Supporting Information

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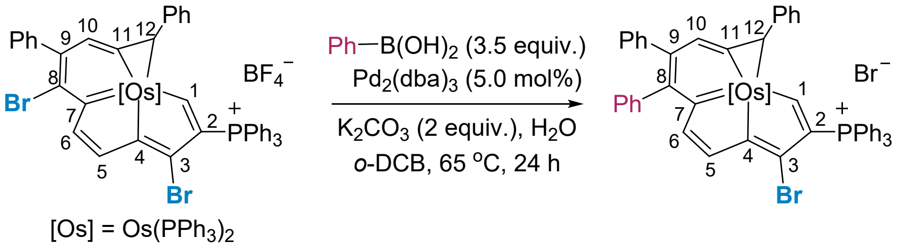
Contents

1. Experimental Procedures and NMR spectra

General information

All air-sensitive or water-sensitive reactions were carried out using the Schlenk technique under inert atmosphere. Solvents were distilled under nitrogen from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane) prior to use. The chemical reagents were obtained from Acros, Innochem, or other commercial resources and used without further purification. Column chromatography was performed on neutral alumina (200–300 mesh) in air. NMR spectra was collected on a Bruker Advance II 500 spectrometer, a Bruker Advance III 600 spectrometer at RT. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P{^{1}H} NMR chemical shifts are relative to 85% H_3PO_4. Elemental analysis (EA) data were collected on a Vario EL III elemental analyzer. The high-resolution mass spectra (HRMS) experiments were performed on a Bruker En Apex Ultra 7.0 T and Agilent 1290-6545XT.

Preparation of 2a



1 **2a**

To a Schlenk tube were added **1** (91.6 mg, 0.06 mmol), phenylboronic acid (25.6 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg) and K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene in nitrogen atmosphere. After the tube was charged with argon through a freeze-pump-thaw cycle for three times, the reaction mixture was stirred for 24 h at 65 °C under argon atmosphere. The reaction system was dried by anhydrous sodium sulfate, and then purified by column chromatography on neutral alumina with dichloromethane/ methanol = 20:1 as eluent to give the desired as yellow-green solid. (**2a**, 77.6 mg, 90%).

^{1}H NMR plus ^{1}H-^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ= 13.3 (d, $J_{P\text{-}H}$ = 21.8 Hz 1H, H1), 7.2 (s,1H, H5), 7.7 (s, 1H, H10), 7.3 ppm (s,1H, H6). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ= 14.1 (t, $J_{P\text{-}P}$ = 6.2 Hz C*P*Ph$_3$), –9.2 (dd, $J_{P\text{-}P}$ = 250.5 Hz, $J_{P\text{-}P}$ = 4.7 Hz, Os*P*Ph$_3$), –17.5 ppm (dd, $J_{P\text{-}P}$ = 250.5 Hz, $J_{P\text{-}P}$ = 7.5 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (125.8 MHz, CD_2Cl_2): δ= 233.7 (t, $J_{P\text{-}C}$ = 7.5 Hz, C7), 218.5 (t, $J_{P\text{-}C}$ = 4.5 Hz, C11), 207.8 (t, $J_{P\text{-}C}$ = 19.7 Hz, C1), 191.7 (dt, $J_{P\text{-}C}$ =20.8 Hz, $J_{P\text{-}C}$ = 4.7 Hz, C4), 161.5 (s, C6), 157.7 (s, C5), 143.9 (s, C9), 139.3.0 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 87.2 Hz, C2), 117.3 (s, C10), 109.7 (d, $J_{P\text{-}C}$ = 25.7 Hz, C3), 14.2 ppm (s, C12). Elemental analysis calcd (%) for $C_{84}H_{65}Br_2OsP_3$: C 66.49, H 4.32; found: C 66.59, H 4.52. HRMS (ESI): m/z calcd for $[C_{84}H_{65}BrOsP_3]^+$, 1437.3081; found: 1437.3069.

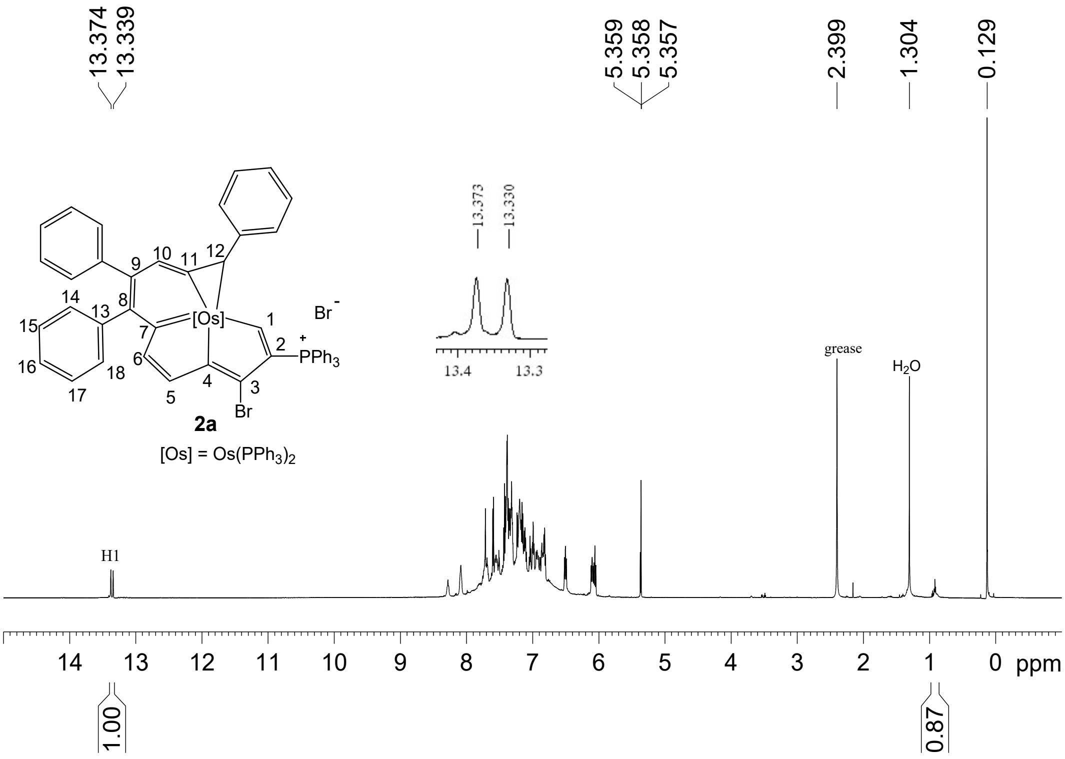


Figure S1 The ^{1}H NMR (500.2 MHz, CD_2Cl_2) spectrum for complex **2a**.

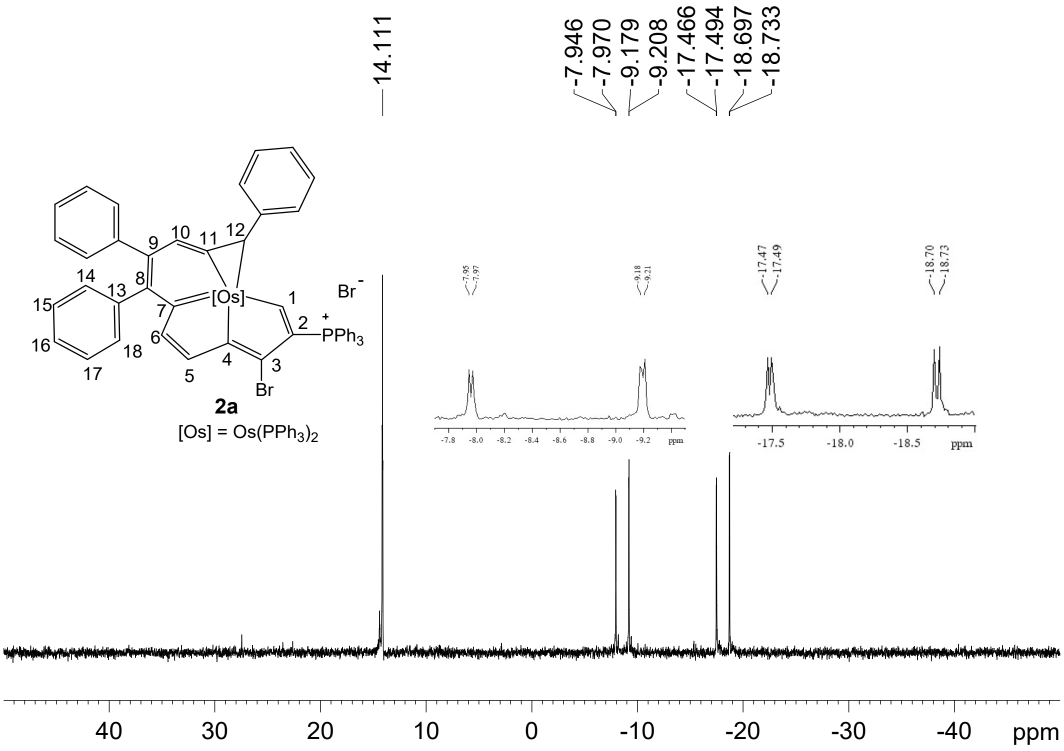


Figure S2 The $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **2a**.

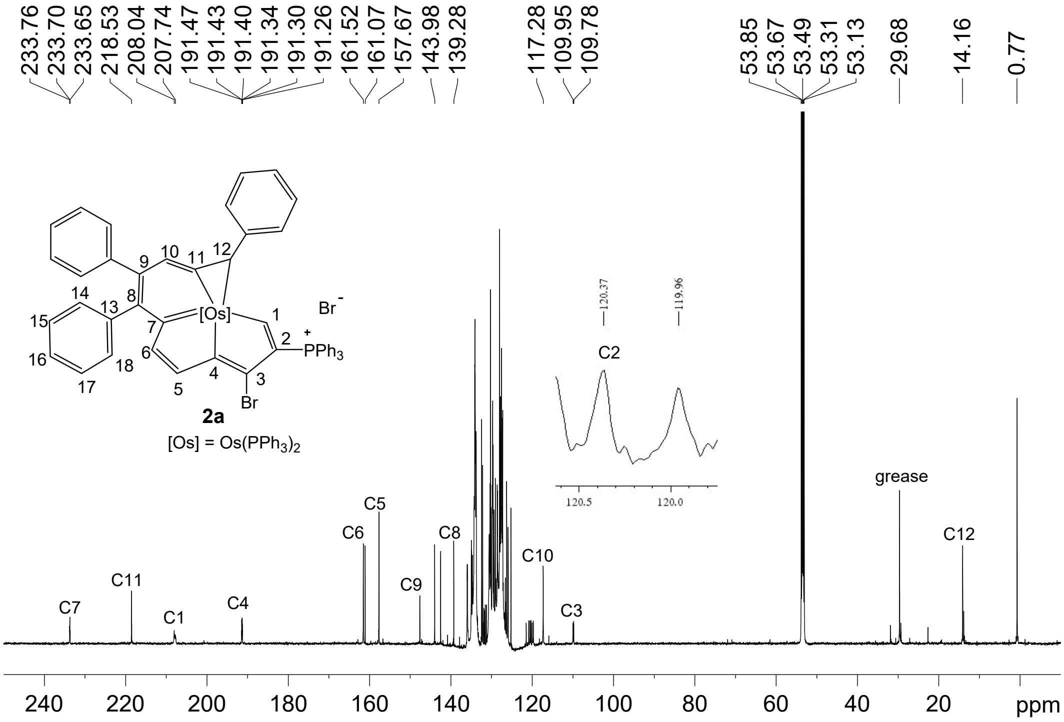


Figure S3 The ^{13}C NMR (125.8 MHz, CD_2Cl_2) spectrum for complex **2a**.

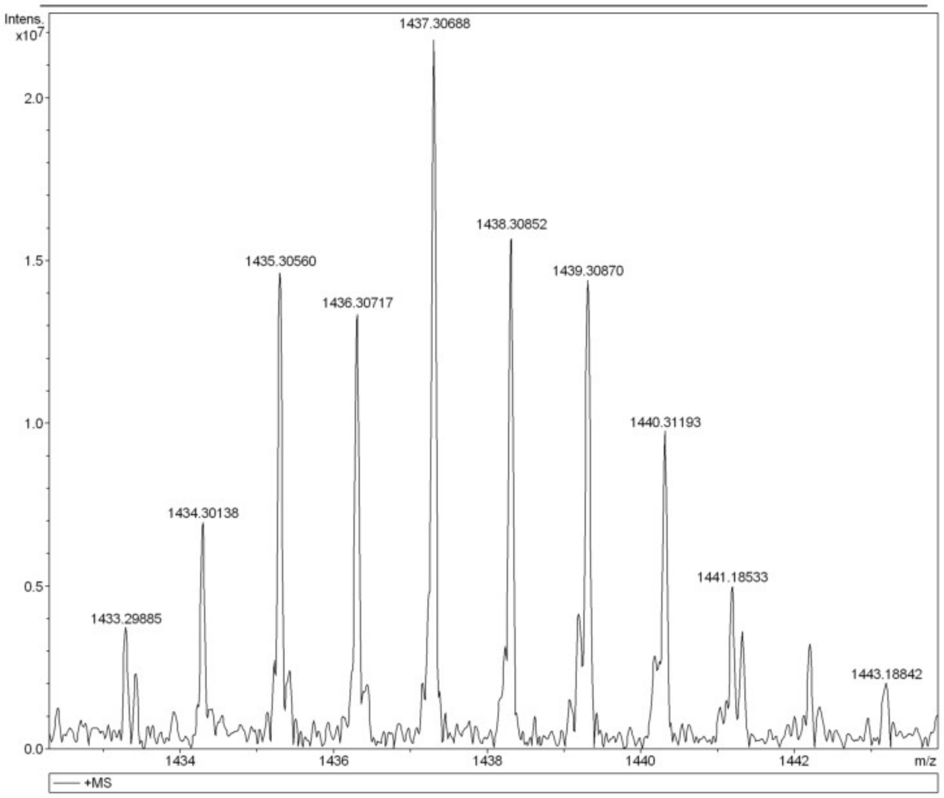


Figure S4 Positive-ion ESI-MS spectrum of **2a** measured in methanol.

Preparation of **2b**

2b: the synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), *p*-tolylboronic acid (28.53 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg) and K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2b**, 74.0 mg, 85%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ= 13.3 (d, $J_{P\text{-}H}$ = 22.15 Hz 1H, H1), 7.2 (s,1H, H5), 7.6 (s, 1H, H10), 7.3 ppm (s,1H, H6), 2.4 ppm (s,3H, H19). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ= 14.0 (t, $J_{P\text{-}P}$ = 5.6 Hz C*P*Ph$_3$), –8.5 (dd, $J_{P\text{-}P}$ = 254.5 Hz, $J_{P\text{-}P}$ = 5.2 Hz, Os*P*Ph$_3$), –18.1 ppm (dd, $J_{P\text{-}P}$ = 250.5 Hz, $J_{P\text{-}P}$ = 6.3 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ= 234.2 (t, $J_{P\text{-}C}$ = 7.2 Hz, C7), 218.2 (t, $J_{P\text{-}C}$ = 4.0 Hz, C11), 207.8 (t, $J_{P\text{-}C}$ = 21.0 Hz, C1), 191.3 (dt, $J_{P\text{-}C}$ =19.9 Hz, $J_{P\text{-}C}$ = 5.6 Hz, C4), 161.6 (s, C6), 157.5 (s, C5), 144.1 (s, C9), 139.2 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 89.2 Hz, C2), 117.3 (s, C10), 109.7 (d, $J_{P\text{-}C}$ = 24.5 Hz, C3), 20.9 ppm (s, C19), 14.0 ppm (s, C12). Elemental analysis calcd (%) for $C_{85}H_{67}Br_2OsP_3$: C 66.67, H 4.41; found: C 67.01, H 4.18. HRMS (ESI): m/z calcd for $[C_{85}H_{67}BrOsP_3]^+$, 1451.3237; found: 1451.3251.

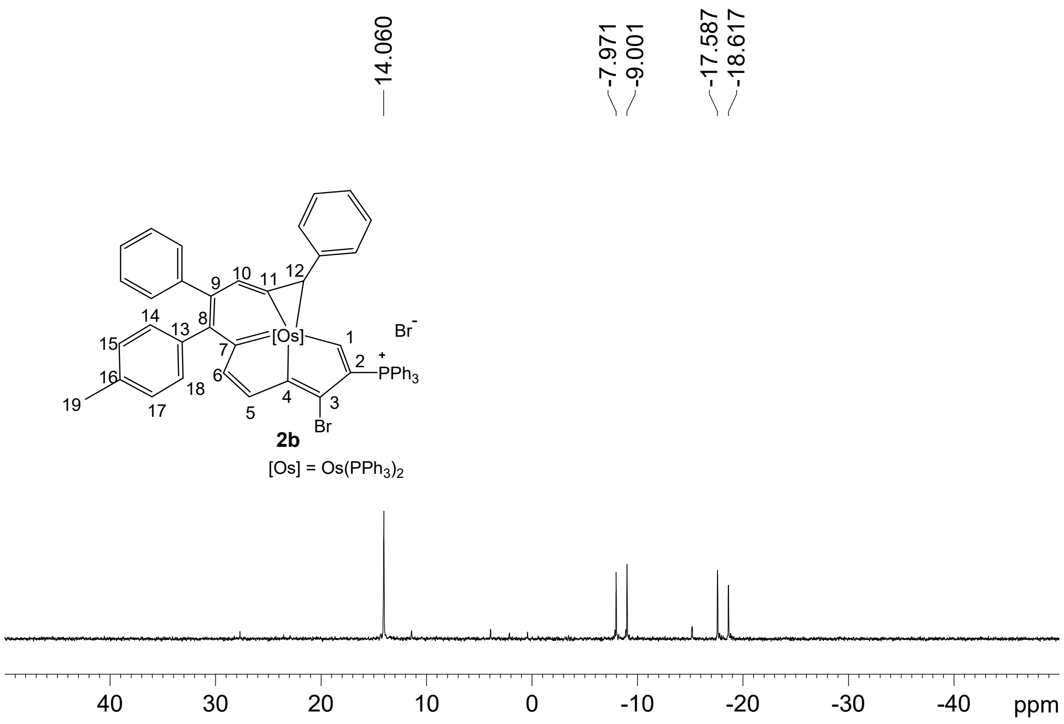


Figure S5 The ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2b**.

