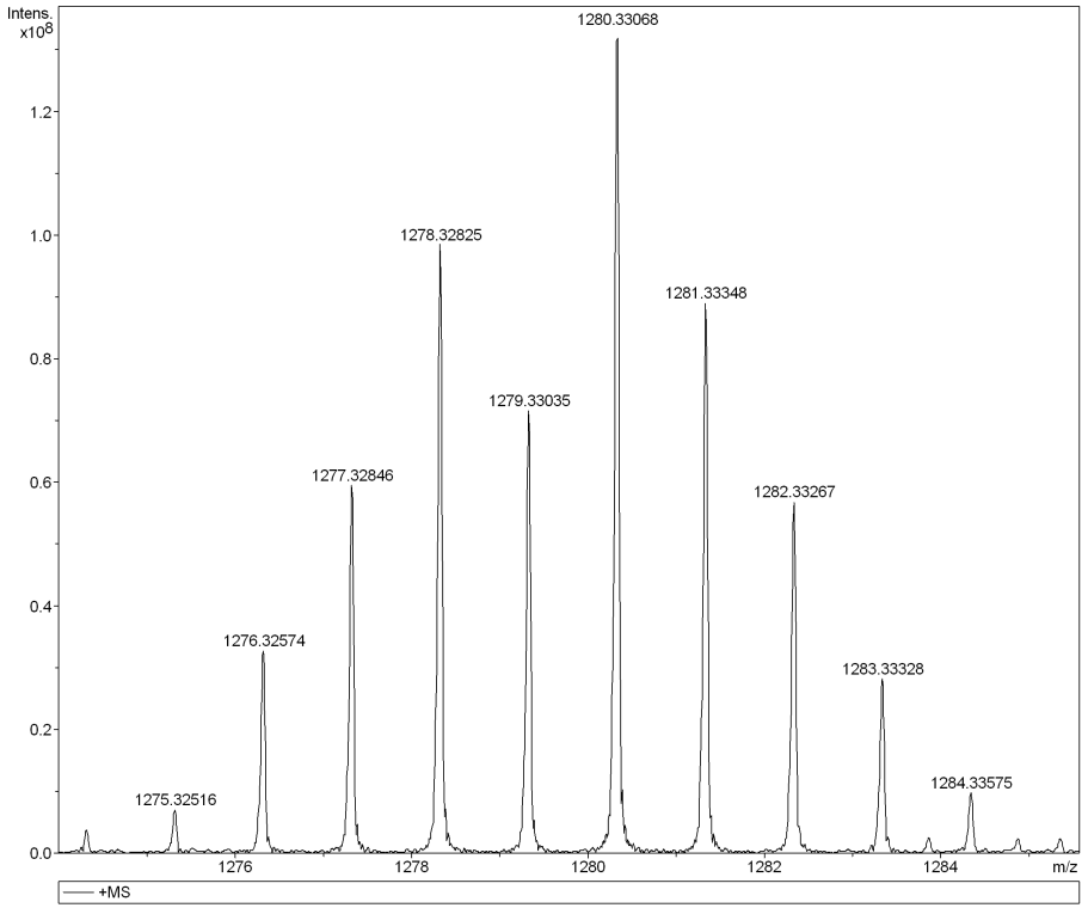


Figure S46. Positive-ion ESI-MS spectrum for complex $[\mathbf{2g}]^+$ measured in methanol.

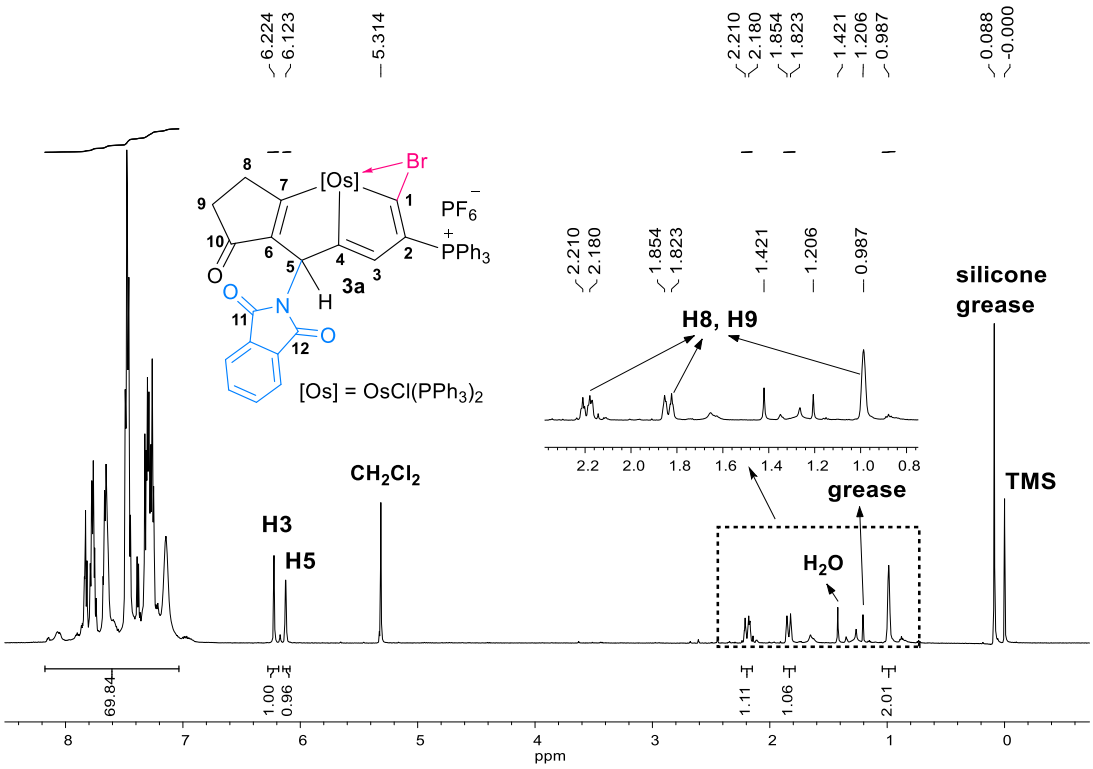


Figure S47. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3a**.

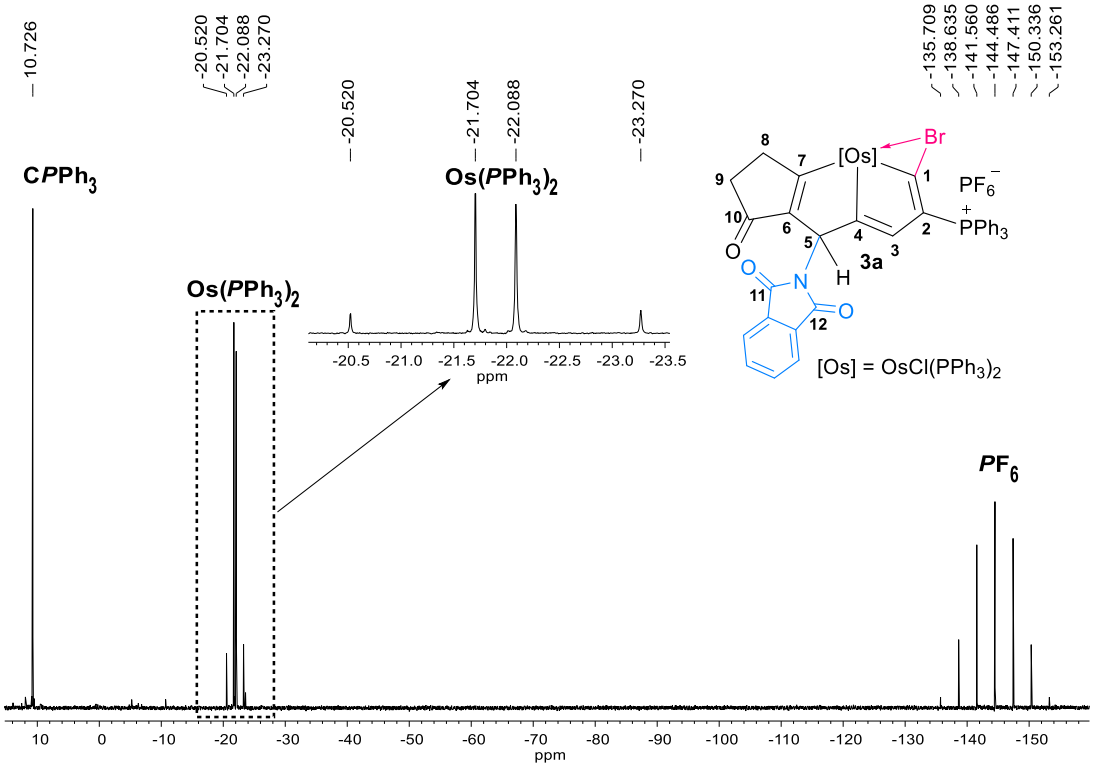


Figure S48. The ^{31}P {^{1}H} NMR *in-situ* spectrum (242.9 MHz, CD_2Cl_2) for complex **3a**.