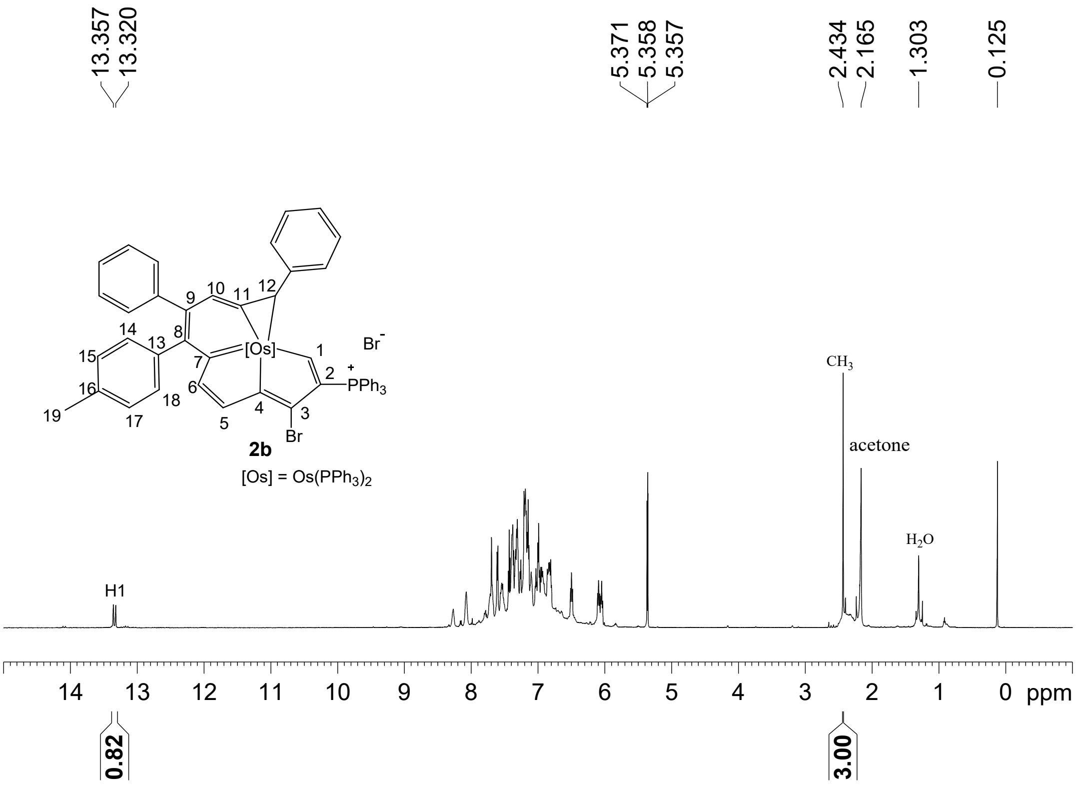


Figure S6 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2b**.

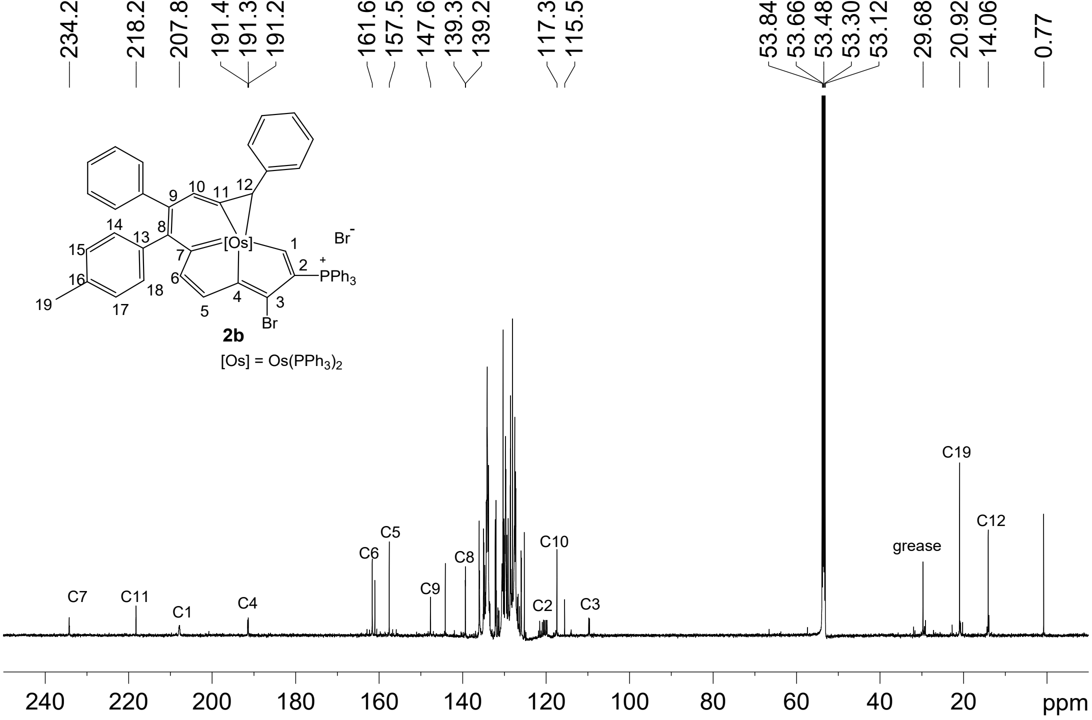


Figure S7 The ^{13}C NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2b**.

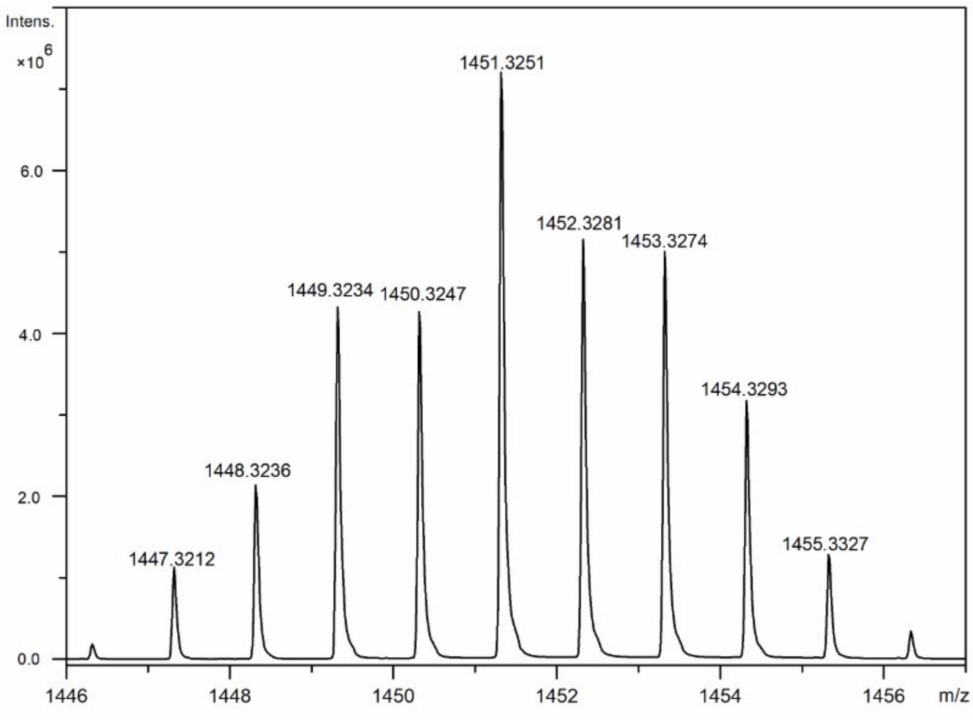


Figure S8 Positive-ion ESI-MS spectrum of **2b** measured in methanol.

Preparation of **2c**

2c: the synthetic procedure is similar to that for **2a**. **1** (91.60 mg, 0.06 mmol), (4-ethylphenyl) boronic acid (31.49 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg) and K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2c**, 72.1 mg, 82%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 13.3 (d, $J_{P\text{-}H}$ = 24.0 Hz 1H, H1), 7.4 ppm (s, 1H, H6), 7.1 (s, 1H, H5), 7.6 (s, 1H, H10), 2.7 ppm (q, $J_{H\text{-}H}$ = 22.8 Hz 2H, H19), 1.32 ppm (t, $J_{H\text{-}H}$ = 7.5 Hz 3H, H20). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ= 14.0 (t, $J_{P\text{-}P}$ = 6.2 Hz C*P*Ph$_3$), –8.5 (dd, $J_{P\text{-}P}$ = 253.0 Hz, $J_{P\text{-}P}$ = 5.1 Hz, Os*P*Ph$_3$), –18.0 ppm (dd, $J_{P\text{-}P}$ = 253.5 Hz, $J_{P\text{-}P}$ = 6.7 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ = 234.1 (t, $J_{P\text{-}C}$ = 7.9 Hz, C7), 218.2 (t, $J_{P\text{-}C}$ = 4.3 Hz, C11), 207.8 (t, $J_{P\text{-}C}$ = 21.0 Hz, C1), 191.4 (dt, $J_{P\text{-}C}$ =20.5 Hz, $J_{P\text{-}C}$ = 5.6 Hz, C4), 161.7 (s, C6), 157.5 (s, C5), 144.1 (s, C9), 139.4 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 89.2 Hz, C2), 117.3 (s, C10), 109.6 (d, $J_{P\text{-}C}$ = 25.7 Hz, C3), 28.4 ppm (s, C19), 15.4 ppm (s, C20).14.0 ppm (s, C12). Elemental analysis calcd (%) for $C_{86}H_{69}Br_2OsP_3$: C 66.84, H 4.50; found: C 66.44, H 4.79. HRMS (ESI): m/z calcd for $[C_{86}H_{69}BrOsP_3]^+$, 1465.3394; found: 1465.3400.

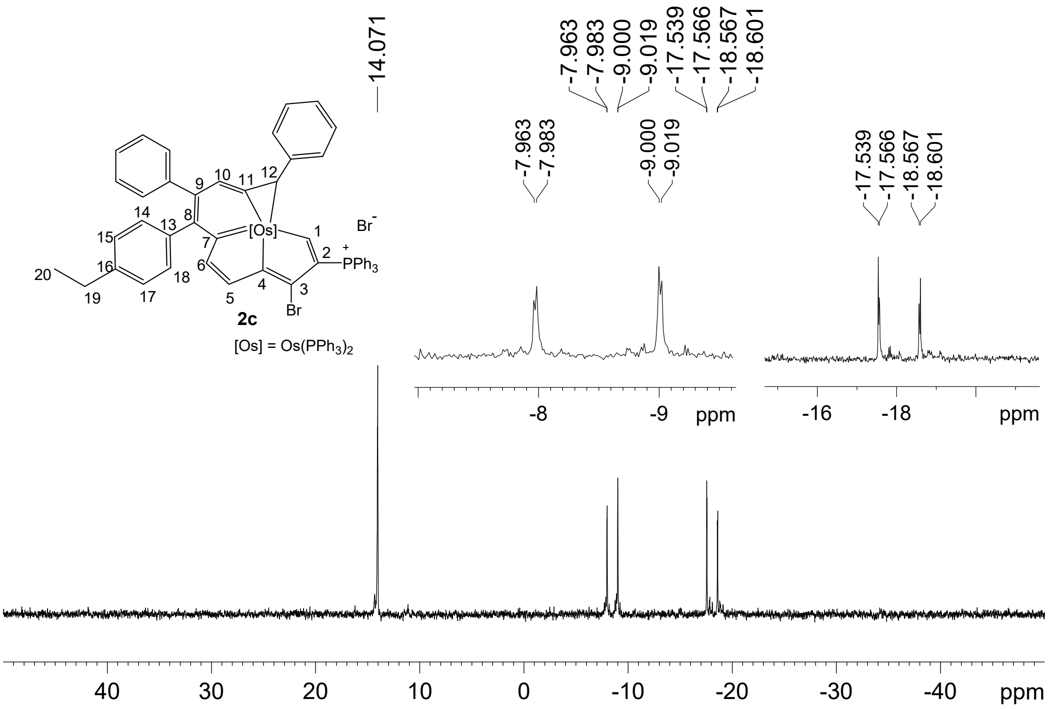


Figure S9 The $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2c**.

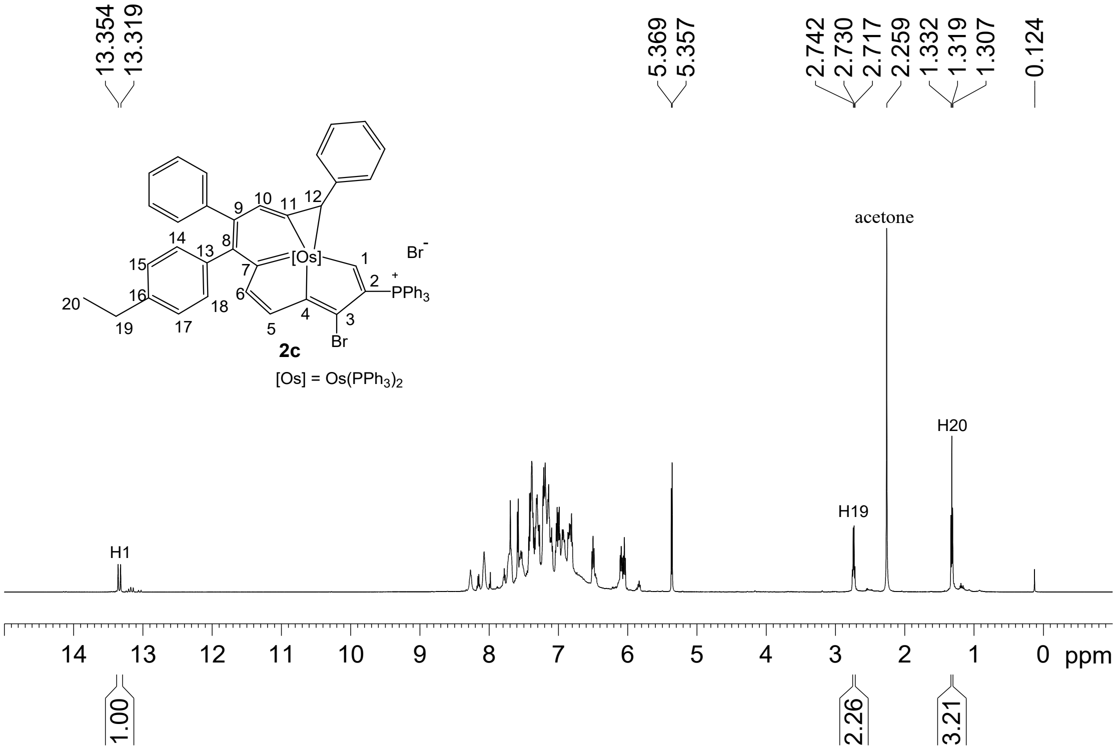


Figure S10 The ^1H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2c**.

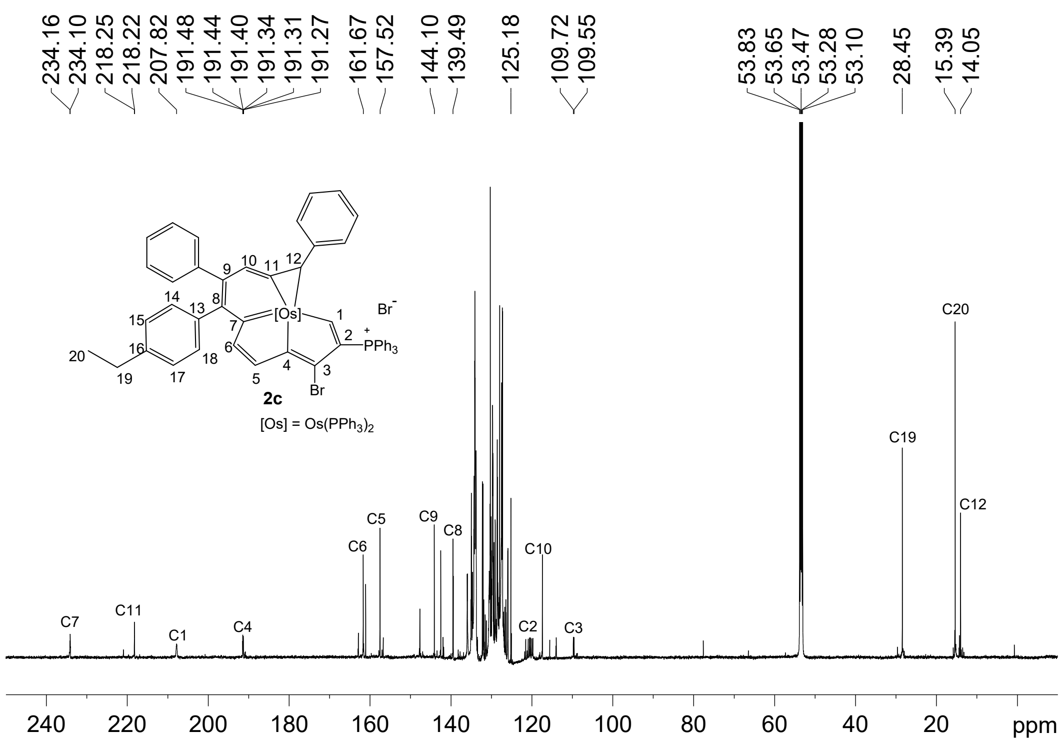


Figure S11 The ^{13}C NMR (150.9 MHz, CD$_2$Cl$_2$) spectrum for complex **2c**.

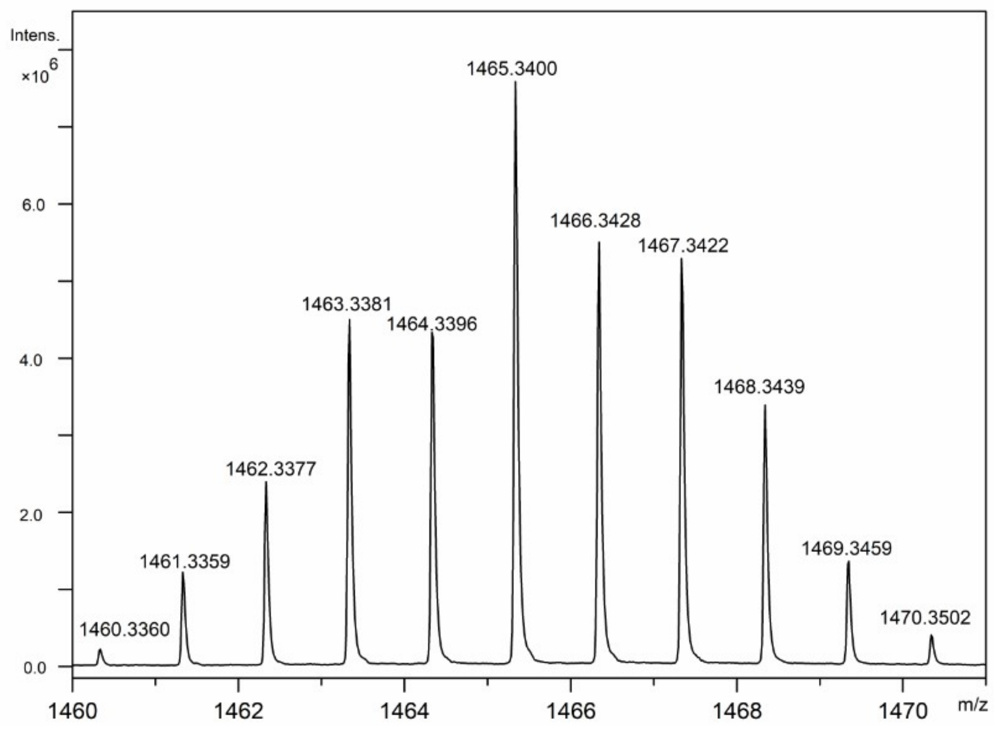


Figure S12 Positive-ion ESI-MS spectrum of **2c** measured in methanol.

Preparation of **2d**

2d: The synthetic procedure is similar to that for **2a**. **1** (91.60 mg, 0.06 mmol), (4-butylphenyl) boronic acid (37.38 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg), K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2d**, 72.2 mg, 87%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 13.3 (d, $J_{P\text{-}H}$ = 20.8 Hz 1H, H1), 7.4 ppm (s, 1H, H6), 7.3 (s, 1H, H5), 7.6 (s, 1H, H10), 2.7 ppm (t, $J_{H\text{-}H}$ = 7.7 Hz 2H, H19), 1.7 ppm (m, 2H, H20), 1.4 ppm (m, 2H, H21), 1.0 ppm (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, H22). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 14.0 (t, $J_{P\text{-}P}$ = 6.0 Hz C*P*Ph$_3$), –8.5 (dd, $J_{P\text{-}P}$ = 250.1 Hz, $J_{P\text{-}P}$ = 5.5 Hz, Os*P*Ph$_3$), –18.0 ppm (dd, $J_{P\text{-}P}$ = 250.1 Hz, $J_{P\text{-}P}$ = 8.1 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ = 234.0 (t, $J_{P\text{-}C}$ = 7.2 Hz, C7), 218.2 (t, $J_{P\text{-}C}$ = 4.3 Hz, C11), 207.7 (t, $J_{P\text{-}C}$ = 21.0 Hz, C1), 191.3 (dt, $J_{P\text{-}C}$ =20.5 Hz, $J_{P\text{-}C}$ = 5.5 Hz, C4), 161.7 (s, C6), 157.5 (s, C5), 144.0 (s, C9), 139.4 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 89.1 Hz, C2), 117.3 (s, C10), 109.6 (d, $J_{P\text{-}C}$ = 25.2 Hz, C3), 35.2 ppm (s, C19), 33.6 ppm (s, C20), 22.1 ppm (s, C21), 14.0 ppm (s, C12), 13.8 ppm (s, C22). Elemental analysis calcd (%) for $C_{88}H_{73}Br_2OsP_3$: C 67.17, H 4.68; found: C 67.36, H 4.52. HRMS (ESI): m/z calcd for $[C_{88}H_{73}BrOsP_3]^+$, 1493.3707; found: 1493.3709.

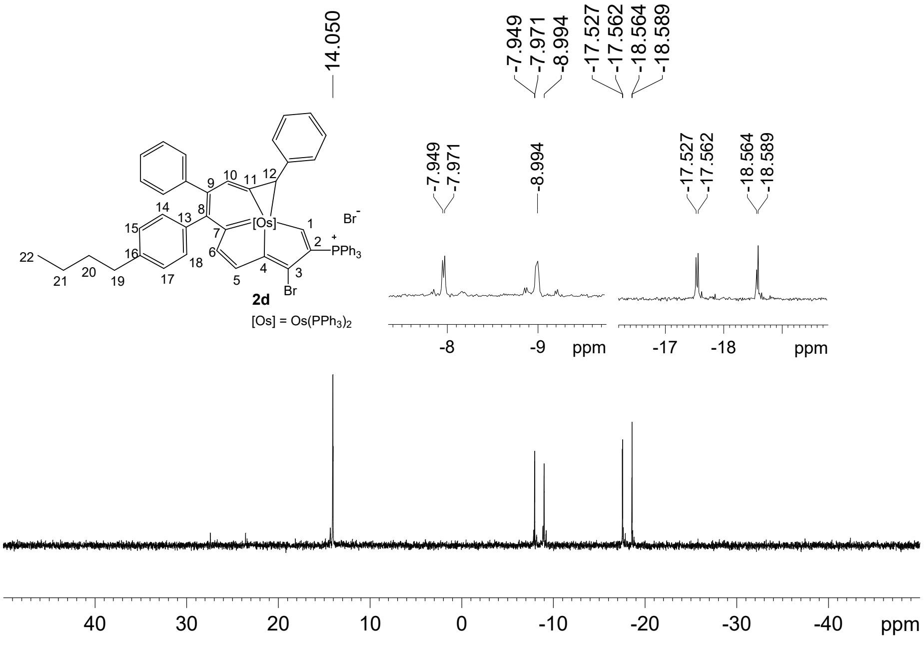


Figure S13 The $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2d**.

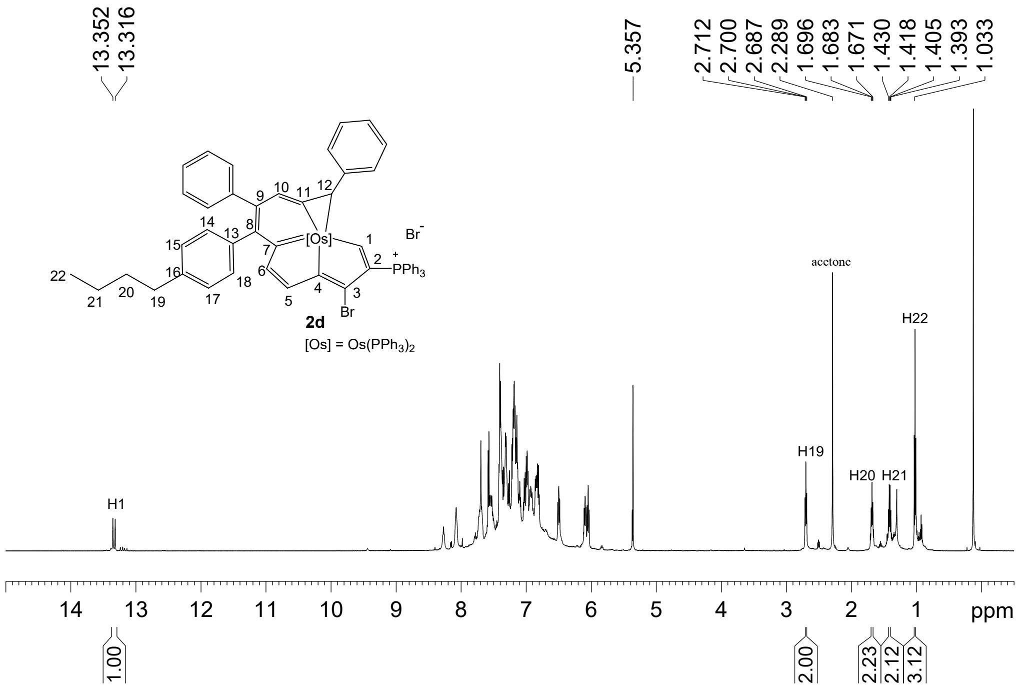


Figure S14 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2d**.

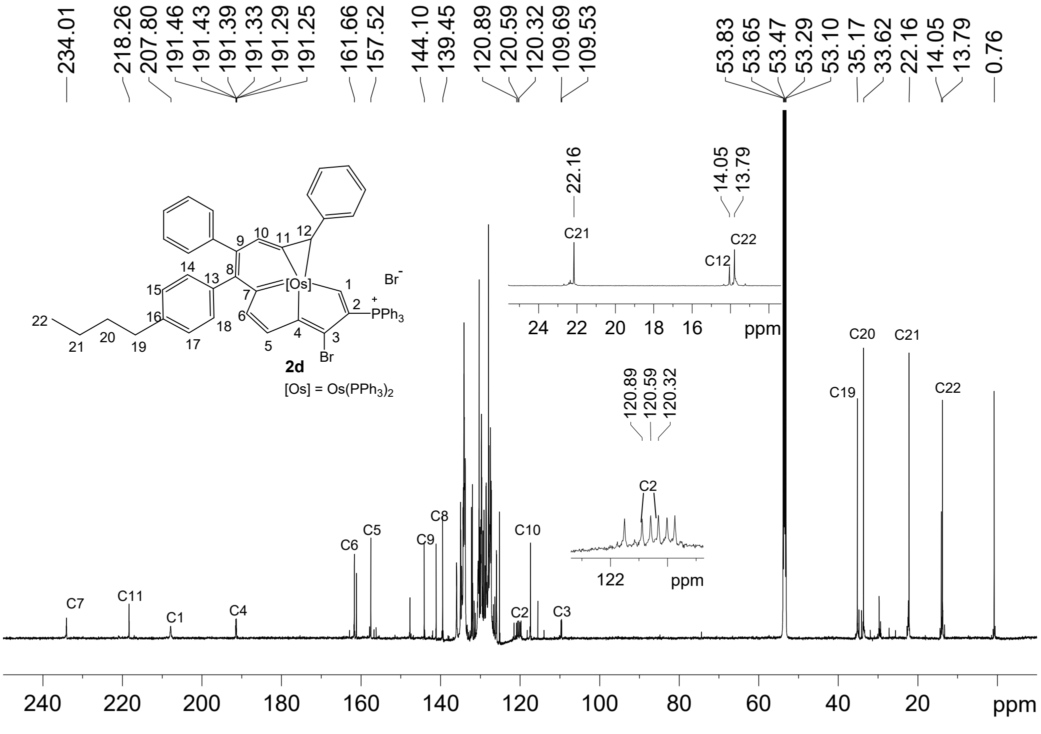


Figure S15 The ^{13}C NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2d**.

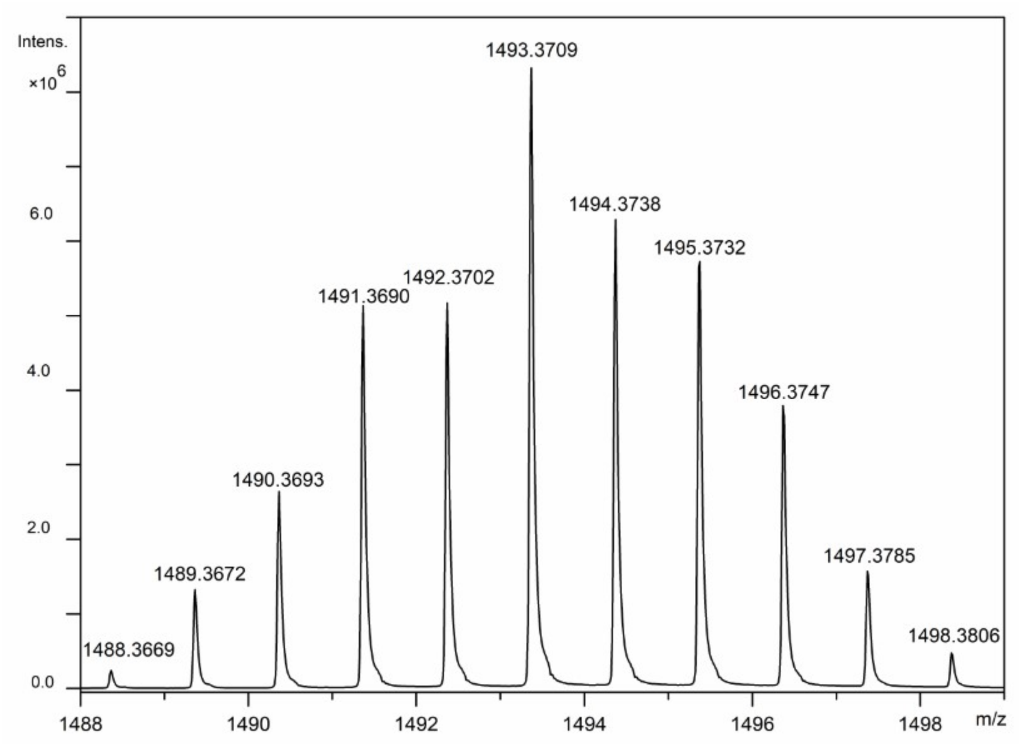


Figure S16 Positive-ion ESI-MS spectrum of **2d** measured in methanol.

Preparation of **2e**

2e: The synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), (4-isopropylphenyl) boronic acid (34.44 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg) and K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2e**, 73.6 mg, 83%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 13.3 (d, $J_{P\text{-}H}$ = 21.6 Hz 1H, H1), 7.4 ppm (s, 1H, H6), 7.2 (s, 1H, H5), 7.6 (s, 1H, H10), 2.9 ppm (m, 1H, H19), 1.3 ppm (d, $J_{H\text{-}H}$ = 6.9 Hz 6H, H20-21). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 14.0 (t, $J_{P\text{-}P}$ = 6.0 Hz C*P*Ph$_3$), –8.0 (dd, $J_{P\text{-}P}$ = 253.1 Hz, $J_{P\text{-}P}$ = 6.5 Hz, Os*P*Ph$_3$), –18.1 ppm (dd, $J_{P\text{-}P}$ = 252.1 Hz, $J_{P\text{-}P}$ = 5.6 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ = 234.1 (t, $J_{P\text{-}C}$ = 8.5 Hz, C7), 218.2 (t, $J_{P\text{-}C}$ = 4.3 Hz, C11), 207.7 (t, $J_{P\text{-}C}$ = 21.0 Hz, C1), 191.3 (dt, $J_{P\text{-}C}$ =20.5 Hz, $J_{P\text{-}C}$ = 5.5 Hz, C4), 161.7 (s, C6), 157.5 (s, C5), 144.0 (s, C9), 139.4 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 89.1 Hz, C2), 117.3 (s, C10), 109.6 (d, $J_{P\text{-}C}$ = 26.2 Hz, C3), 33.7 ppm (s, C19), 23.8 ppm (s, C20-21).14.0 ppm (s, C12). Elemental analysis calcd (%) for $C_{87}H_{71}Br_2OsP_3$: C 67.01, H 4.59; found: C 67.40, H 4.52. HRMS (ESI): m/z calcd for $[C_{87}H_{71}BrOsP_3]^+$, 1479.3551; found: 1479.3552.

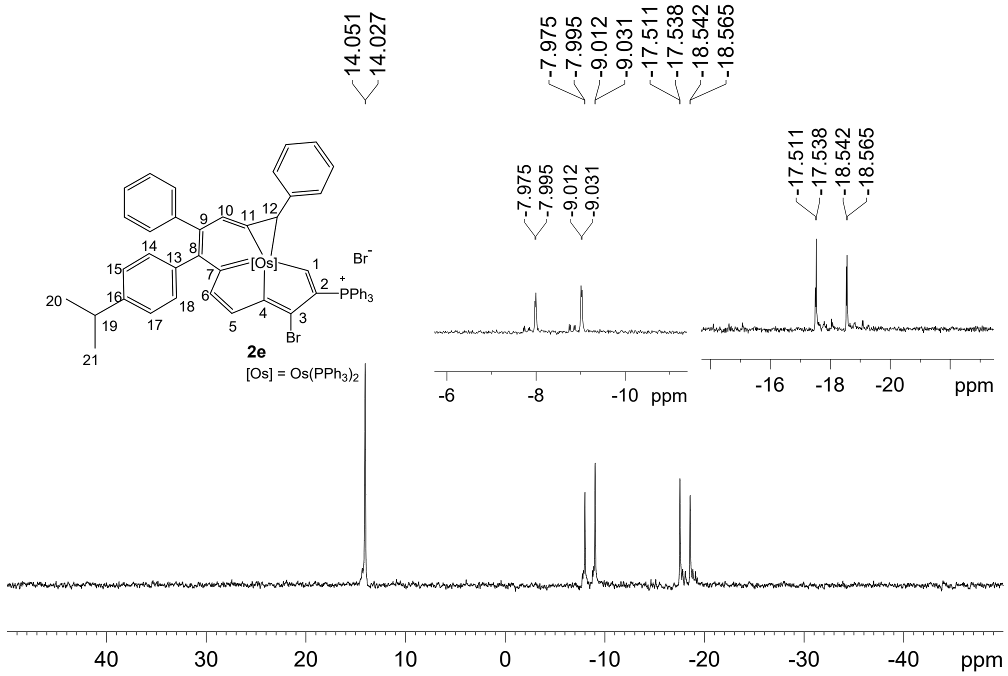


Figure S17 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2e.**

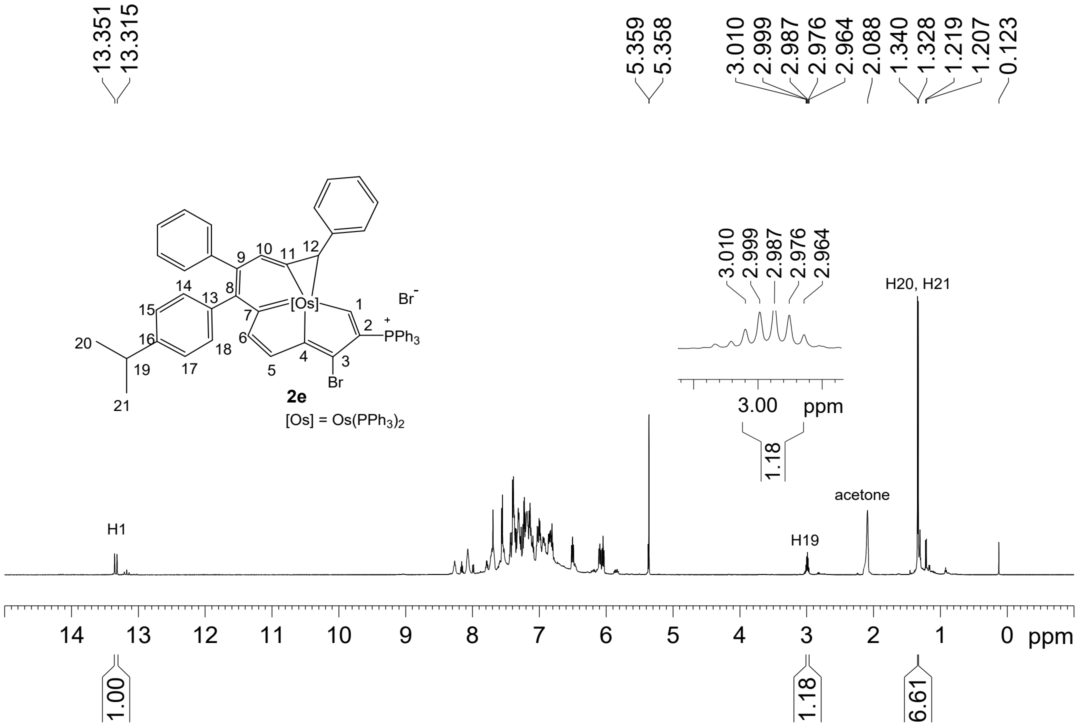


Figure S18 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2e**.