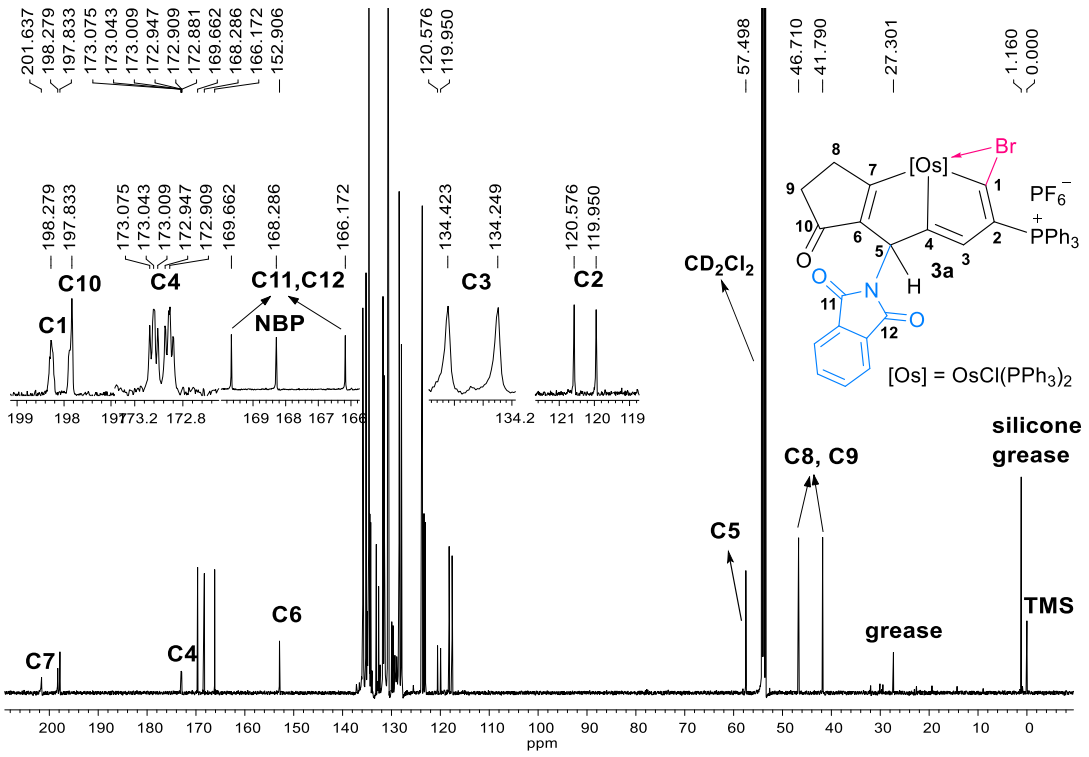


Figure S49. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3a**.

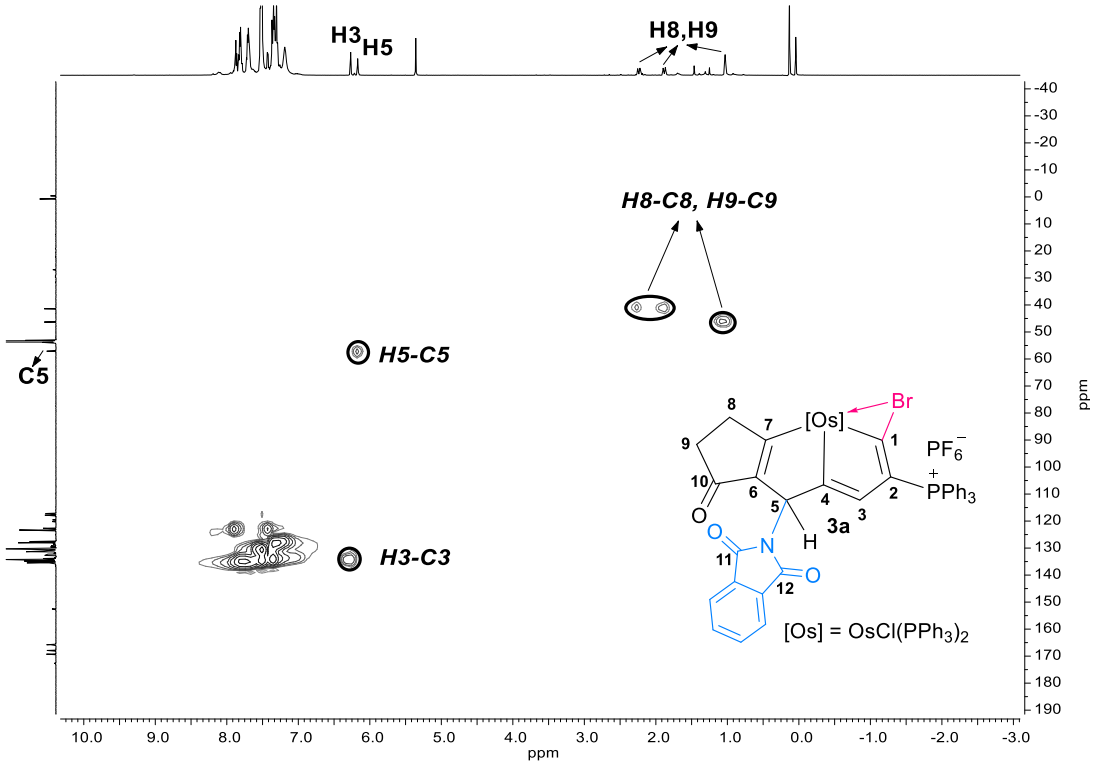


Figure S50. The ^{1}H-^{13}C HSQC (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3a**.

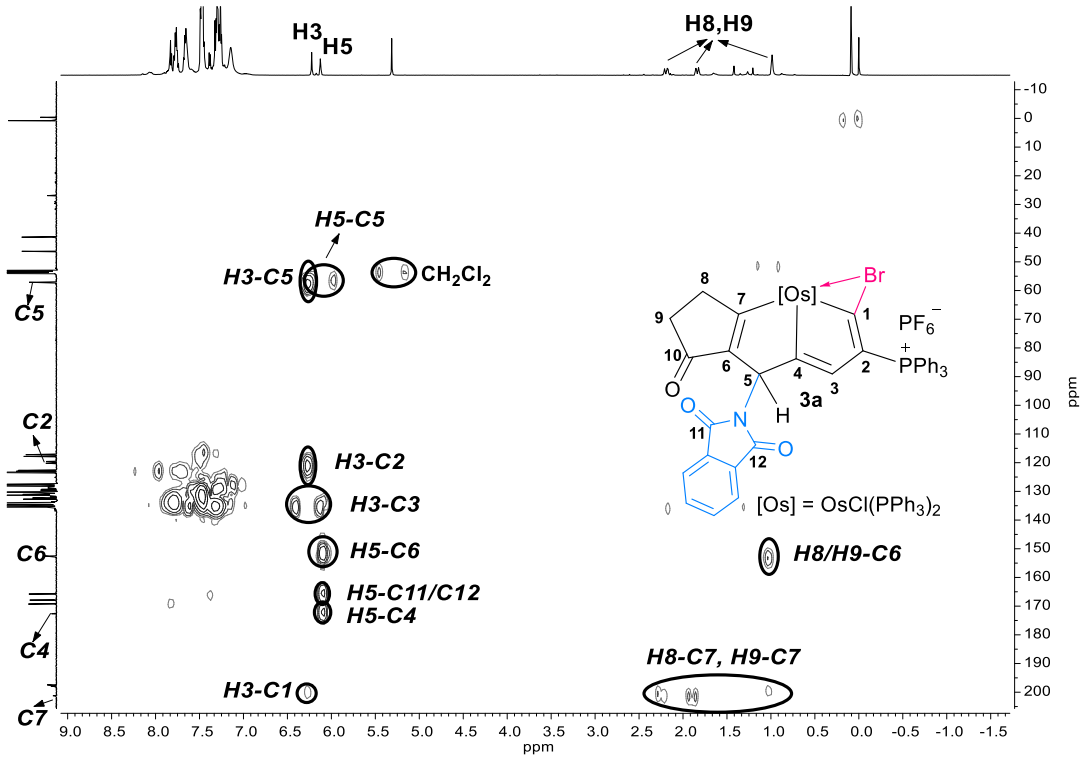


Figure S51. The ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3a**.

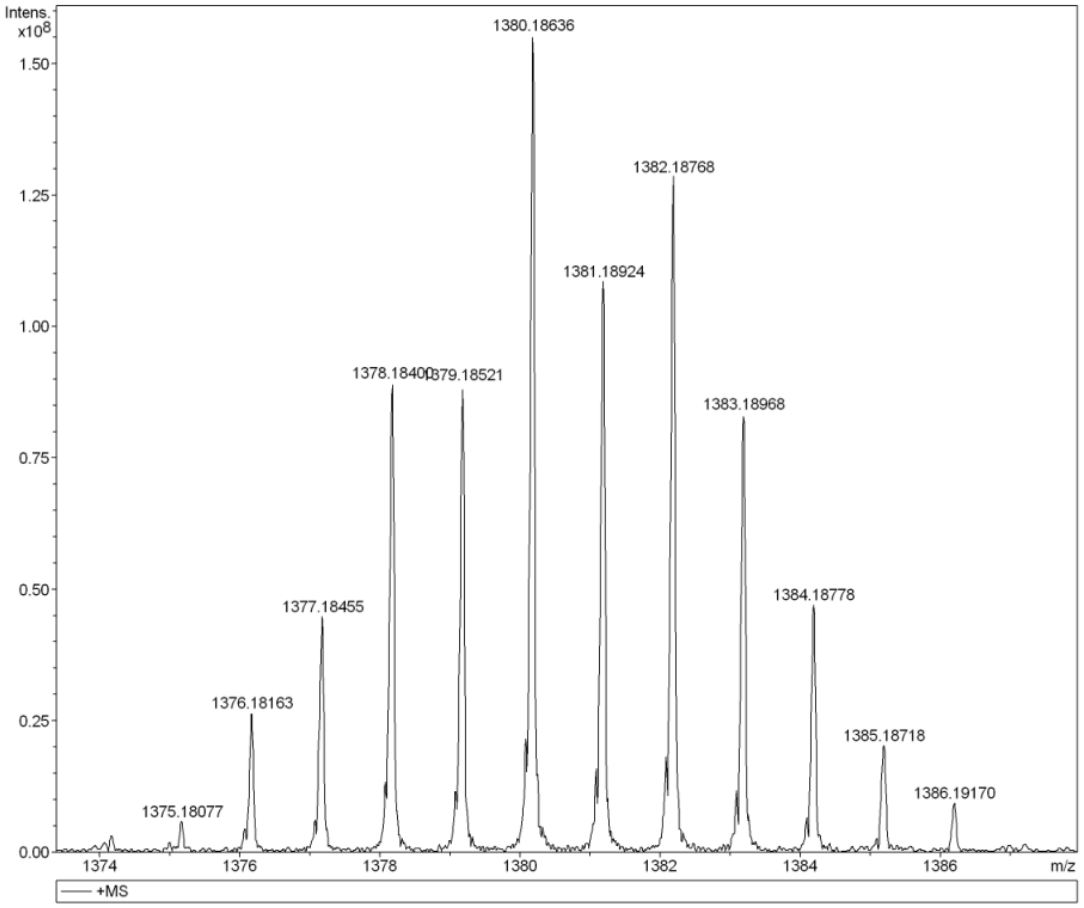


Figure S52. Positive-ion ESI-MS spectrum for complex [**3a**]$^{+}$ measured in methanol.