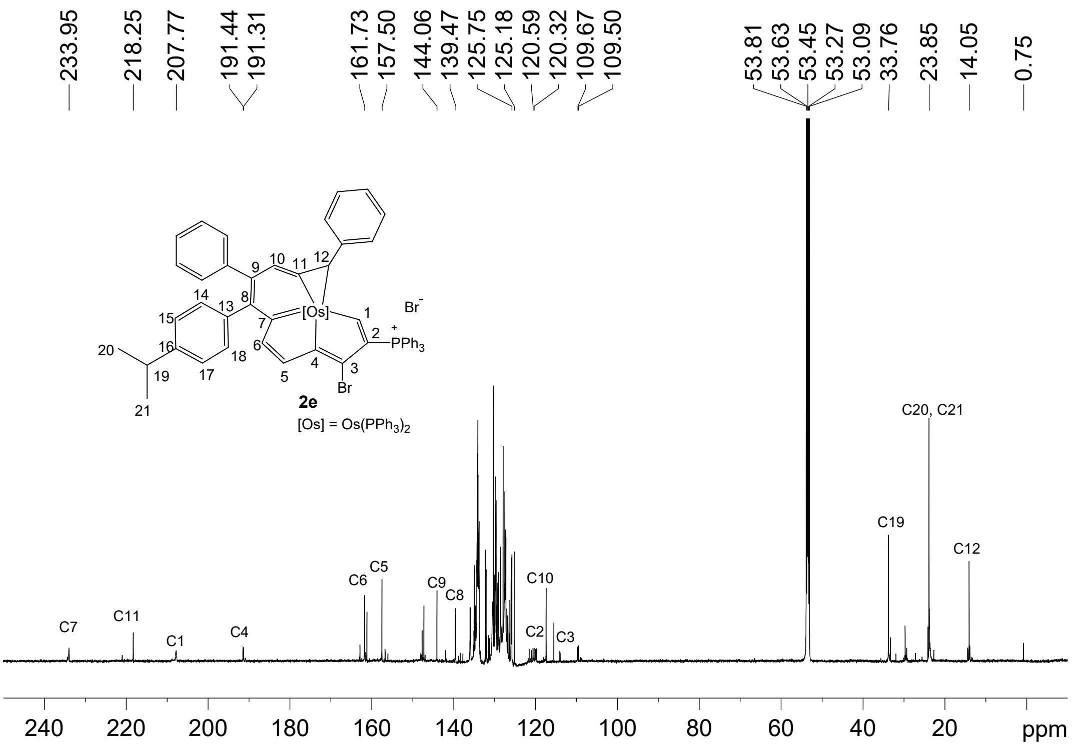


Figure S19 The ^{13}C NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2e**.

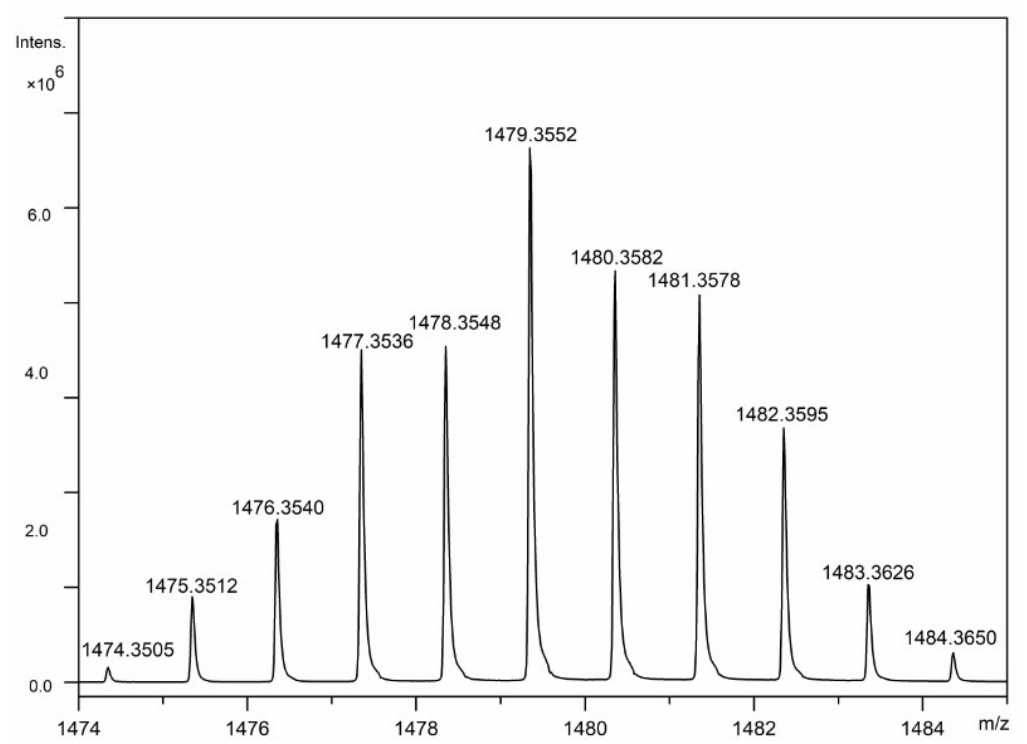


Figure S20 Positive-ion ESI-MS spectrum of **2e** measured in methanol.

Preparation of **2f**

2f: The synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), (4-(*tert*-

butyl)phenyl) boronic acid (37.38 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg), K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2f**, 76.2 mg, 85%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ= 13.3 (d, $J_{P\text{-}H}$ = 21.4 Hz 1H, H1), 7.4 ppm (s, 1H, H6), 7.2 (s, 1H, H5), 7.6 (s, 1H, H10), 1.4 ppm (s, 9H, H20-22). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ= 14.0 (t, $J_{P\text{-}P}$ = 5.1 Hz C*P*Ph$_3$), –8.5 (dd, $J_{P\text{-}P}$ = 250.1 Hz, $J_{P\text{-}P}$ = 5.9 Hz, Os*P*Ph$_3$), –18.0 ppm (dd, $J_{P\text{-}P}$ = 250.1 Hz, $J_{P\text{-}P}$ = 5.8 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ= 233.8 (t, $J_{P\text{-}C}$ = 8.7 Hz, C7), 218.2 (t, $J_{P\text{-}C}$ = 4.7 Hz, C11), 207.7 (t, $J_{P\text{-}C}$ = 21.6 Hz, C1), 191.4 (dt, $J_{P\text{-}C}$ =20.1 Hz, $J_{P\text{-}C}$ = 5.2 Hz, C4), 161.7 (s, C6), 157.5 (s, C5), 144.0 (s, C9), 139.4 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 86.2 Hz, C2), 117.3 (s, C10), 109.6 (d, $J_{P\text{-}C}$ = 26.2 Hz, C3), 34.3 ppm (s, C19), 31.2 ppm (s, C20-22), 14.0 ppm (s, C12). Elemental analysis calcd (%) for $C_{88}H_{73}Br_2OsP_3$: C 67.17, H 4.68; found: C 67.26, H 4.49. HRMS (ESI): m/z calcd for $[C_{88}H_{73}BrOsP_3]^+$, 1493.3707; found: 1493.3711.

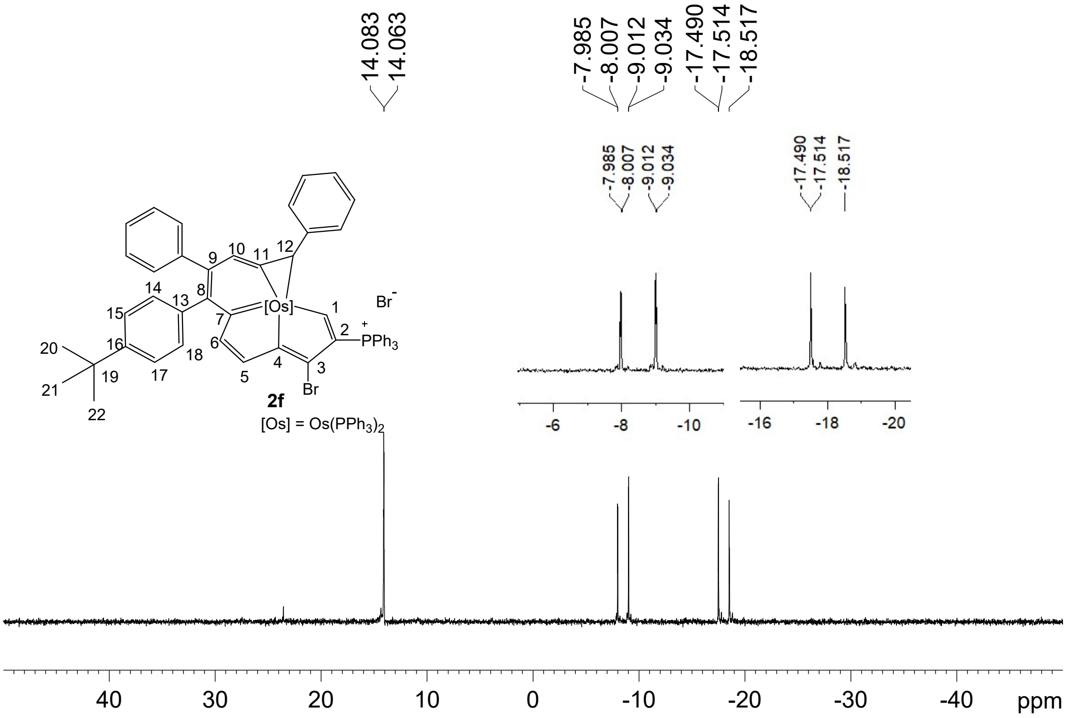


Figure S21 The ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2f**.

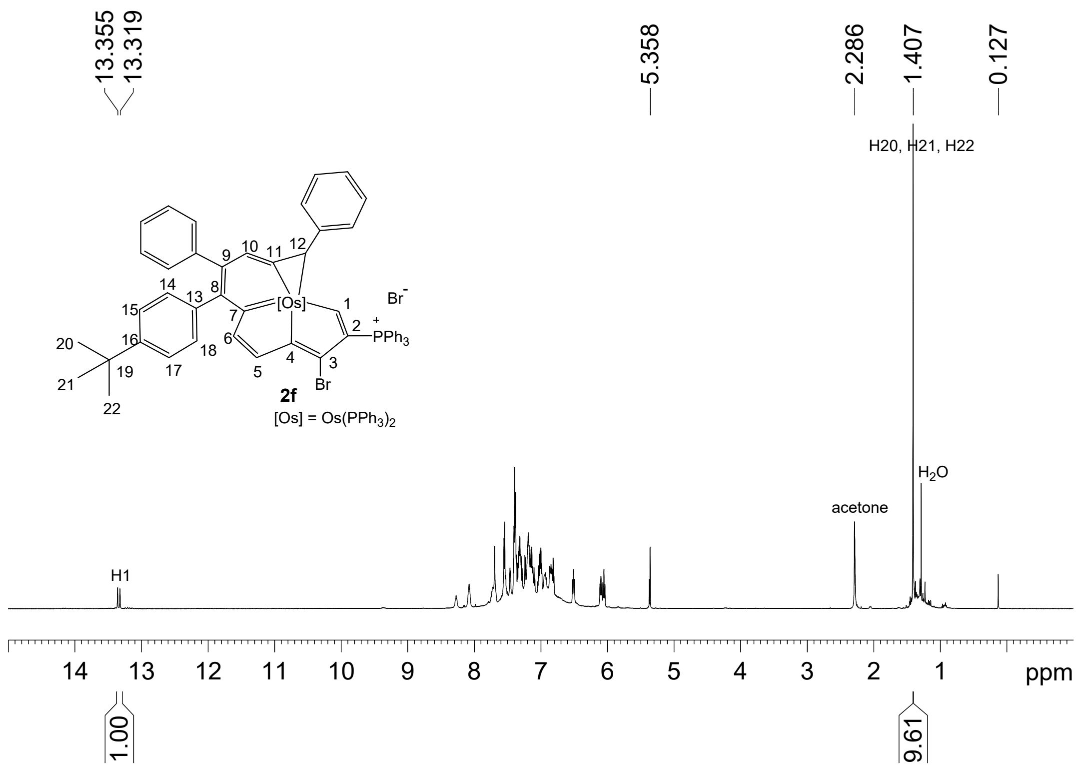


Figure S22 The ^1H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2f**.

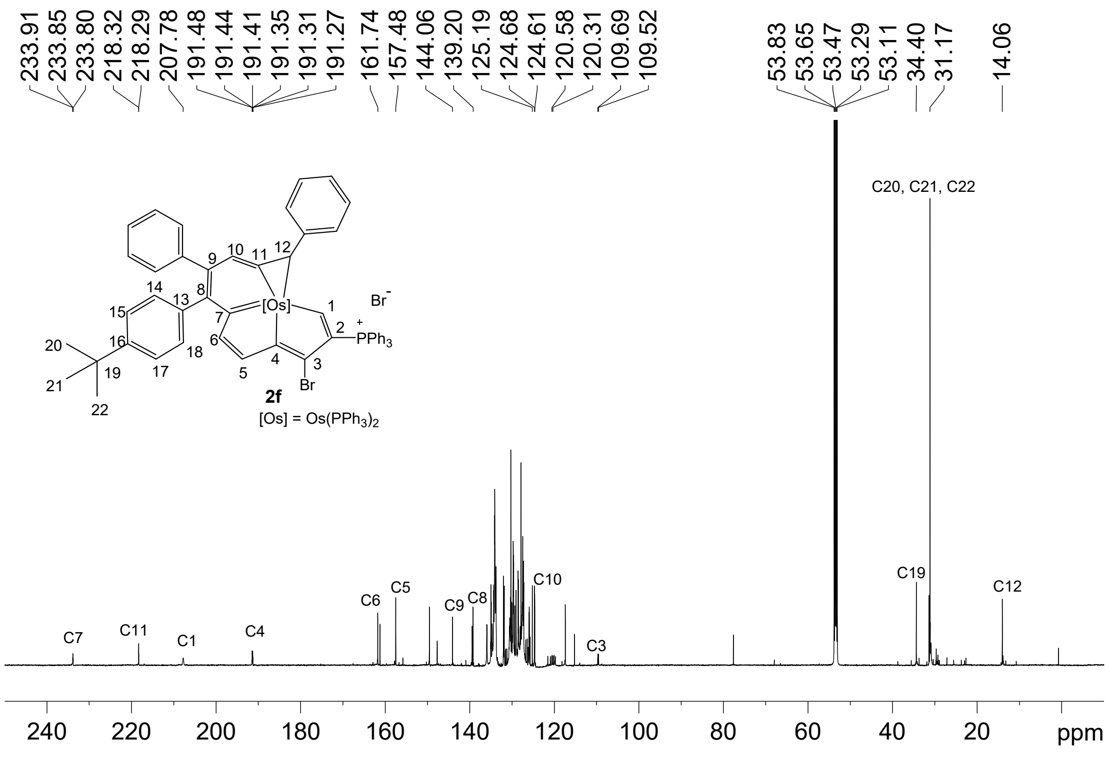


Figure S23 The ^{13}C NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2f**.

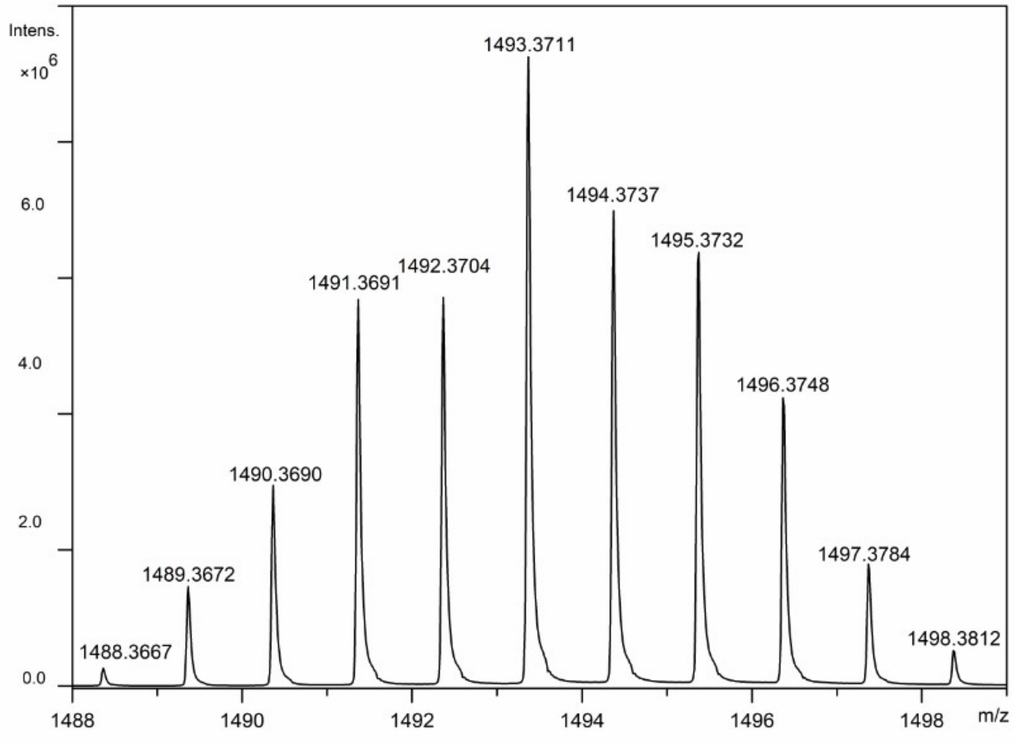


Figure S24 Positive-ion ESI-MS spectrum of **2f** measured in methanol.

Preparation of **2g**

2g: The synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), (4-methoxyphenyl)boronic acid (31.90 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg), K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2g**, 80.9 mg, 92%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ = 13.3 (d, $J_{P\text{-}H}$ = 21.9 Hz 1H, H1), 7.7 (s, 1H, H10), 7.4 ppm (s,1H, H6) 7.2 (s,1H, H5), 3.9 (s,3H, H17) ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ= 14.1 (t, $J_{P\text{-}P}$ = 5.8 Hz C*P*Ph$_3$), –8.9 (dd, $J_{P\text{-}P}$ = 248.9 Hz, $J_{P\text{-}P}$ =5.3 Hz, Os*P*Ph$_3$), –17.6 ppm (dd, $J_{P\text{-}P}$ = 248.9 Hz, $J_{P\text{-}P}$ = 5.3 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (125.8 MHz, CD_2Cl_2): δ= 234.5 (t, $J_{P\text{-}C}$ = 8.4 Hz, C7), 218.1 (t, $J_{P\text{-}C}$ = 4.3 Hz, C11), 207.8 (t, $J_{P\text{-}C}$ = 12 Hz, C1), 191.3 (dt, $J_{P\text{-}C}$ =18.5 Hz, $J_{P\text{-}C}$ = 4.7 Hz, C4), 161.6 (s, C6), 157.6 (s, C5), 144.2 (s, C9), 138.9 (s, C8), 120.3 (d, $J_{P\text{-}C}$ = 88.2 Hz, C2), 117.5 (s, C10), 109.5 (d, $J_{P\text{-}C}$ = 26.3 Hz, C3), 55.2 ppm (s, C19)，14.1 ppm (s, C12). Elemental analysis calcd (%) for $C_{85}H_{67}Br_2OOsP_3$: C 65.98, H 4.36; found: C 65.78, H 4.11. HRMS (ESI): m/z calcd for $[C_{85}H_{67}BrOOsP_3]^+$: 1467.3186; found: 1467.3187.

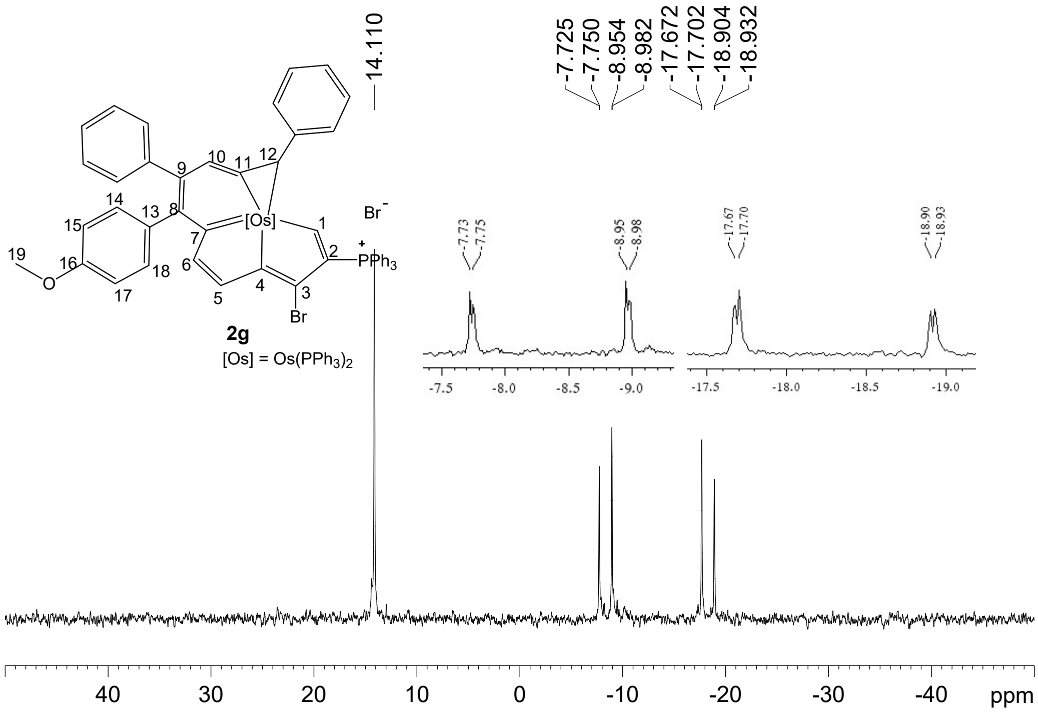


Figure S25 The $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **2g**.

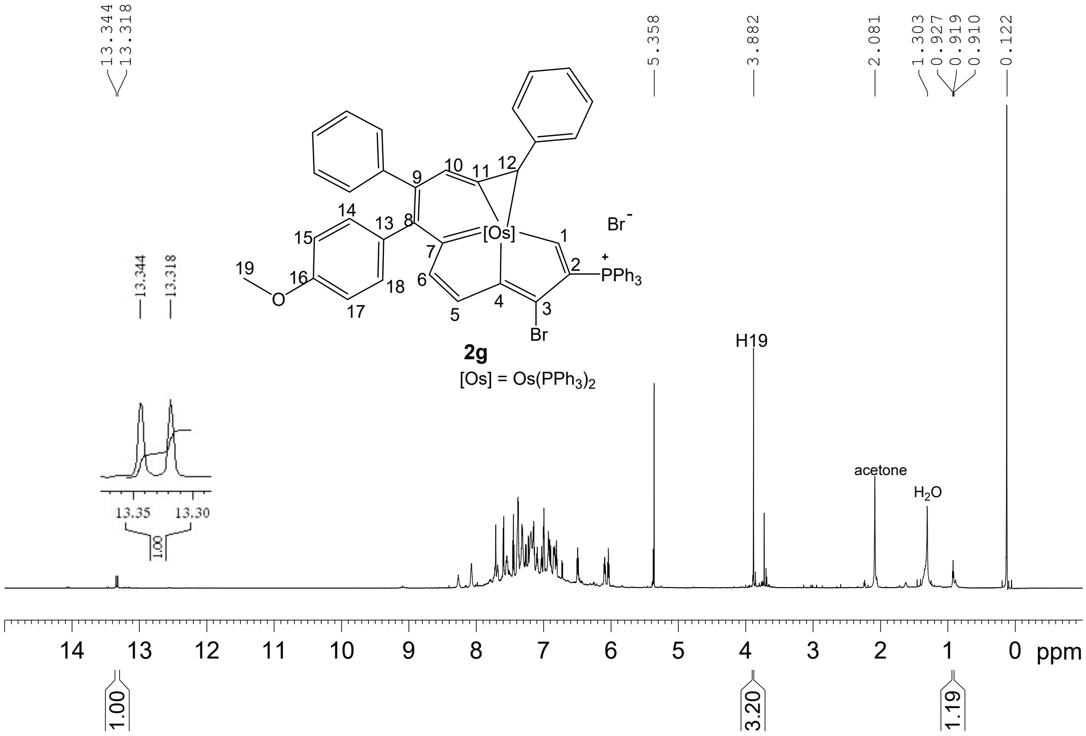


Figure S26 The ^1H NMR (500.2 MHz, CD_2Cl_2) spectrum for complex **2g**.

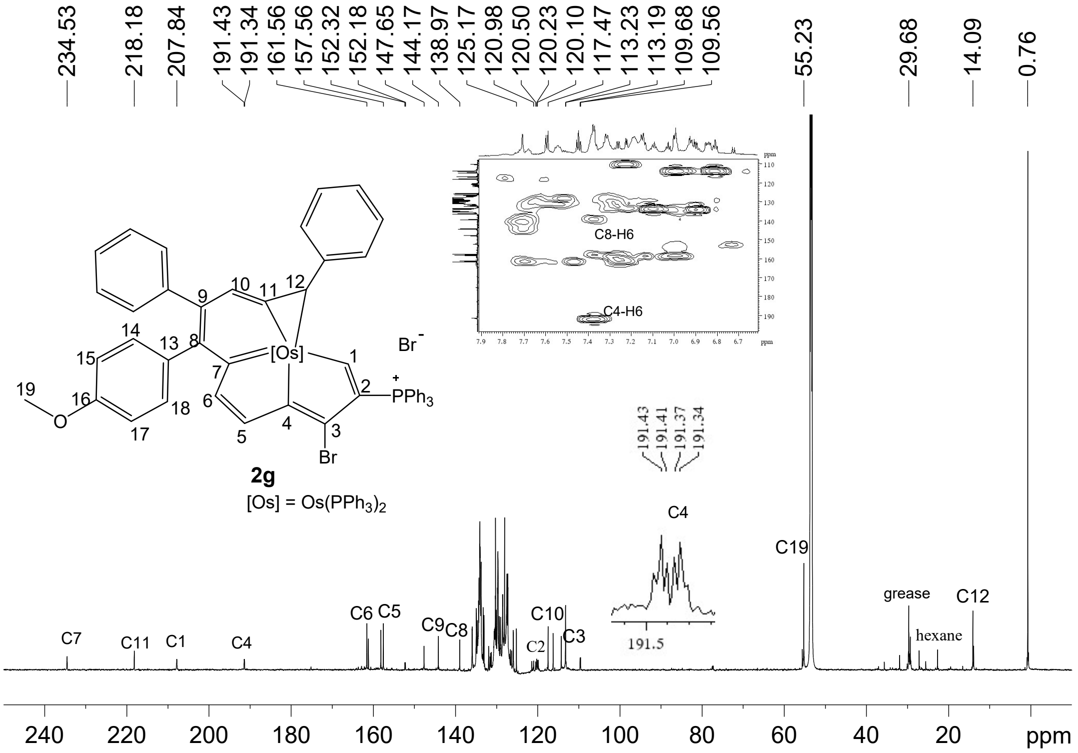


Figure S27 The ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$) spectrum for complex **2g**.

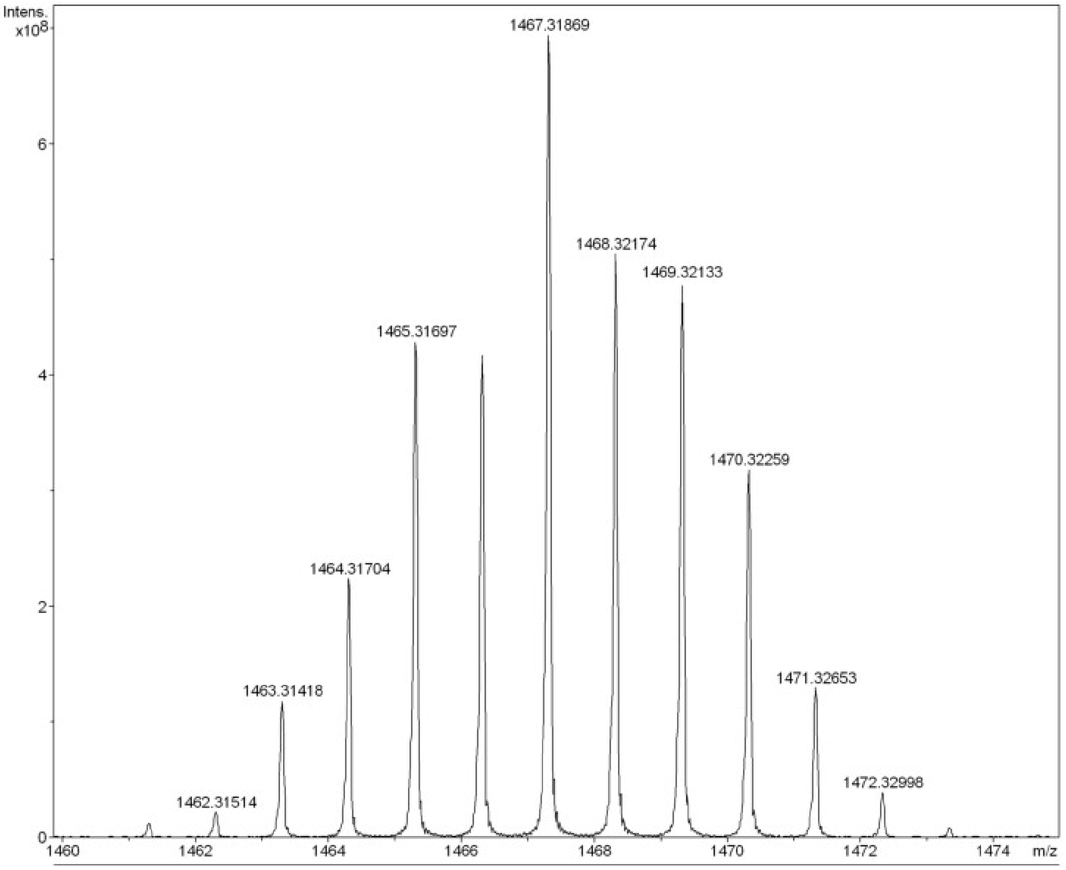


Figure S28 Positive-ion ESI-MS spectrum of **2g** measured in methanol.

Preparation of **2h**

2h: The synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), (4-(diphenylamino)phenyl) boronic acid (60.72 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg), K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2h**, 84.6 mg, 88%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ= 13.4 (d, $J_{P\text{-}H}$ = 21.6 Hz 1H, H1), 7.7 (s, 1H, H10), 7.6 ppm (s,1H, H6) 7.3 (s,1H, H5). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ= 14.1 (t, $J_{P\text{-}P}$ = 6.8 Hz C*P*Ph$_3$), –9.2 (dd, $J_{P\text{-}P}$ = 250.7 Hz, $J_{P\text{-}P}$ =5.7 Hz, Os*P*Ph$_3$), –17.4 ppm (dd, $J_{P\text{-}P}$ = 250.7 Hz, $J_{P\text{-}P}$ = 5.7 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (125.8 MHz, CD_2Cl_2): δ= 233.6 (t, $J_{P\text{-}C}$ = 7.1 Hz, C7), 218.6 (t, $J_{P\text{-}C}$ = 4.2 Hz, C11), 207.7 (t, $J_{P\text{-}C}$ = 12 Hz, C1), 191.3 (dt, $J_{P\text{-}C}$ =19.9 Hz, $J_{P\text{-}C}$ = 6.2 Hz, C4), 161.5 (s, C6), 157.7 (s, C5), 146.1 (s, C16),144.2 (s, C9), 138.1 (s, C8), 117.4 (s, C10), 109.8 (d, $J_{P\text{-}C}$ = 25.1 Hz, C3), 14.3 ppm (s, C12). Elemental analysis calcd (%) for $C_{96}H_{74}Br_2NOsP_3$: C 68.45, H 4.43, N 0.83; found: C 68.50, H 4.84, N 0.79. HRMS (ESI): m/z calcd for $[C_{96}H_{74}BrNOsP_3]^+$, 1604.3825; found: 1604.3827.

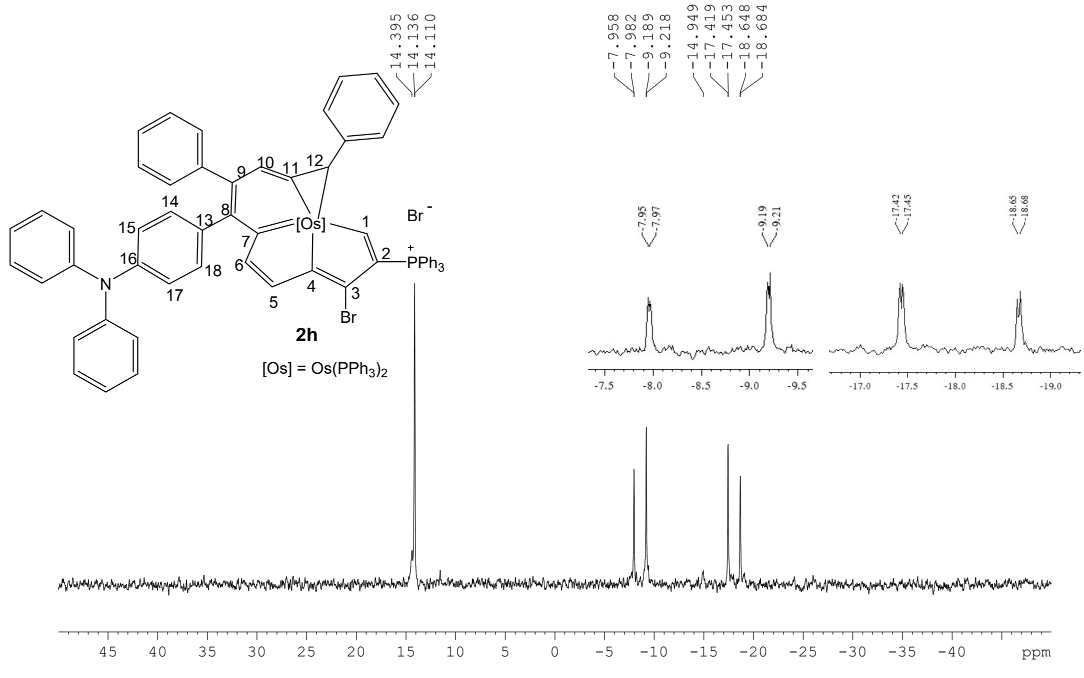


Figure S29 The ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **2h**.