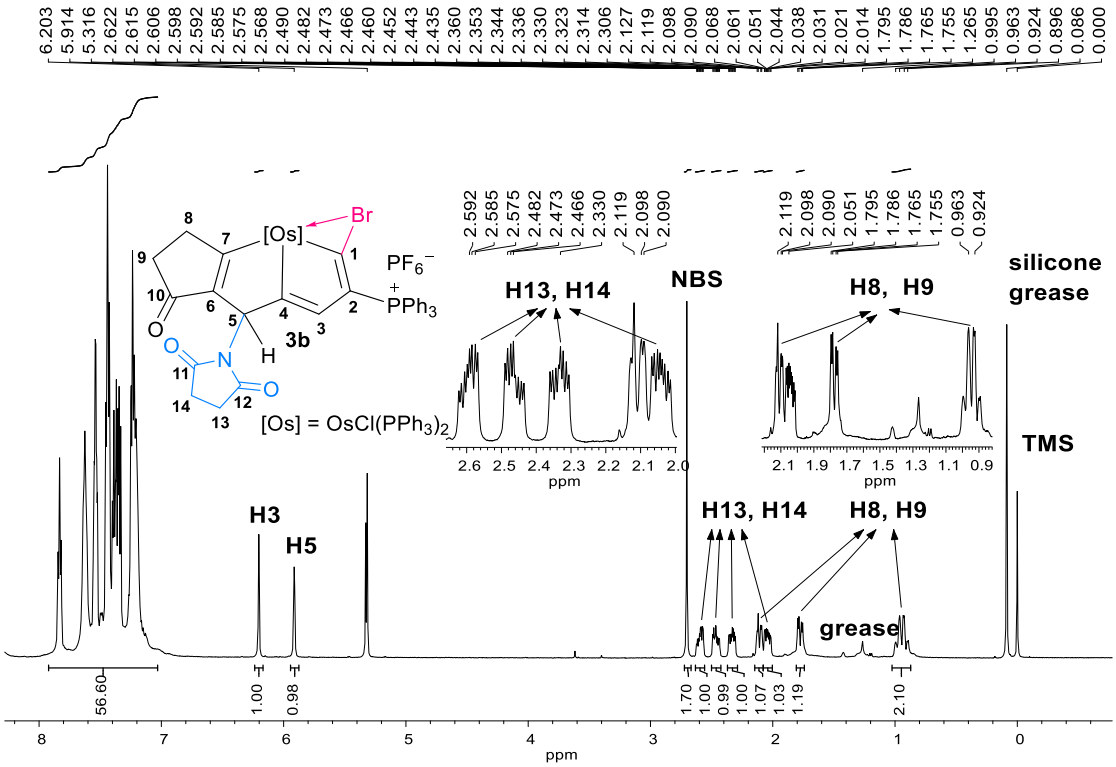


Figure S53. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3b**.

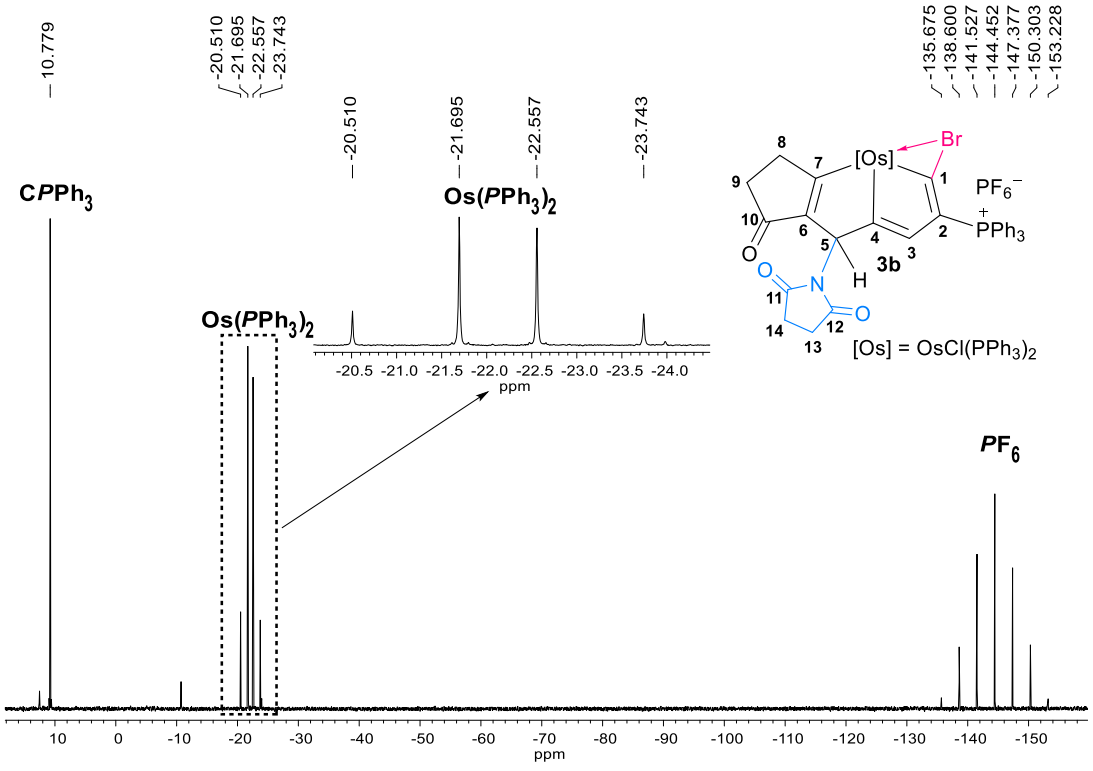


Figure S54. The ^{31}P{^{1}H} NMR *in-situ* spectrum (242.9 MHz, CD_2Cl_2) for complex **3b**.

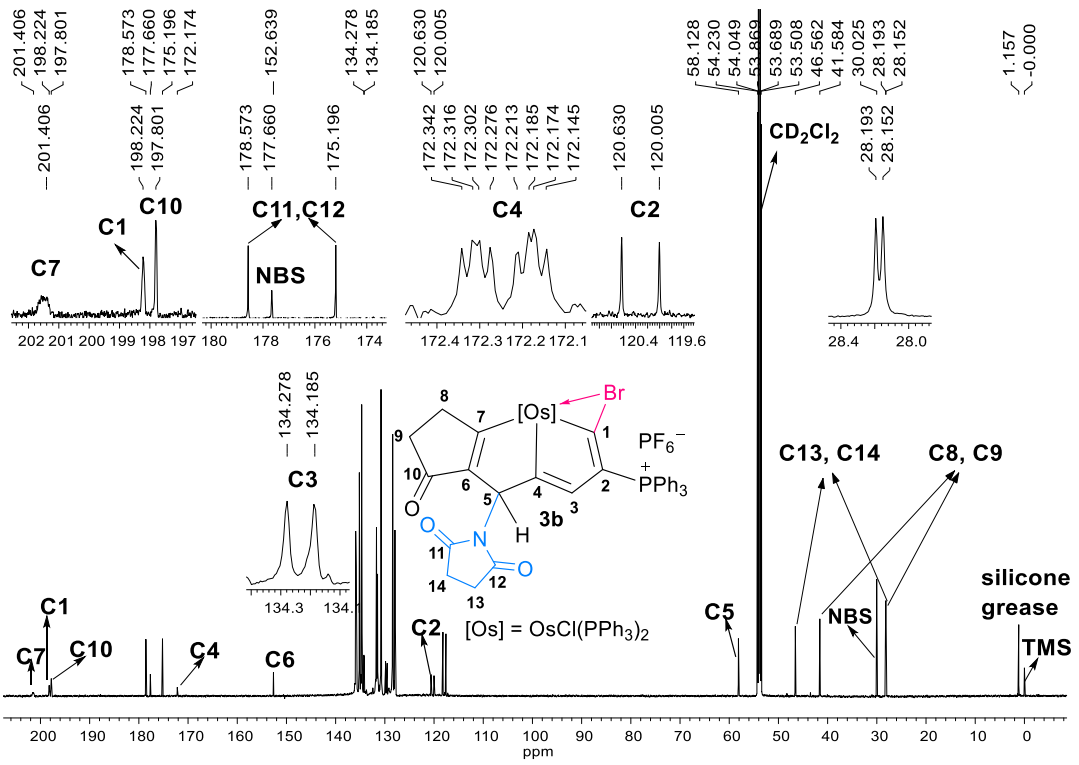


Figure S55. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3b**.