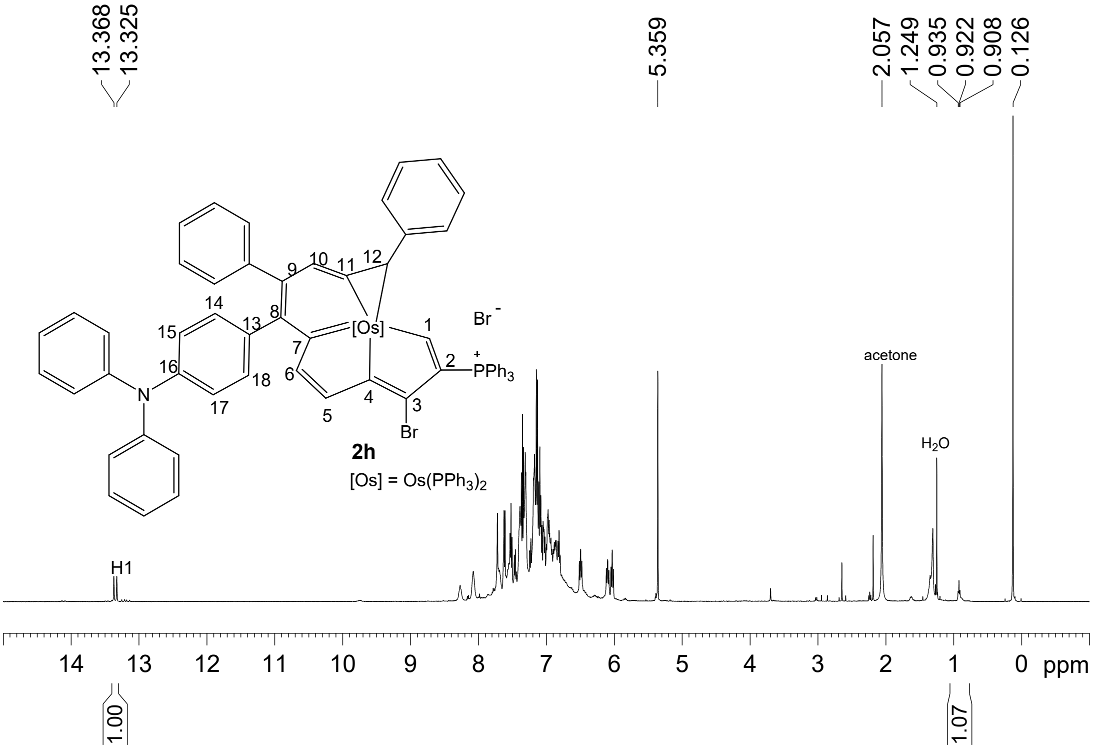


Figure S30 The ^{1}H NMR (500.2 MHz, CD_2Cl_2) spectrum for complex **2h**.

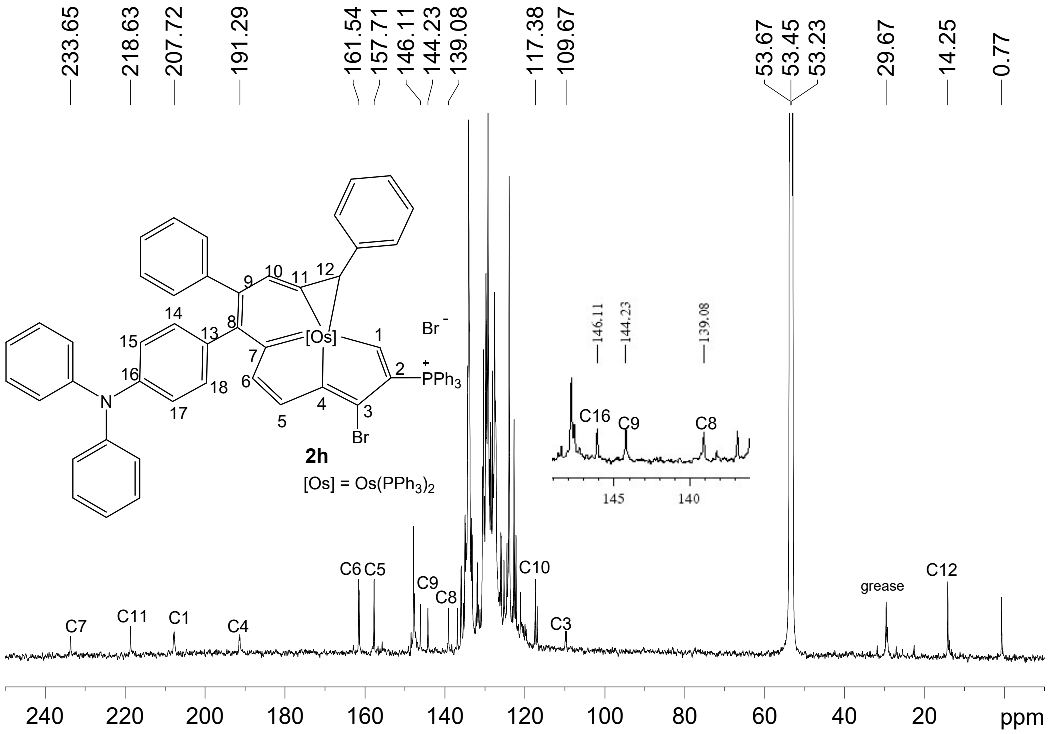


Figure S31 The ^{13}C NMR (125.8 MHz, CD_2Cl_2) spectrum for complex **2h**.

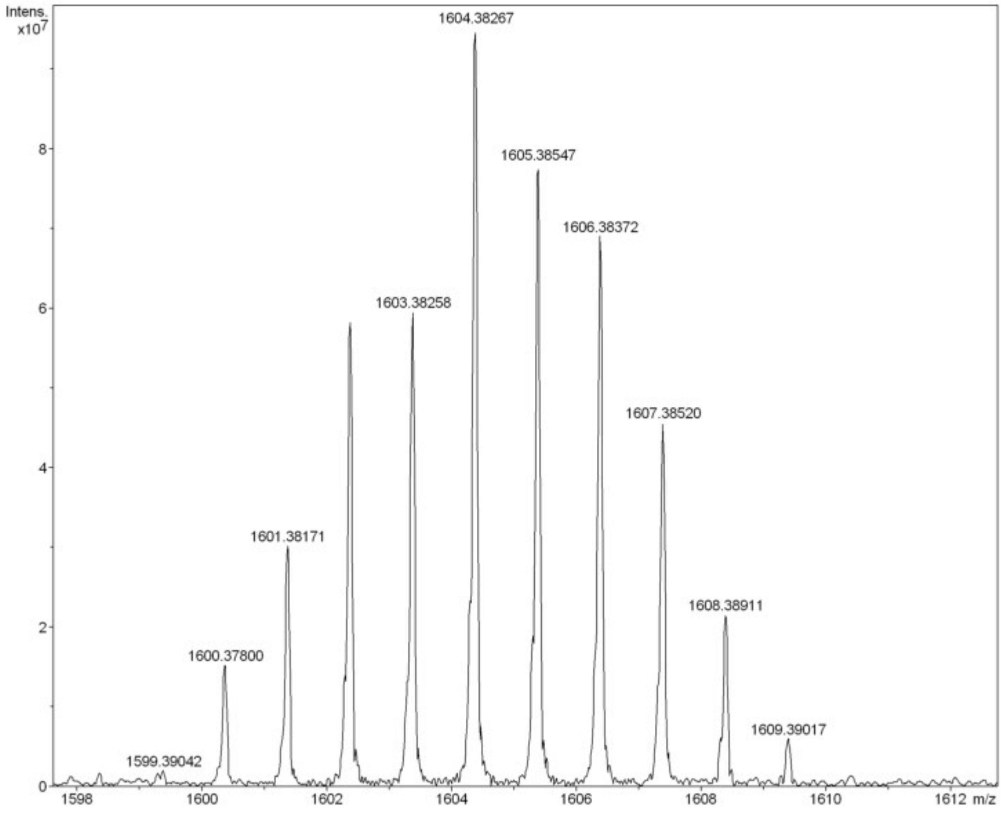


Figure S32 Positive-ion ESI-MS spectrum of **2h** measured in methanol.

Preparation of **2i**

2i: The synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), (4-fluorophenyl) boronic acid (29.38 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg), K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2i**, 75.9 mg, 87%). ^1H NMR plus ^1H-^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ = 13.3 (d, $J_{P\text{-}H}$ = 21.1 Hz 1H, H1), 7.7 (s, 1H, H10), 7.3 ppm (s,1H, H6) 7.2 (s,1H, H5), 1.36 (s,1H, H12) ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ = 14.2 (t, $J_{P\text{-}P}$ = 5.6 Hz C*P*Ph$_3$), –9.3 (dd, $J_{P\text{-}P}$ = 251.7 Hz, $J_{P\text{-}P}$ =5.7 Hz, Os*P*Ph$_3$), –17.5 ppm (dd, $J_{P\text{-}P}$ = 251.7 Hz, $J_{P\text{-}P}$ = 5.7 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^1H-^{13}C HSQC and ^1H-^{13}C HMBC (125.8 MHz, CD_2Cl_2): δ = 233.6 (t, $J_{P\text{-}C}$ = 9.5 Hz, C7), 218.8 (t, $J_{P\text{-}C}$ = 4.7 Hz, C11), 207.9 (t, $J_{P\text{-}C}$ = 12.3 Hz, C1), 191.3 (dt, $J_{P\text{-}C}$ =21.1 Hz, $J_{P\text{-}C}$ = 6.1 Hz, C4), 161.2 (s, C6), 157.9 (s, C5), 143.8 (s, C9), 138.4 (s, C8), 117.3 (s, C10), 110.1 (d, $J_{P\text{-}C}$ = 25.1 Hz, C3), 14.4 ppm (s, C12). Elemental analysis calcd (%) for $C_{84}H_{64}Br_2FOsP_3$: C 65.71, H 4.20; found: C 65.83, H 4.09. HRMS (ESI): m/z calcd for $[C_{84}H_{64}BrFOsP_3]^+$: 1455.2986;

found: 1455.2968.

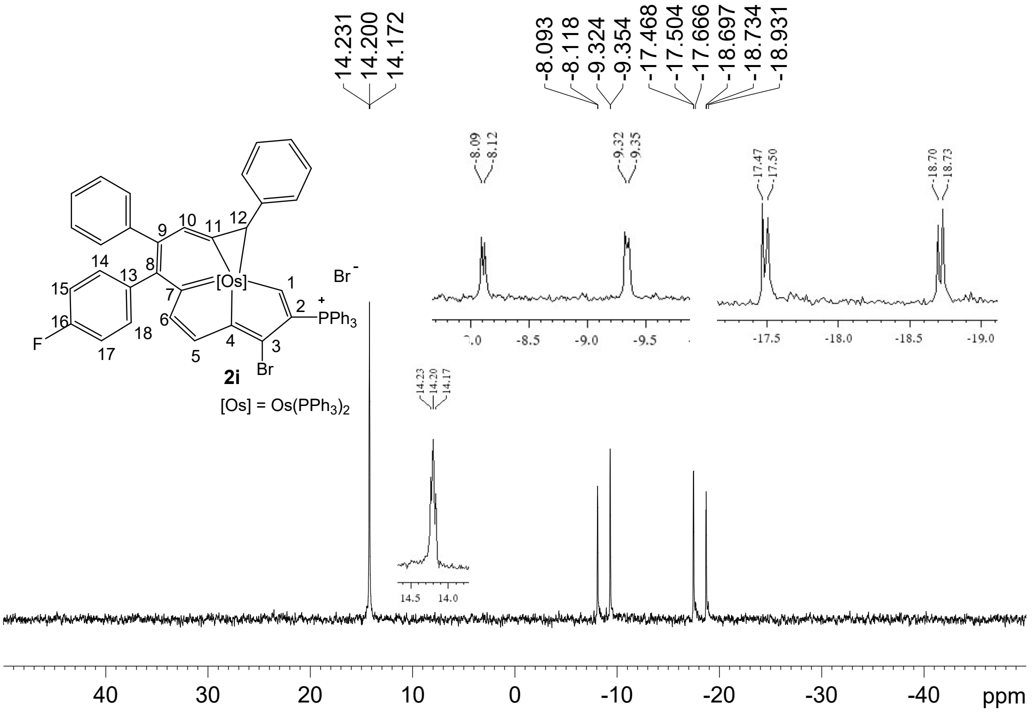


Figure S33 The $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **2i**.

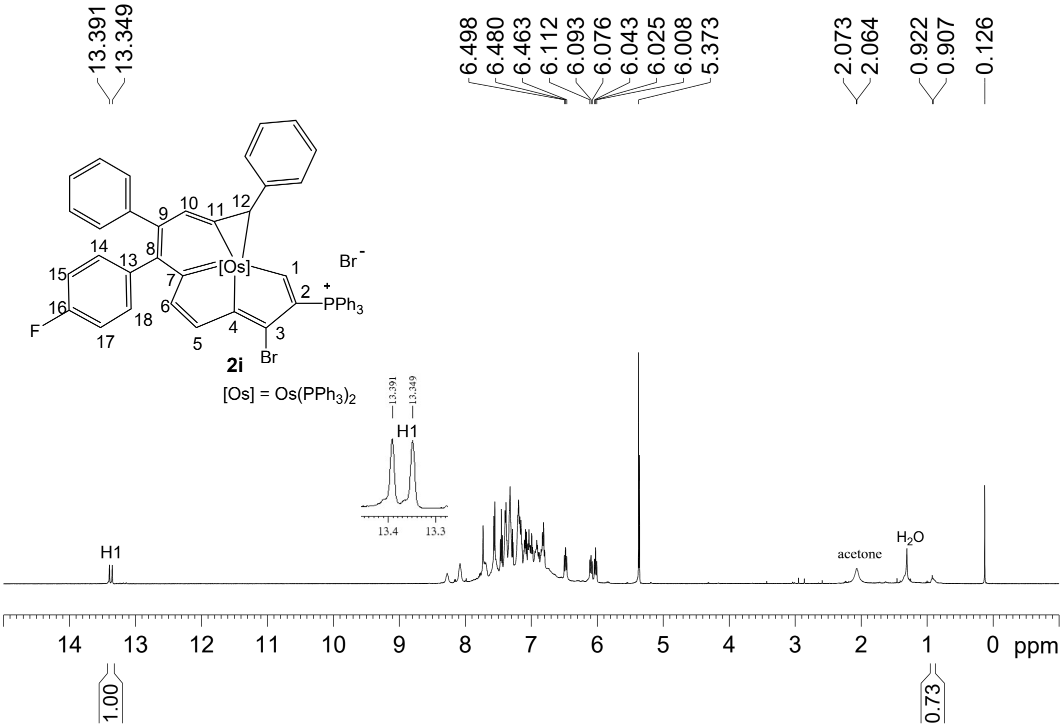


Figure S34 The ^1H NMR (500.2 MHz, CD_2Cl_2) spectrum for complex **2i**.

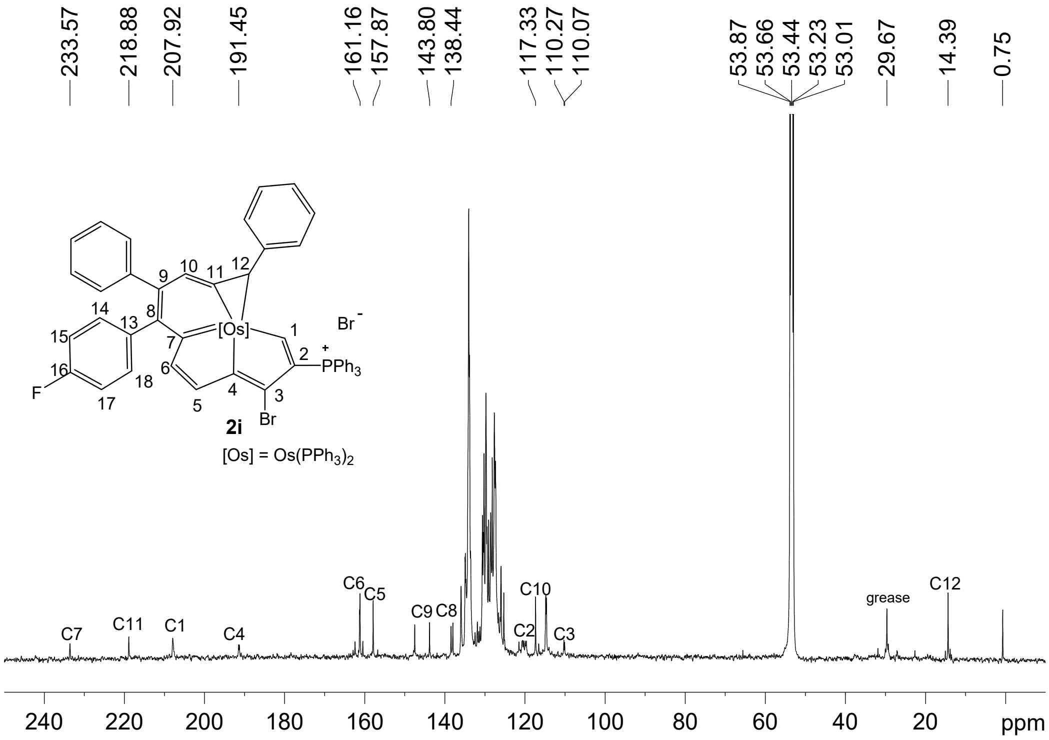


Figure S35 The ^{13}C NMR (125.8 MHz, CD2Cl2) spectrum for complex **2i**.

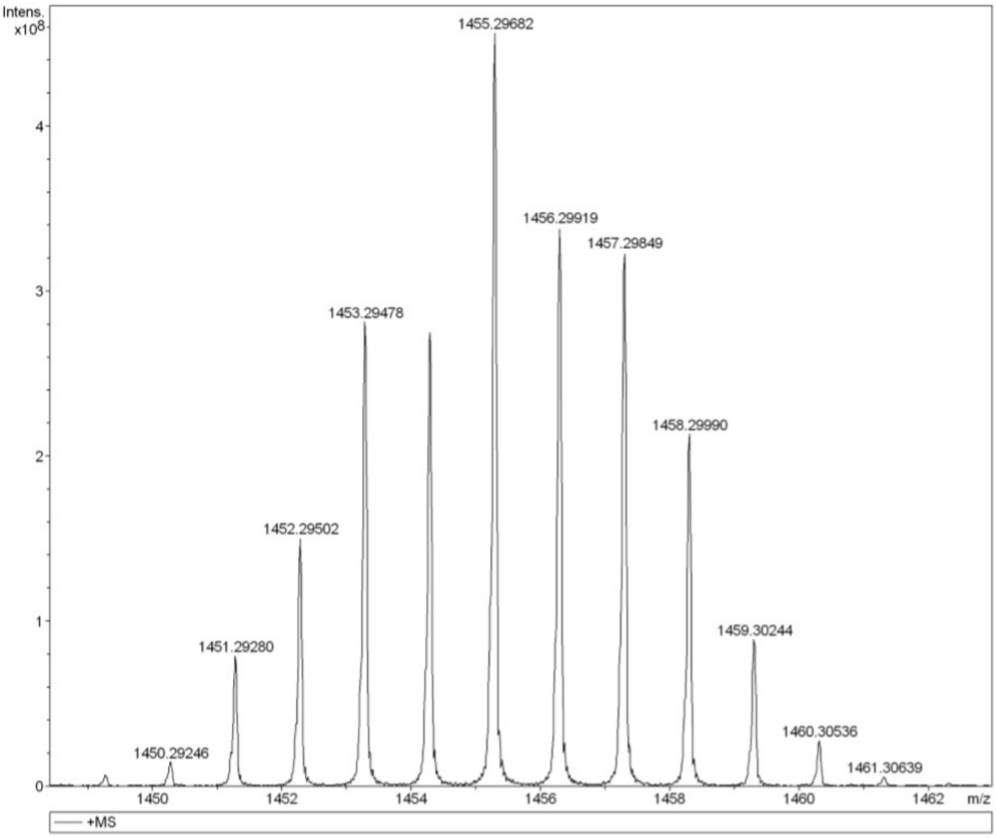


Figure S36 Positive-ion ESI-MS spectrum of **2i** measured in methanol.

Preparation of **2j**

2j: The synthetic procedure is similar to that for **2a**. **1** (91.6 mg, 0.06 mmol), naphthalen-2-ylboronic acid (36.12 mg 0.21 mmol), $Pd_2(dba)_3$ (5 mol%, 2.75 mg), K_2CO_3 (16.6 mg, 0.12 mmol) and 3 mL of 1,2-dichlorobenzene, afforded as yellow-green solid (**2j**, 72.3 mg, 81%). ^{1}H NMR plus ^{1}H-^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 13.4 (d, $J_{\text{P-H}}$ = 20.8 Hz 1H, H1), 7.3 ppm (s, 1H, H6), 7.2 (s, 1H, H5), 7.6 (s, 1H, H10). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ= 14.2 (d, $J_{\text{P-P}}$ = 10.2 Hz C*P*Ph$_3$), –8.6 (ddd, $J_{\text{P-P}}$ = 248.1 Hz, $J_{\text{P-P}}$ = 5.9 Hz, Os*P*Ph$_3$), –18.5 ppm (ddd, $J_{\text{P-P}}$ = 249.8 Hz, $J_{\text{P-P}}$ = 6.1 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (150.9 MHz, CD_2Cl_2): δ= 233.8 (dt, $J_{\text{P-C}}$ = 32.0 Hz, C7), 218.2 (t, $J_{\text{P-C}}$ = 9.2 Hz, C11), 207.7 (t, $J_{\text{P-C}}$ = 6.8 Hz, C1), 191.4 (dt, $J_{\text{P-C}}$ =19.5 Hz, $J_{\text{P-C}}$ = 5.2 Hz, C4), 161.6 (s, C6), 157.8 (s, C5), 143.8 (s, C9), 138.9 (s, C8), 120.3 (d, $J_{\text{P-C}}$ = 91.2 Hz, C2), 117.4 (s, C10), 109.9 (d, $J_{\text{P-C}}$ = 25.5 Hz, C3) 14.4 (s, C12). Elemental analysis calcd (%) for $C_{88}H_{67}Br_2OsP_3$: C 67.43, H 4.31; found: C 67.25, H 4.58. HRMS (ESI): m/z calcd for $[C_{88}H_{67}BrOsP_3]^+$: 1487.3238; found: 1487.3250.

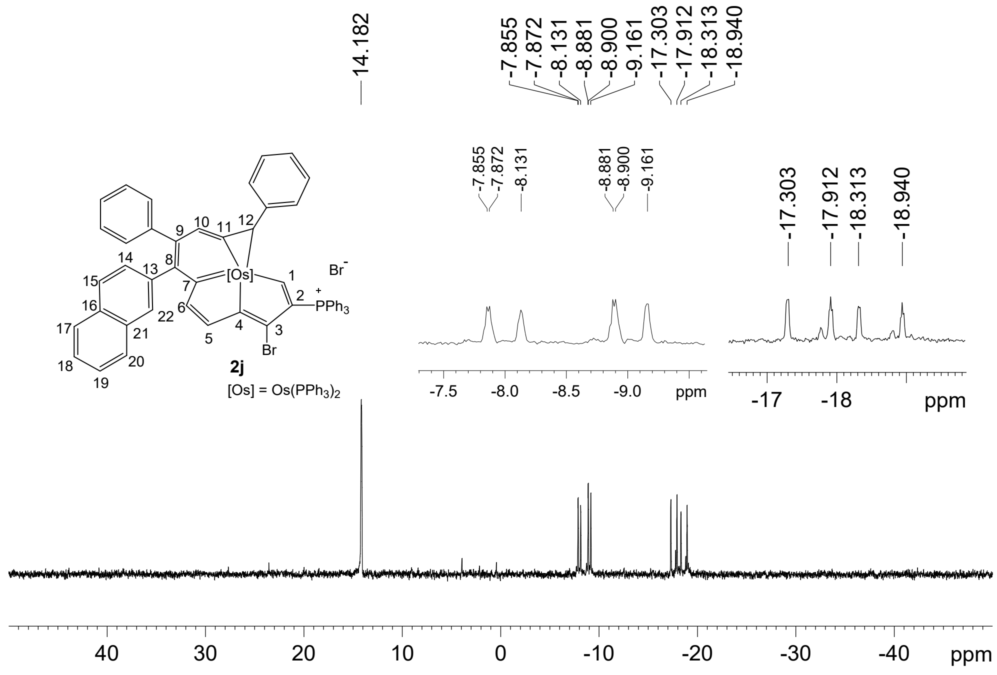


Figure S37 The ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2j**.

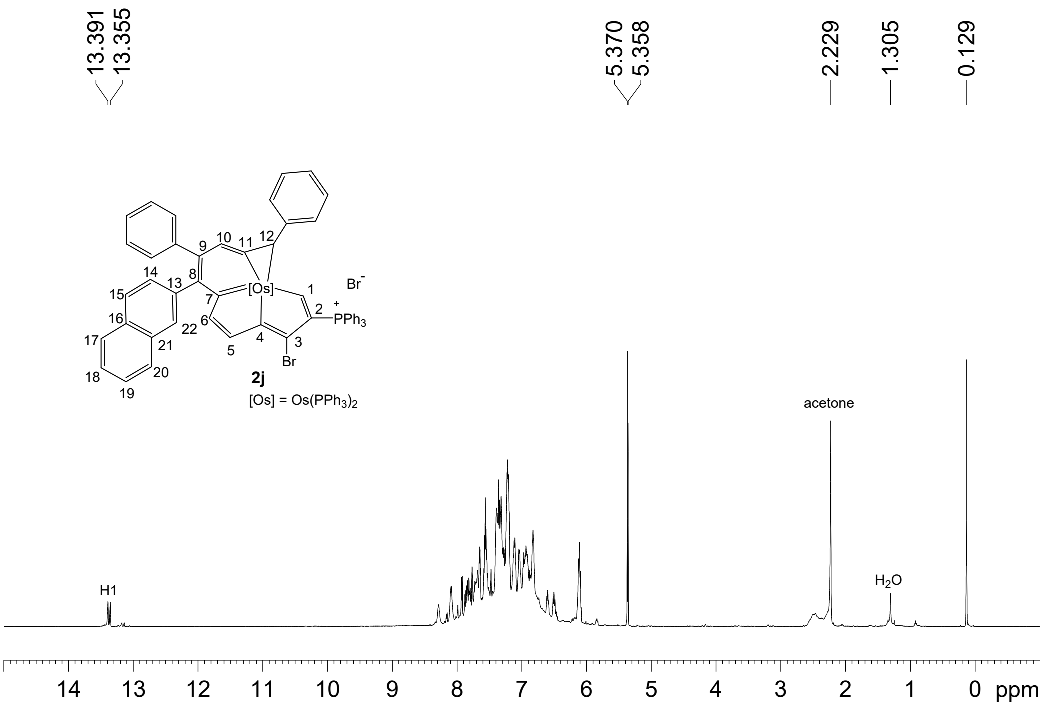


Figure S38 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2j**.

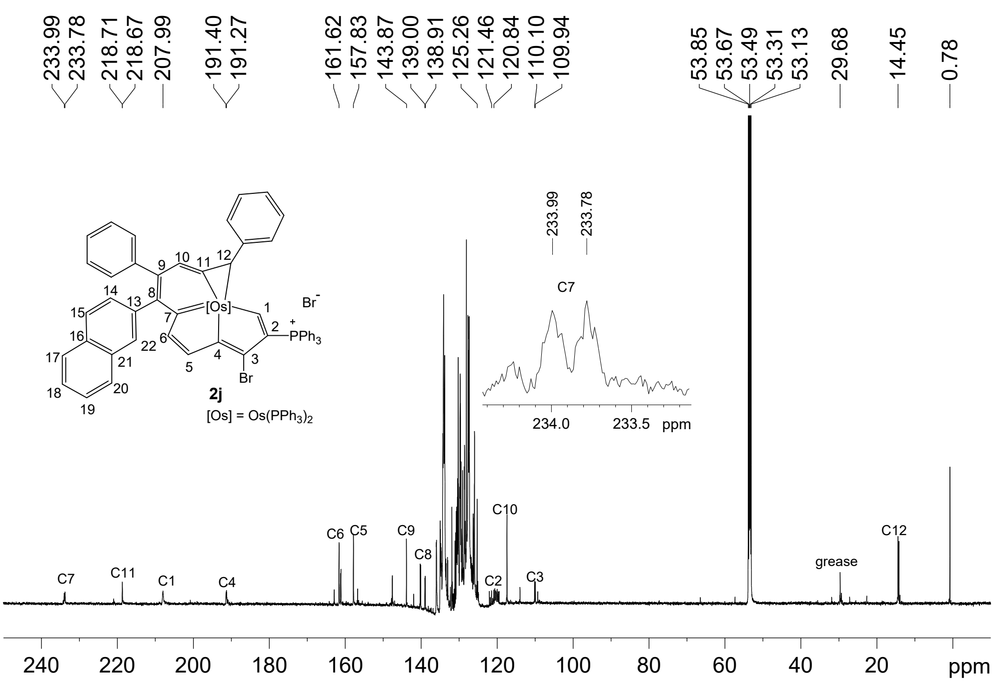


Figure S39 The ^{13}C NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **2j**.

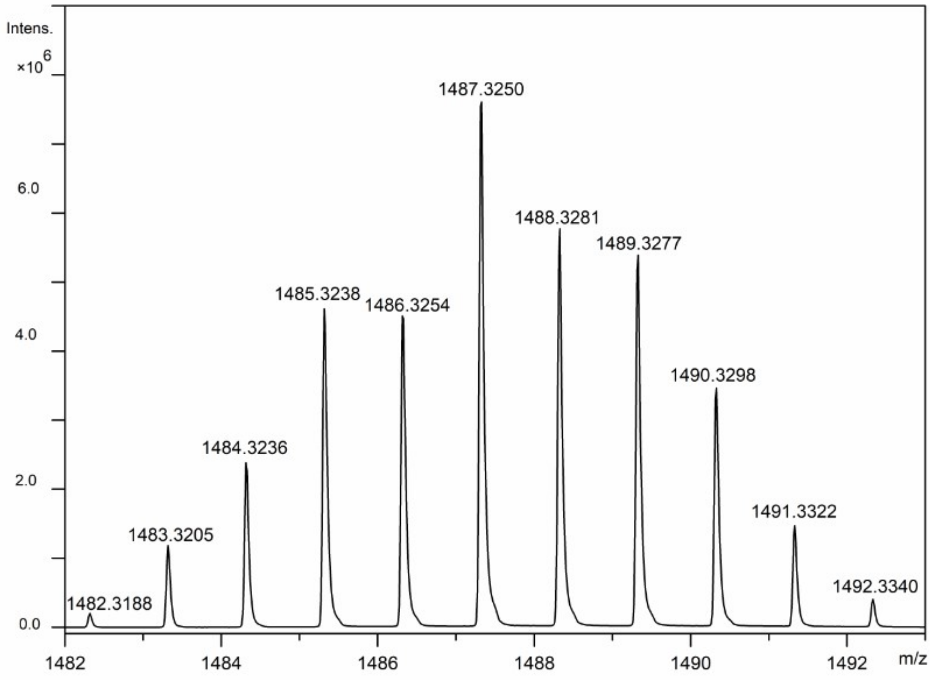
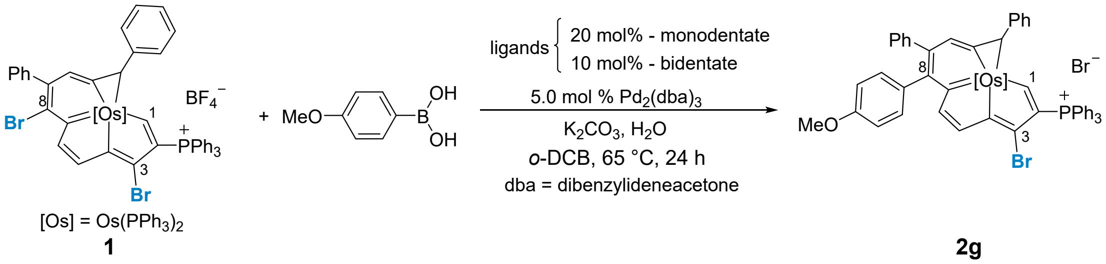


Figure S40 Positive-ion ESI-MS spectrum of **2j** measured in methanol.

2. Ligand Screen



entry	[a]ligands	Yield(%)
1	$P(^tBu)_3$	0
2	P(*o*-tol)$_3$	0
3	PPh_3	0
4	DPPF	0
5	Sphos	0
6	BIPHEP	0

Reaction conditions: **1** (0.1 mmol), 4-methoxyphenyl boronic acid (0.35 mmol), K_2CO_3 (0.2 mmol), $Pd_2(dba)_3$ (5.0 mol %), *o*-DCB (5 mL).
[a]Monodentate ligands were loaded at 20 mol %, bidentate at 10 mol %.

Ligand study: Reaction was performed according to the standard procedure for metalla-aromatics suzuki-miyaura coupling. The effect of additional phosphine ligands on the reaction was probed systematically, almost obtaining triphenylphosphine oxide and **2'**, no cross-coupling product **2g**.

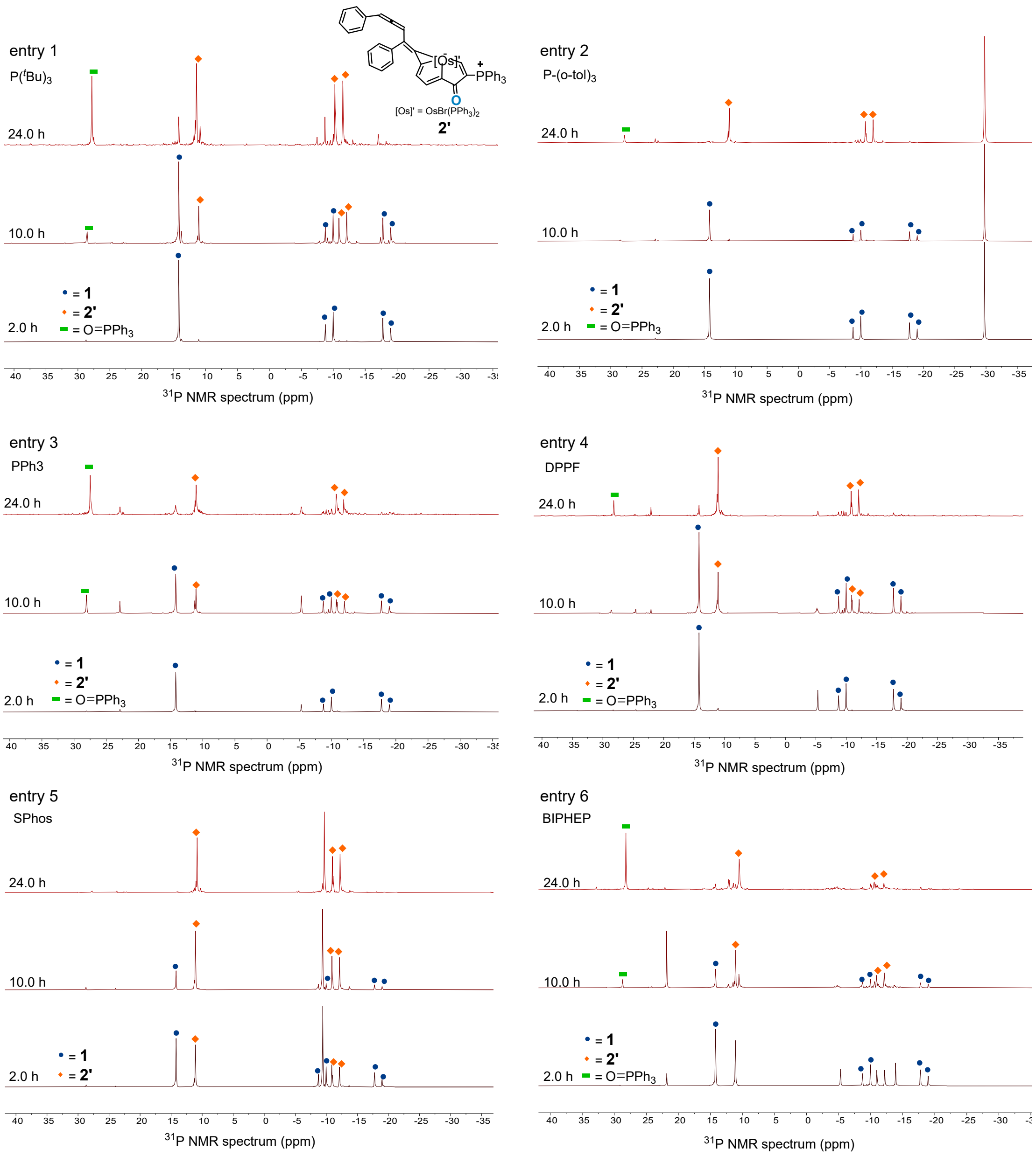
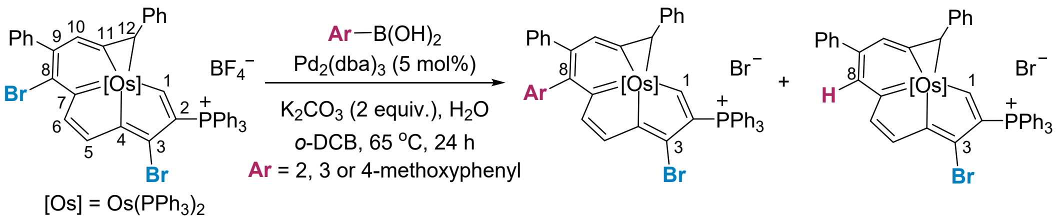


Figure S41 Overlapping $^{31}P\ \{^{1}H\}$ NMR Spectrums.