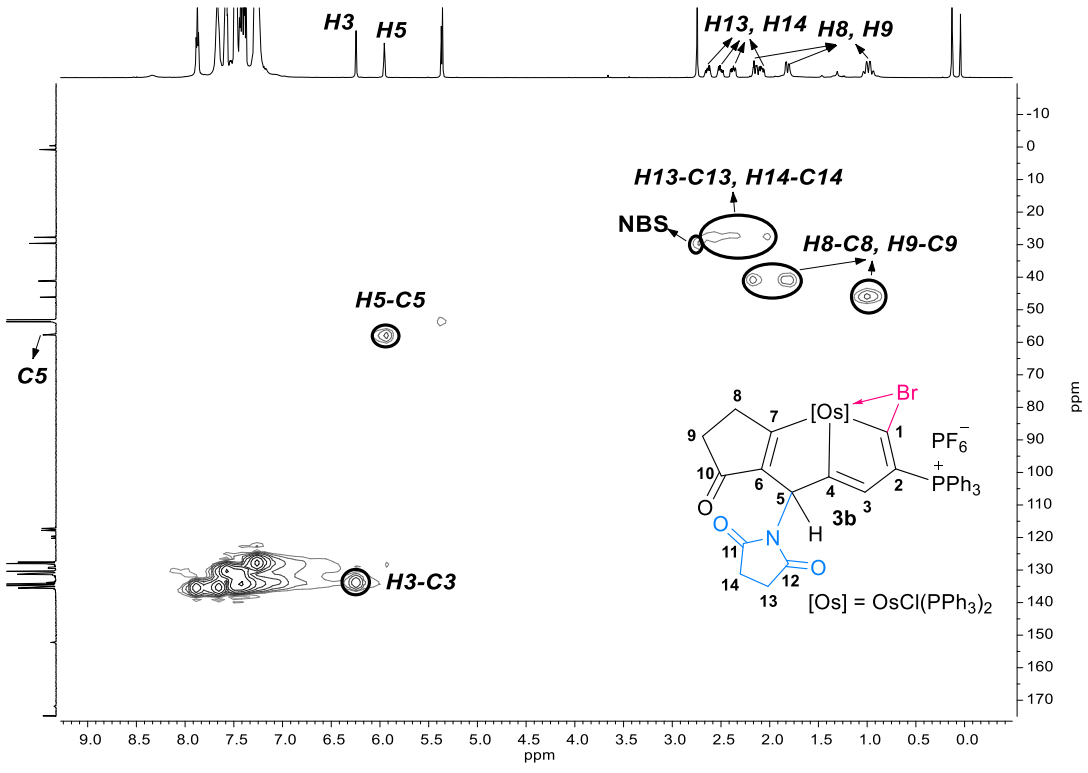


Figure S56. The ^{1}H-^{13}C HSQC (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3b**.

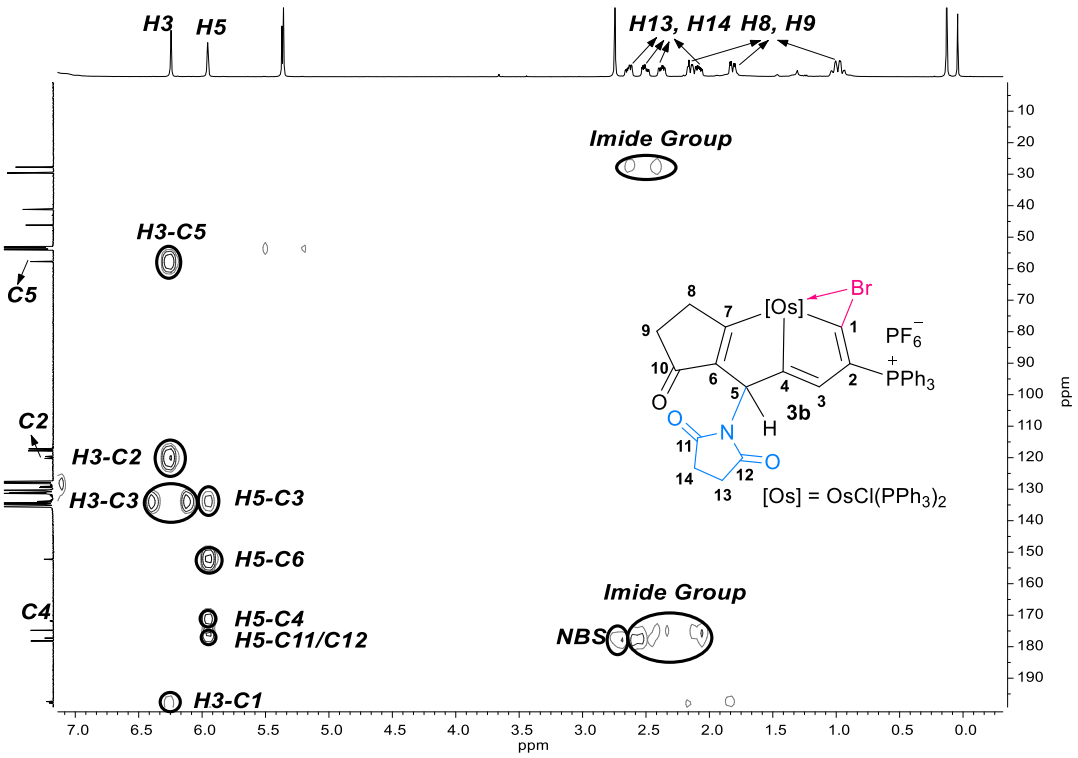


Figure S57. The ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **3b**.

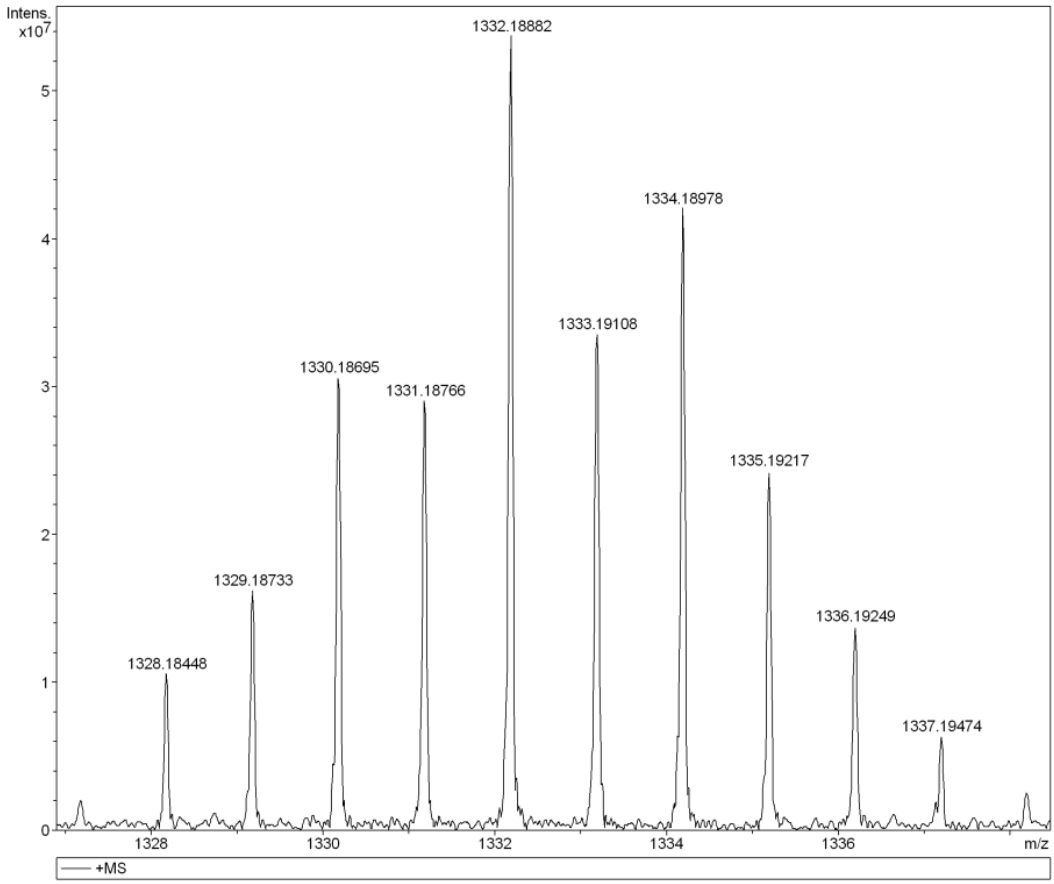


Figure S58. Positive-ion ESI-MS spectrum for complex [**3b**]$^{+}$ measured in methanol.

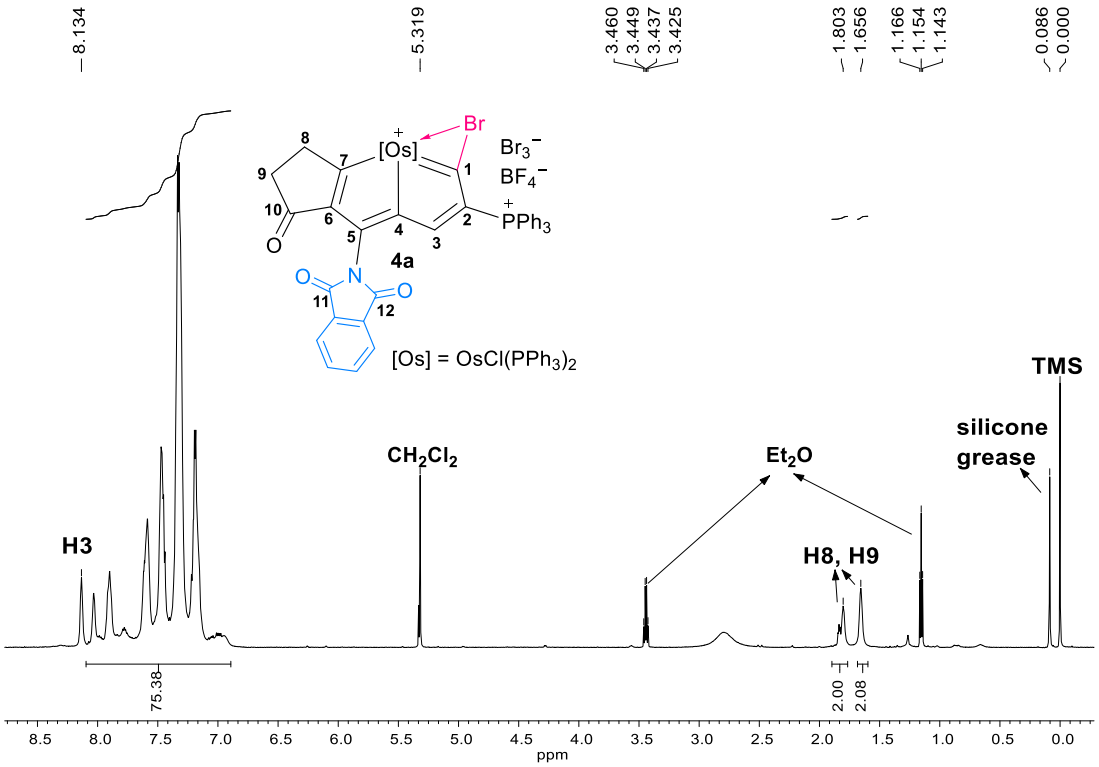


Figure S59. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) *in-situ* spectrum for complex **4a**.(The signal of H3 was observed in aromatic region and could not be integrated reliably.)

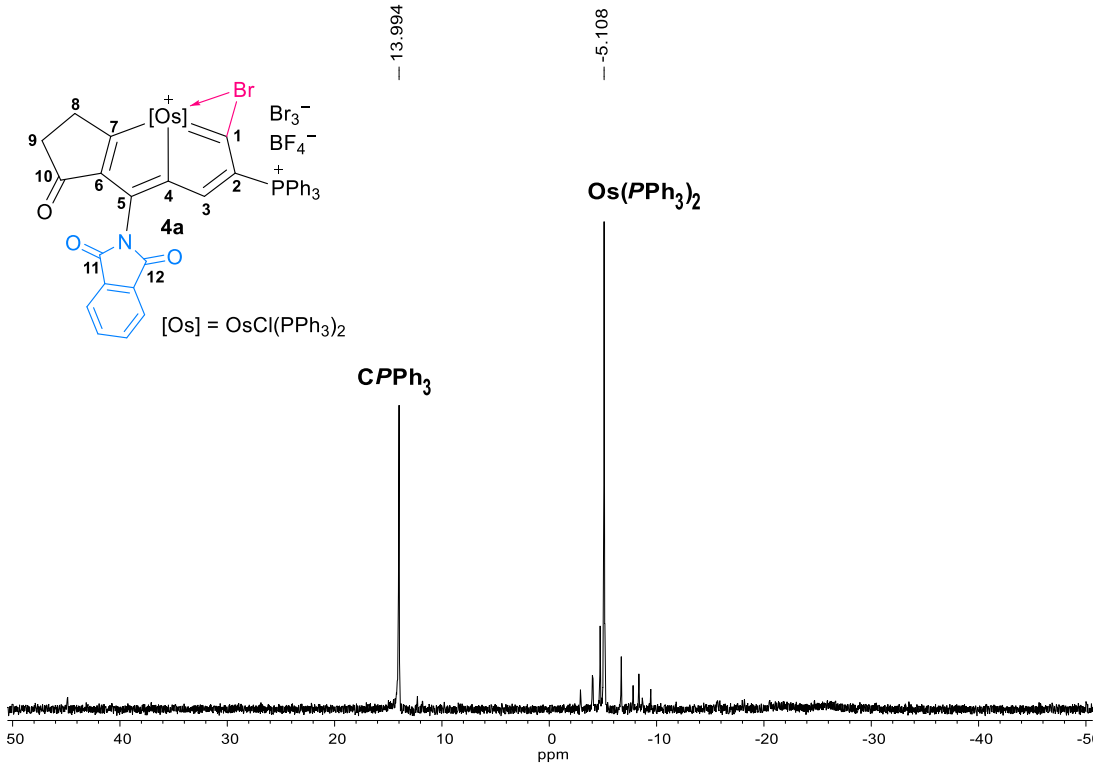


Figure S60. The $^{31}P\{^{1}H\}$ NMR *in-situ* spectrum (242.9 MHz, CD_2Cl_2) for complex **4a**.

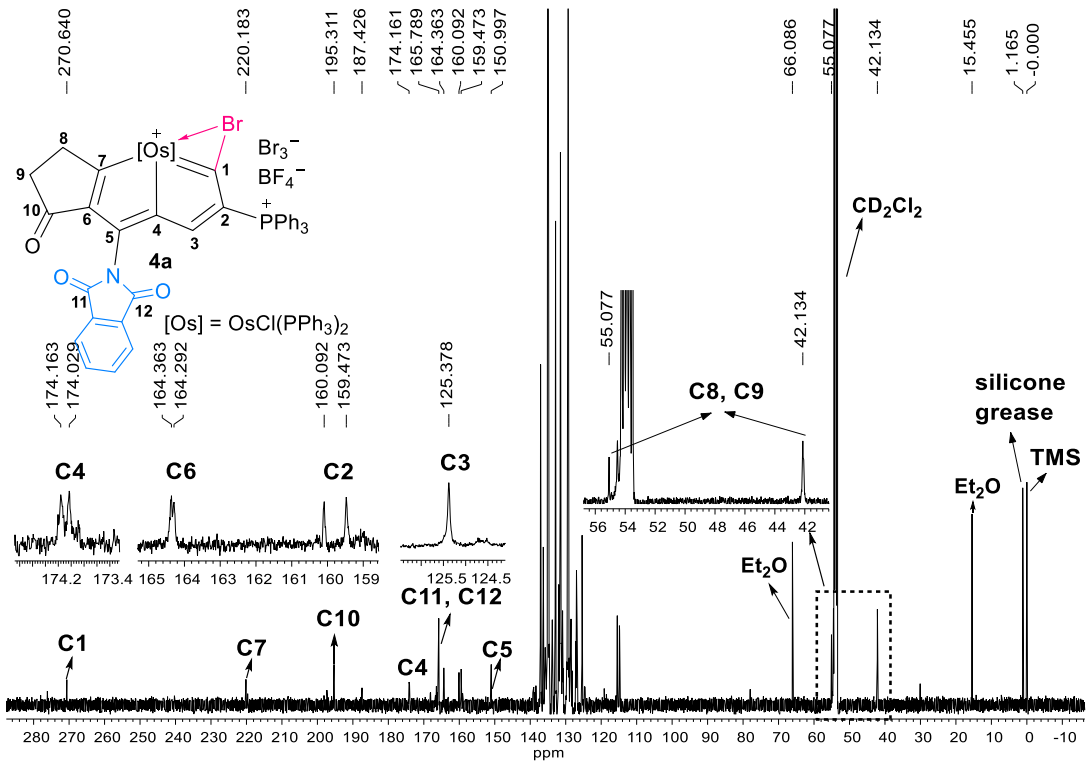


Figure S61. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) *in-situ* spectrum for complex **4a**.

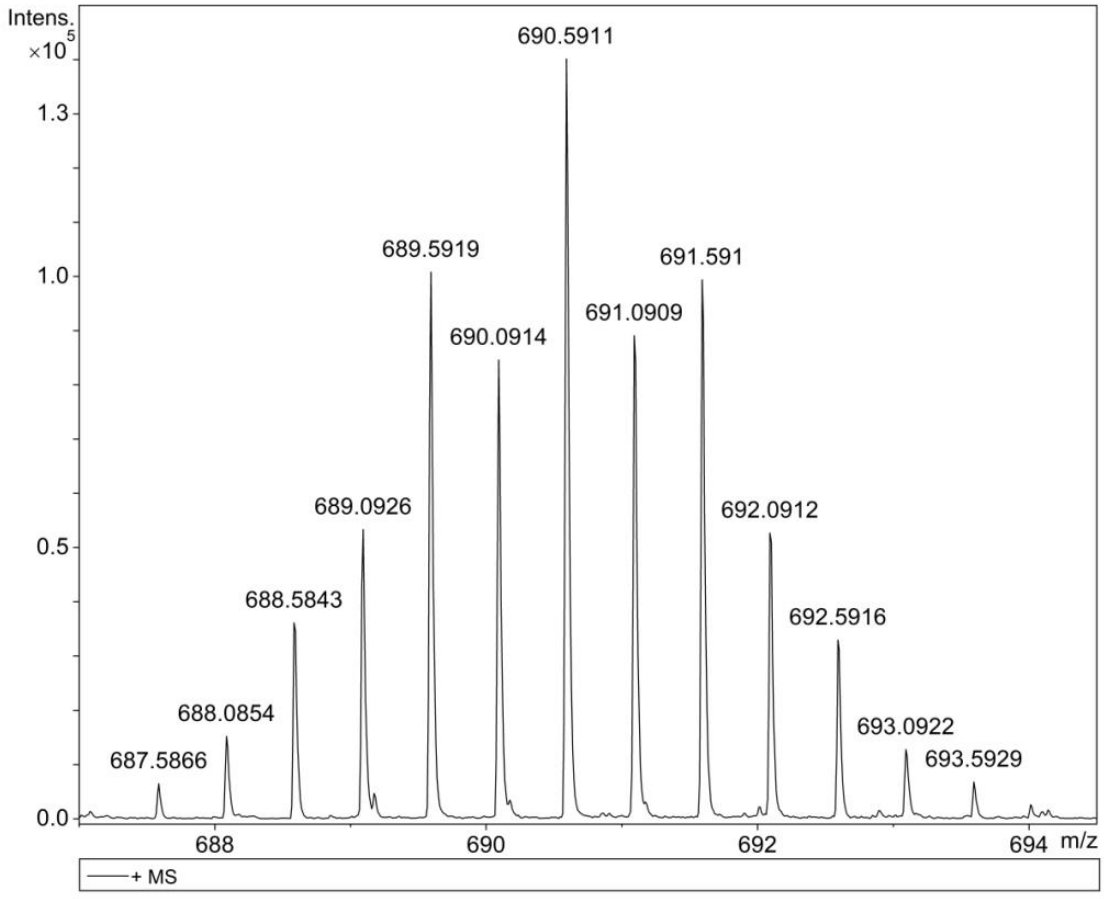


Figure S62. Positive-ion ESI-MS spectrum for complex $[\mathbf{4a}]^{2+}$ measured in methanol.

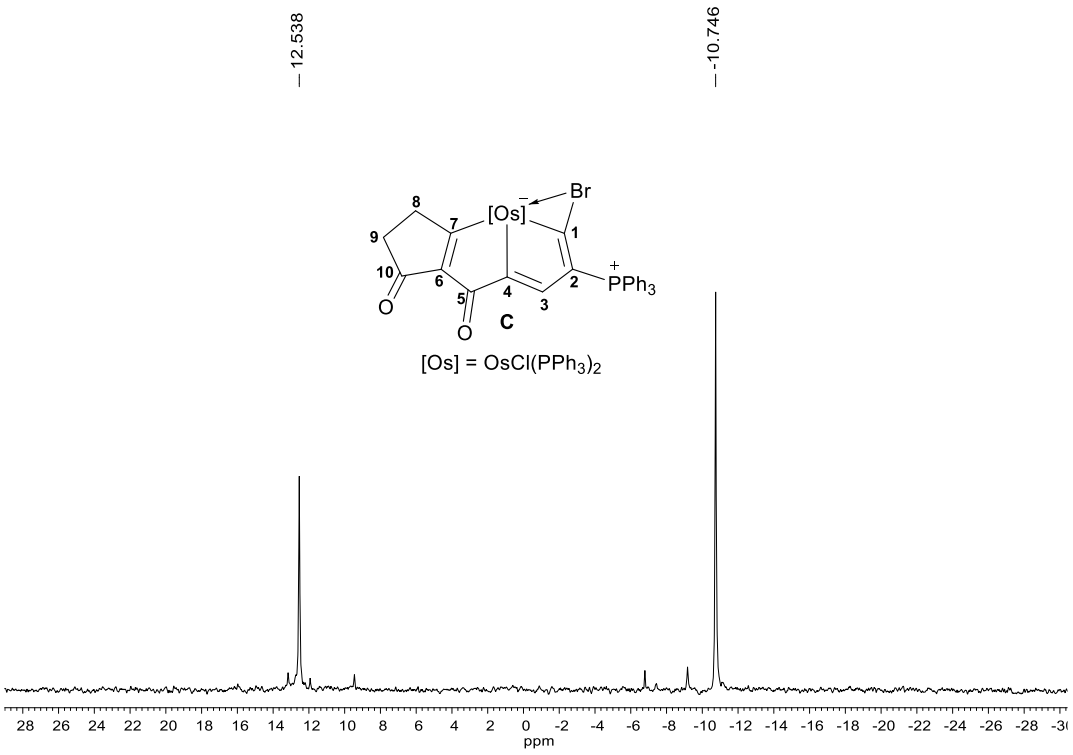


Figure S63. The $^{31}P\{^{1}H\}$ NMR spectrum (202.5 MHz, CD_2Cl_2) for intermediate **C**.

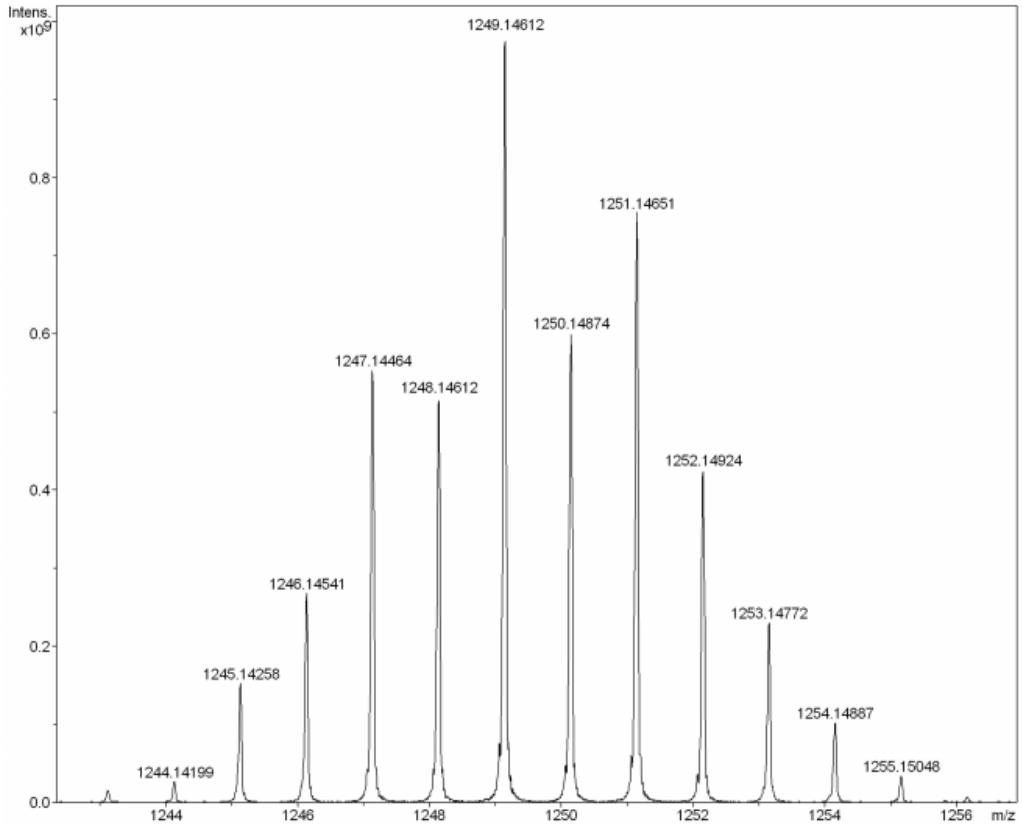


Figure S64. Positive-ion ESI-MS spectrum for complex $[\mathbf{C}]^+$ measured in methanol, (*m/z*) Calcd for $[C_{64}H_{50}ClO_2BrOsP_3]^+$ requires 1249.1483, Found 1249.1461.

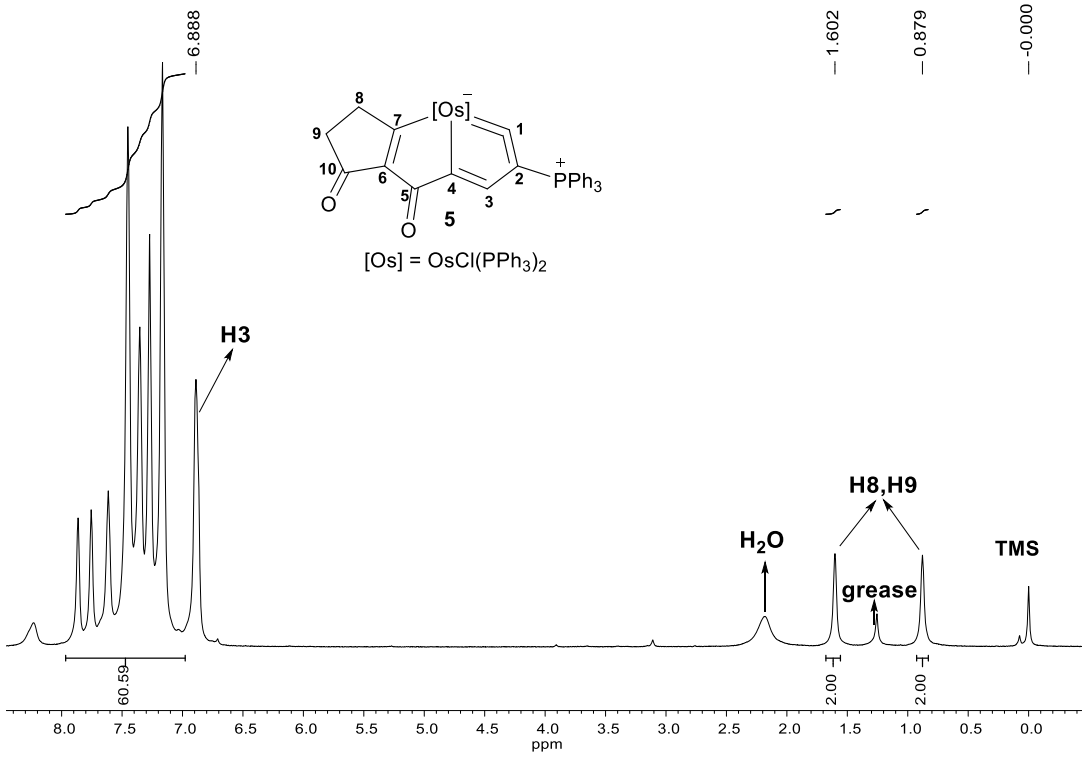


Figure S65. The ^{1}H NMR (600.1 MHz, $CDCl_3$) spectrum for complex **5**. (The signal of H3 was observed in aromatic region and could not be integrated reliably.)

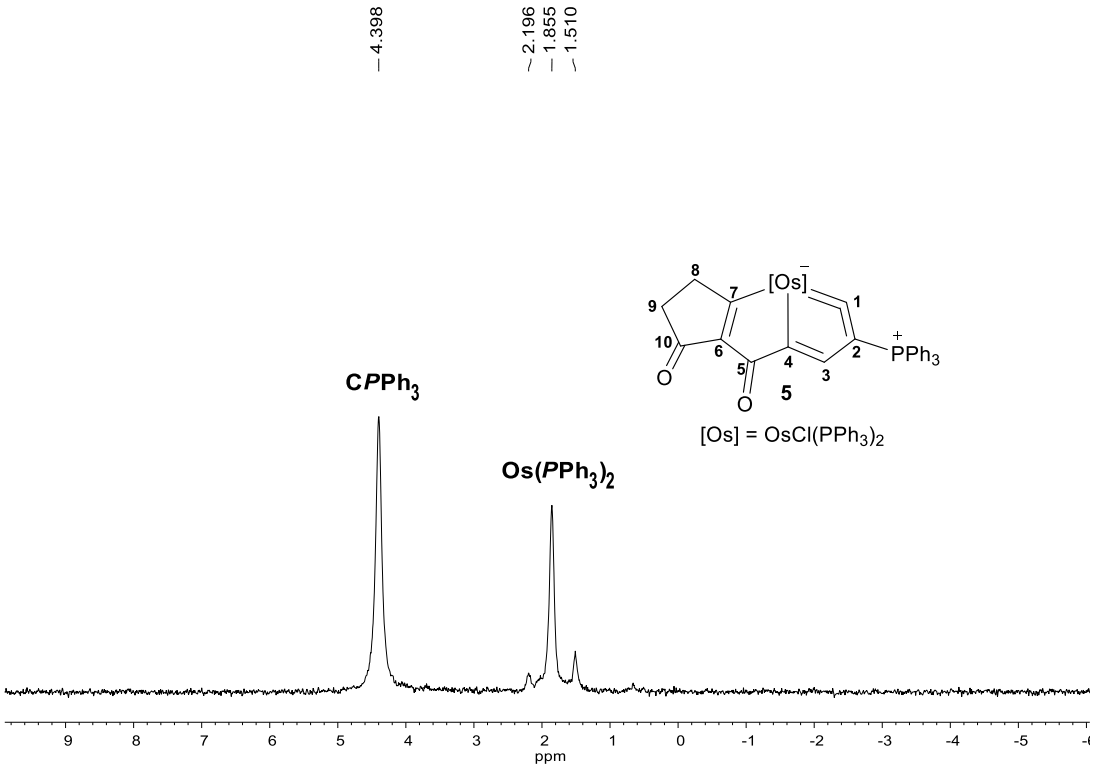


Figure S66. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, $CDCl_3$) for complex **5**.

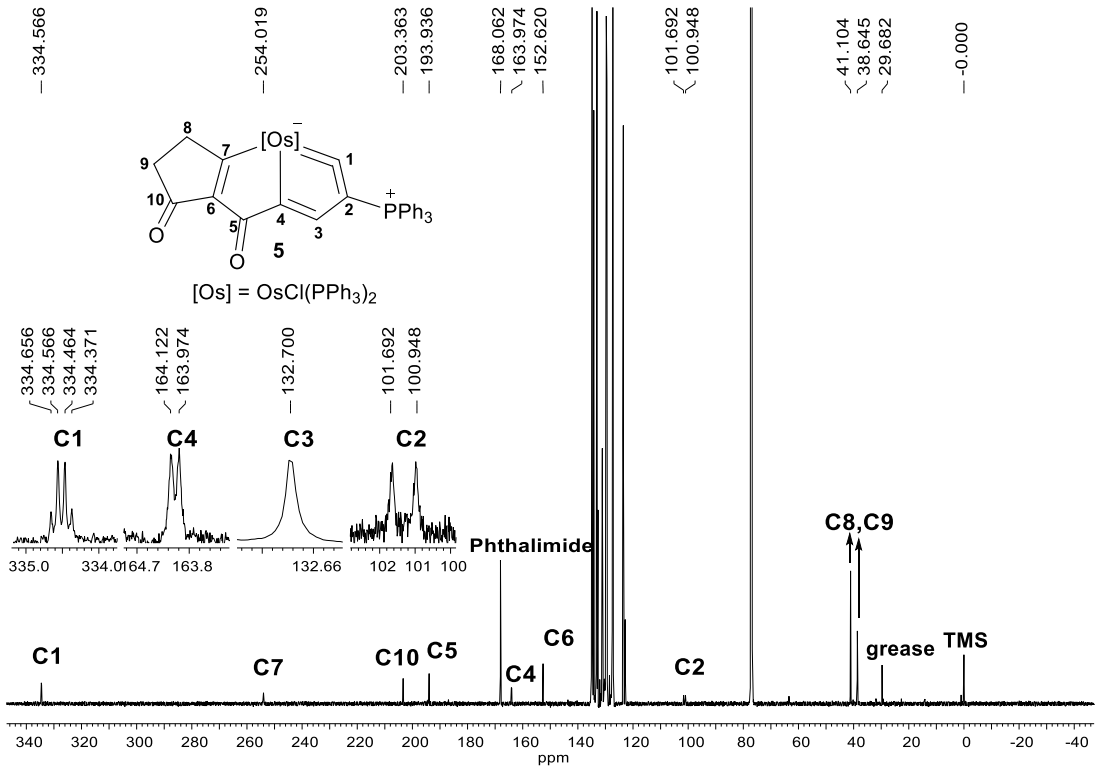


Figure S67. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$) spectrum for complex **5**.

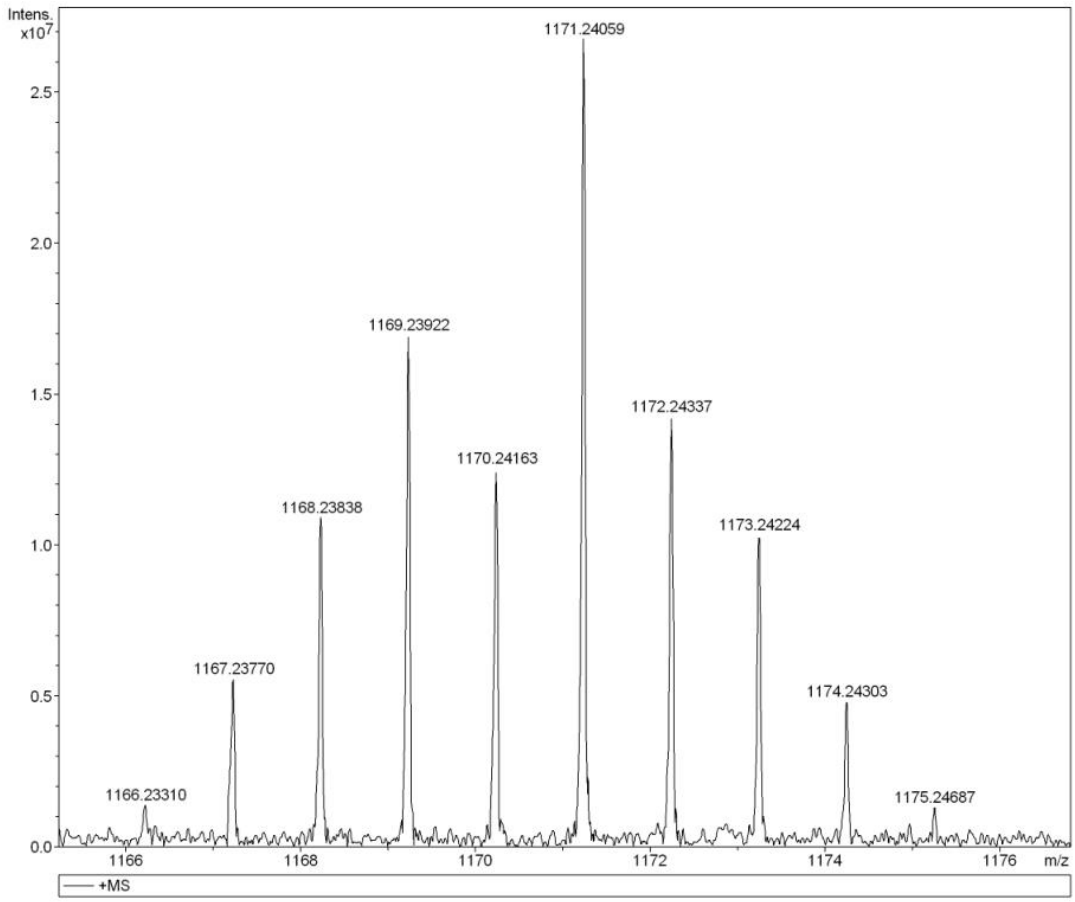


Figure S68. Positive-ion ESI-MS spectrum for complex [**5**+**H**]$^{+}$ measured in methanol.

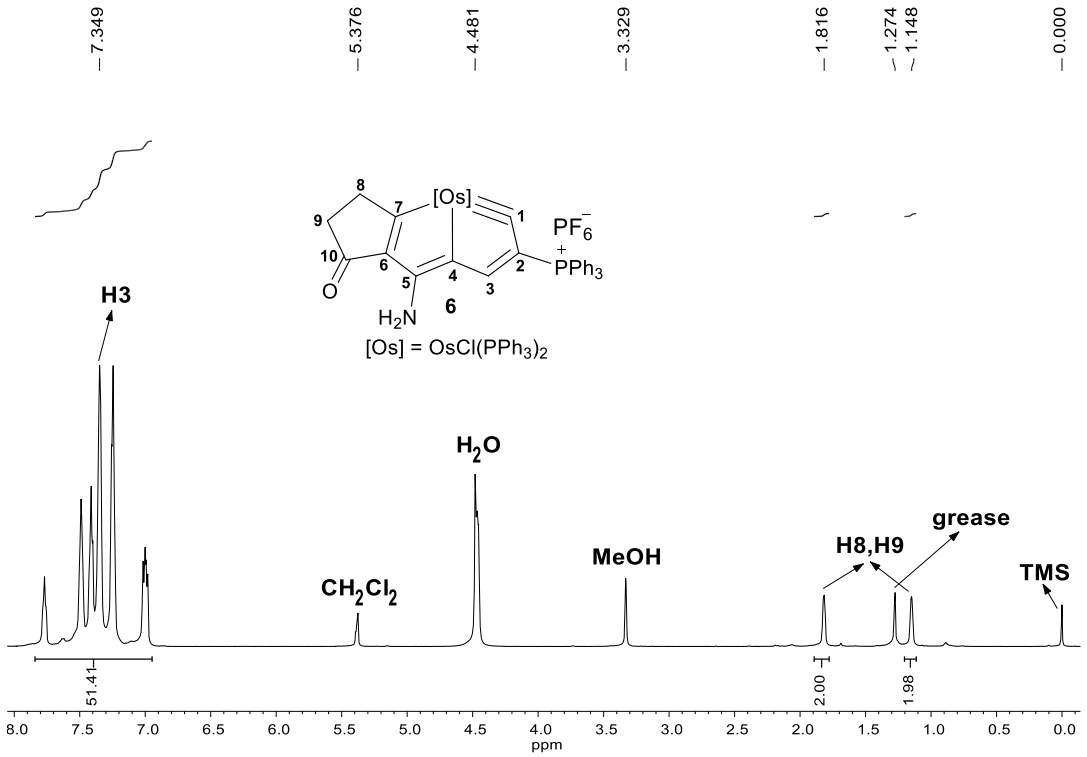


Figure S69. The ^{1}H NMR (600.1 MHz, CD_2Cl_2+MeOD) spectrum for complex **6**. (The signal of H3 was observed in aromatic region and could not be integrated reliably.)

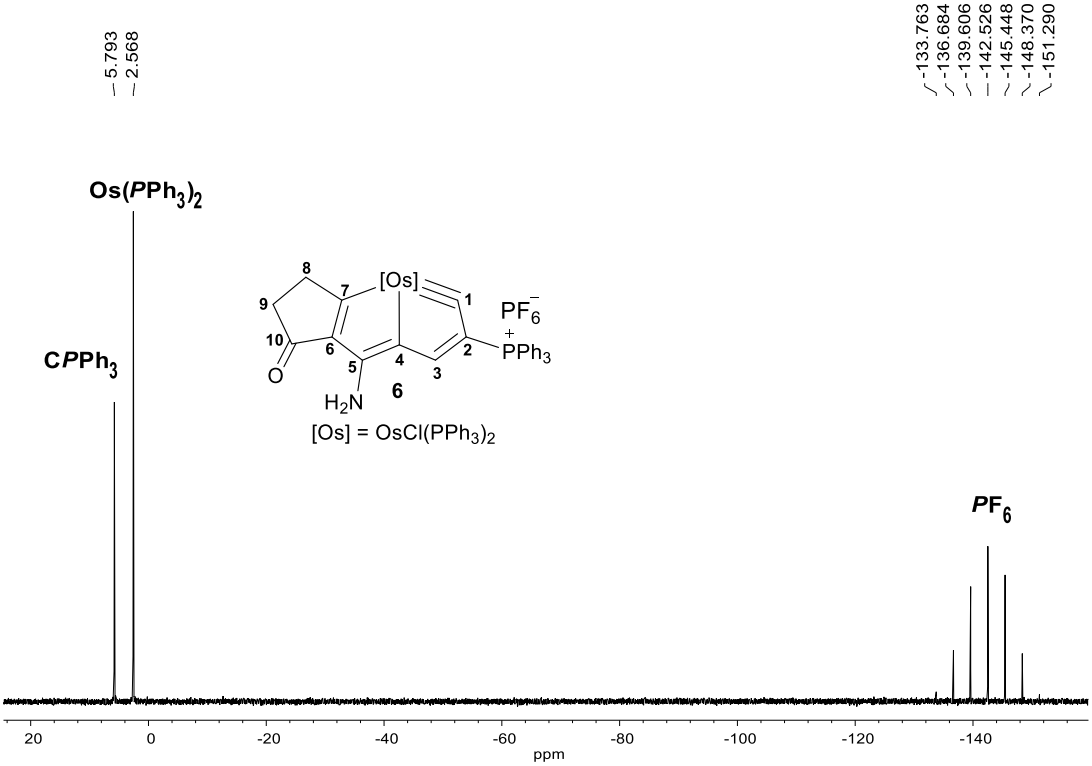


Figure S70. The $^{31}P\{^{1}H\}$ NMR spectrum (242.9 MHz, CD_2Cl_2+MeOD) for complex **6**.

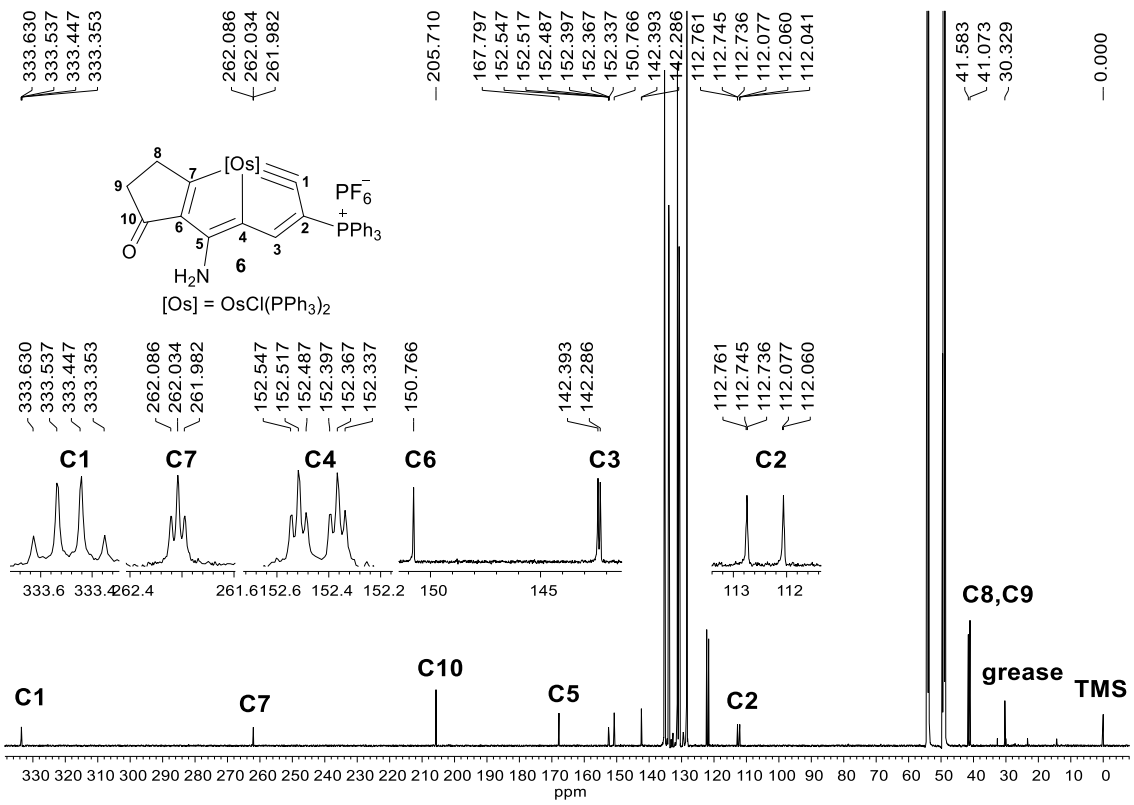


Figure S71. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2+MeOD) spectrum for complex **6**.

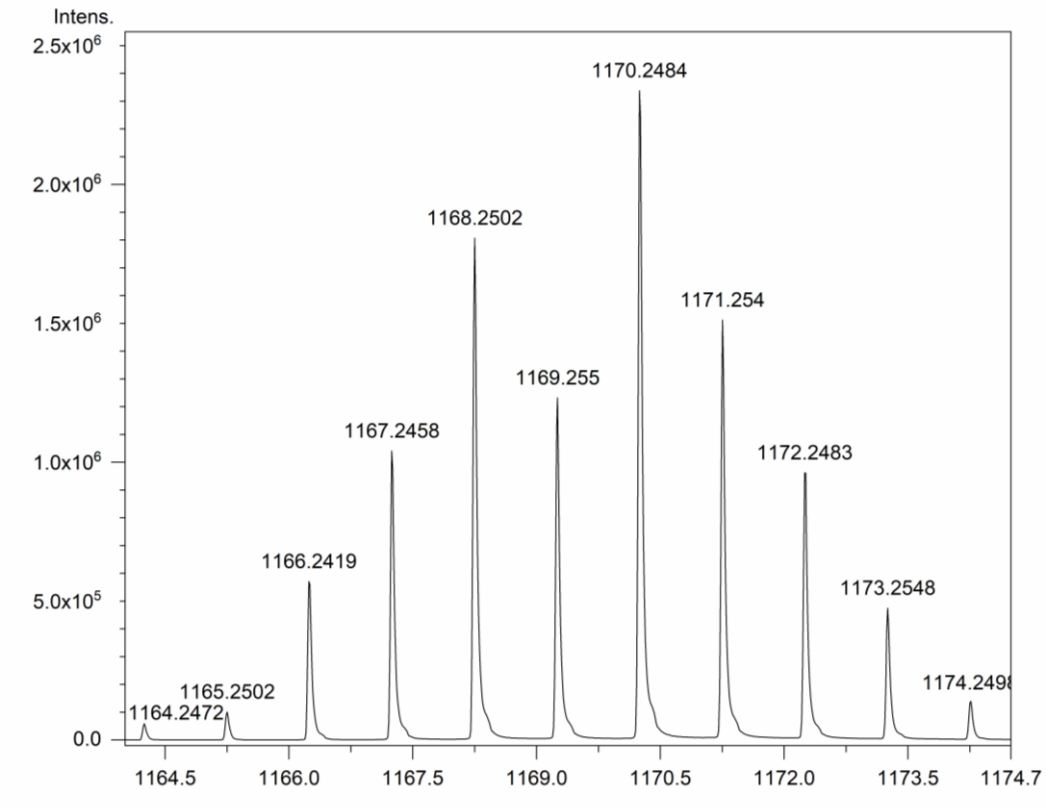


Figure S72. Positive-ion ESI-MS spectrum for complex $[\mathbf{6}]^+$ measured in methanol.

7. Reference

[1] Sheldrick, G. M. *SHELXTL*; Siemens Analytical X-ray Systems: Madison, Wisconsin, USA.