3. Aryl Boronic Acid with Methoxy Group Located in Different Positions



1 **6** **7**

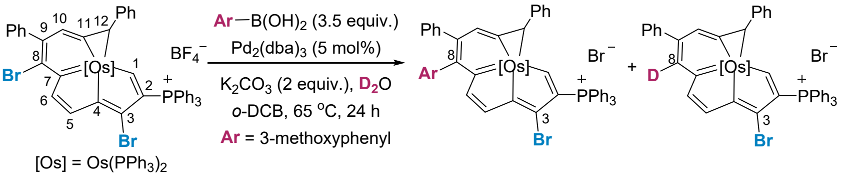
entry	aryl boronic acid	conv. (%)	ratio (**6**/**7**)
1	(2-methoxyphenyl)boronic acid	89	7/93
2	(3-methoxyphenyl)boronic acid	86	38/62
3	(4-methoxyphenyl)boronic acid	92	96/4

Entry 1: Reaction was performed according to the standard procedure for metalla-aromatics suzuki-miyaura coupling. (2-methoxyphenyl) boronic acid was used for the reaction, almost obtaining byproduct **7**. The ratio of product **6a** to byproduct **7** is 7/93 by integral of the characteristic hydrogen spectrum (H1).

Entry 2: Reaction was performed according to the standard procedure for metalla-aromatics suzuki-miyaura coupling. (3-methoxyphenyl) boronic acid was used for the reaction, byproduct **7** sharply decreasing. The ratio of product **6b** to byproduct **7** is 38/62 by integral of the characteristic hydrogen spectrum (H1).

Entry 3: Reaction was performed according to the standard procedure for metalla-aromatics suzuki-miyaura coupling. (4-methoxyphenyl) boronic acid was used for the reaction, almost obtaining product **6c**. The ratio of product **6c** to byproduct **7** is 96/4 by integral of the characteristic hydrogen spectrum (H1).

4. Isotopic-labeling Experiments



1 **8** **9**

Reaction was performed according to the standard procedure for deuterium-labeling experiments. In this case, D_2O neat was used instead of regular H_2O. 100% deuterium incorporation has taken place at C8, affording byproduct **9**. **9** was characterized by high-resolution mass spectrometry (Figure S42).

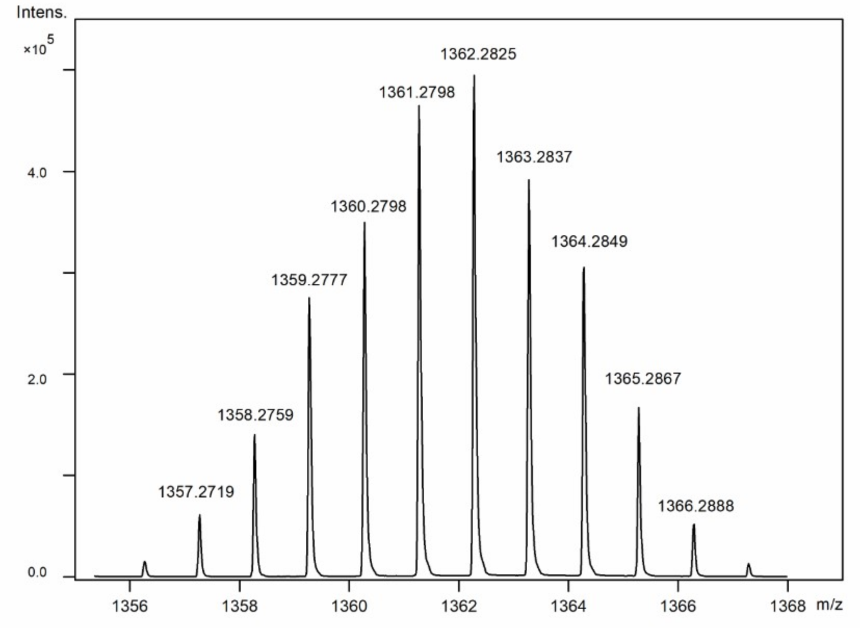
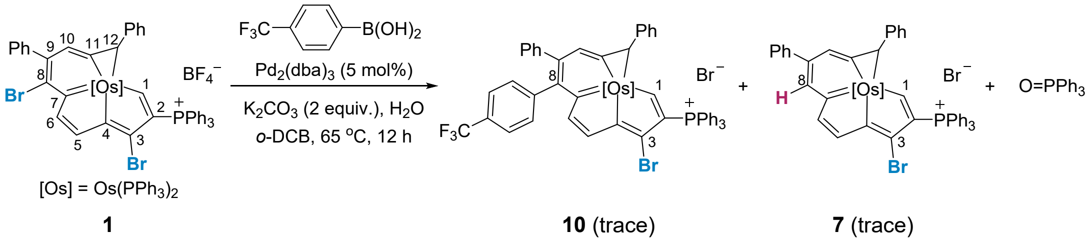


Figure S42 Positive-ion ESI-MS spectrum of **9** measured in methanol

5. Reaction of 1 with (4-(trifluoromethyl)phenyl) boronic acid



Reaction was performed according to the standard procedure for metalla-aromatics suzuki-miyaura coupling. (4-(trifluoromethyl)phenyl) boronic acid was used for the reaction, as monitored by in situ NMR (Figure S43), almost obtaining triphenylphosphine oxide, only trace cross-coupling product **10** and byproduct **7**. Cross-coupling product **10** was characterized by high-resolution mass spectrometry (Figure S44).

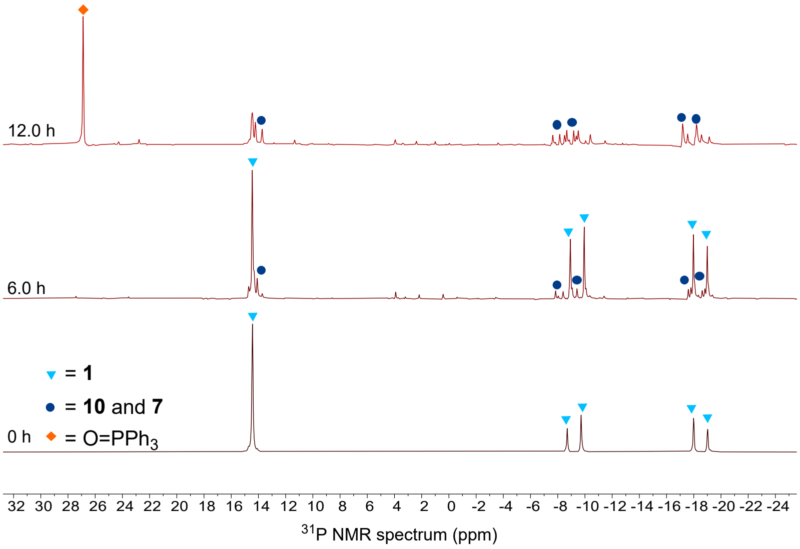


Figure S43 Overlapping $^{31}P\ \{^1H\}$ NMR Spectrums.

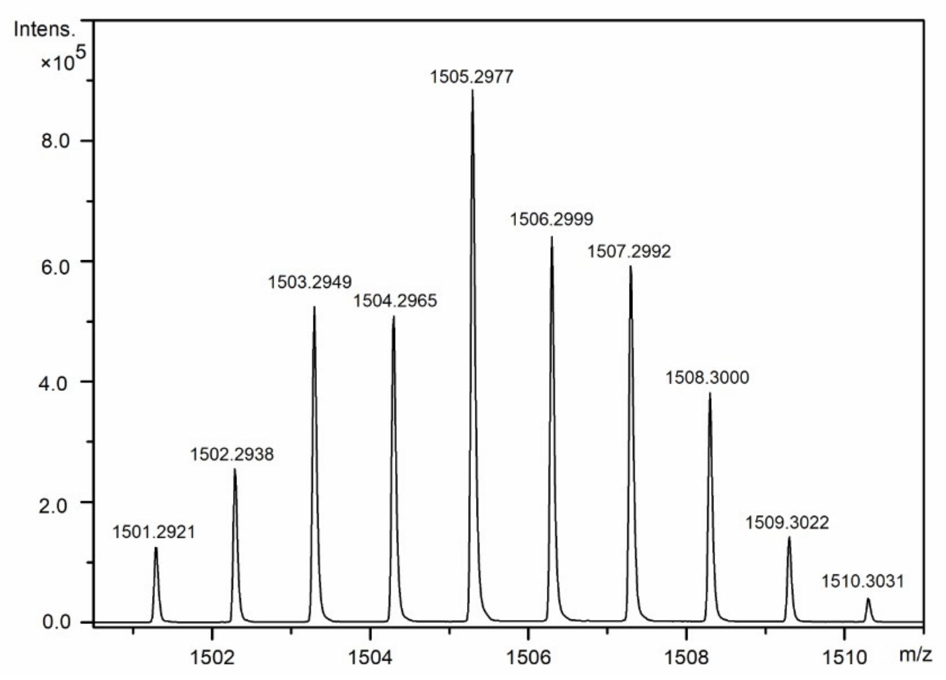


Figure S44 Positive-ion ESI-MS spectrum of **10** measured in methanol

6. X-ray Crystallographic Analysis

All single crystals suitable for X-ray diffraction were grown from 1,2-dichloroethane solution layered with hexane unless otherwise stated. Single-Crystal X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer with mirror-monochromated Cu Kα radiation (λ = 1.54184 Å) for **2a** and **2h**. With Olex2 [1], the structures of **2a** and **2h** were solved with ShelXT[2] structure solution program using

Direct methods and refined with the ShelXL [3] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. Some of the solvent molecules and phenyl groups were disordered and refined with suitable restrains. CCDC-2194944 (**2a**) and CCDC-2194946 (**2h**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table S1. Crystallographic details for complex **2a** and **2h**

	2a	**2h**
Empirical formula	$C_{86}H_{69}Br_2Cl_2OsP_3$	$C_{98}H_{77}Br_2Cl_2NOsP_3$
Formula weight	1571.78	1782.43
Temperature/K	100.00(10)	99.99(10)
Radiation	CuKα (1.54184)	CuKα (1.54184)
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a/Å	13.8929(3)	37.0917(4)
b/Å	15.2075(3)	10.98180(10)
c/Å	18.0219(4)	43.2112(5)
α/°	93.513(2)	90
β/°	96.836(2)	106.0800(10)
γ/°	101.444(2)	90
V/Å^3	3691.24(14)	16912.7(3)
Z	2	8
d_{calc}/g cm^{-3}	1.414	1.400
μ/mm^{-1}	5.848	5.428
F(000)	1584.0	7176.0
Reflections collected	100729	81743
Independent reflections	12300	14941
Data/restraints/parameters	12300/600/856	14941/132/1168
Goodness-of-fit on F_2	1.064	1.063
Final R indexes [I>=2σ(I)]	R1 = 0.0547, wR2 = 0.1540	R1 = 0.0495, wR2 = 0.1288
peak/hole/e Å^{-3}	1.84/-1.72	1.68/-1.67

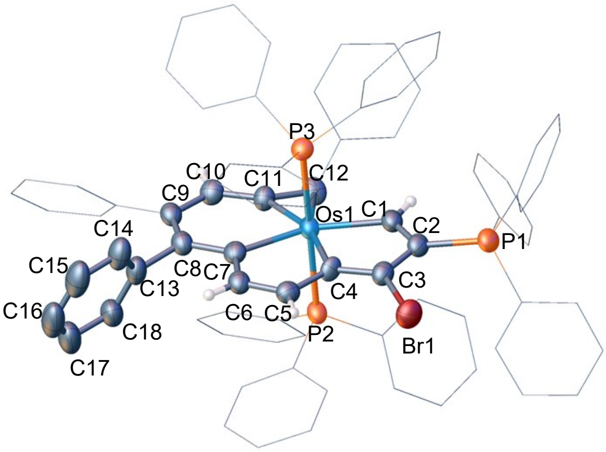


Figure S45 X-ray molecular structure for the cation of complex **2a** drawn with 50% probability level. The hydrogen atoms on the phenyl group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.094(6), Os1–C4 2.109(5), Os1–C7 2.110(6), Os1–C11 2.025(6), Os1–C12 2.238(5), C1–C2 1.356(9), C2–C3 1.437(8), C3–C4 1.351(8), C4–C5 1.410(8), C5–C6 1.346(8), C6–C7 1.419(8), C7–C8 1.457(8), C8–C9 1.378(8), C9–C10 1.439(8), C10–C11 1.338(9), C11–C12 1.391(8), C8–C13 1.513(8), C13–C14 1.380(10), C14–C15 1.380(10), C15–C16 1.351(13), C16–C17 1.356(13), C17–C18 1.404(10), C3–Br1 1.910(6).

Os1-C1-C2 119.0(4), C1-C2-C3 112.8(5), C2-C3-C4 115.8(5), C3-C4-Os1 117.3(4), C4-Os1-C1 74.9(2), Os1-C4-C5 114.9(4), C4-C5-C6 115.8 (5), C5-C6-C7 118.7(5), C6-C7-Os1 113.0(4), C7-Os1-C4 77.6(2), Os1-C7-C8 129.8(4), C7-C8-C9 124.2(5), C8-C9-C10 122.8(5), C9-C10-C11 123.3(6), C10-C11-Os1 136.9(4), C11-Os1-C7 82.6(2), Os1-C11-C12 79.5(3), C11-C12-Os1 62.8(3), C12-Os1-C11 37.7(2), P1-Os1-P2 171.49(5).

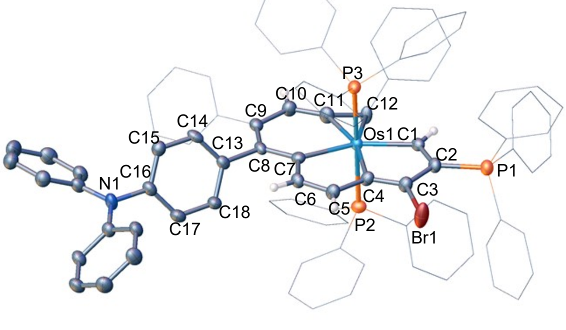
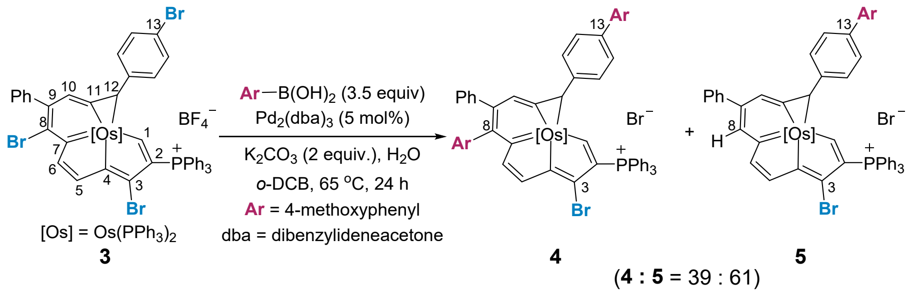


Figure S46 X-ray molecular structure for the cation of complex **2h** drawn with 50%

probability level. The hydrogen atoms on the phenyl group is omitted are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.086(5), Os1–C4 2.113(5), Os1–C7 2.125(5), Os1–C11 2.022(5), Os1–C12 2.256(13), C1–C2 1.373(7), C2–C3 1.449(7), C3–C4 1.356(7), C4–C5 1.421(7), C5–C6 1.366(7), C6–C7 1.443(7), C7–C8 1.442(7), C8–C9 1.403(7), C9–C10 1.437(7), C10–C11 1.337(7), C11–C12 1.434(14), C8–C13 1.507(6), C13–C14 1.401(7), C14–C15 1.389(7), C15–C16 1.387(7), C16–C17 1.388(7), C17–C18 1.394(7), C16–N1 1.432(6), C3–Br1 1.924(5).

Os1-C1-C2 118.9(3), C1-C2-C3 112.4(4), C2-C3-C4 116.6(5), C3-C4-Os1 116.2(4), C4-Os1-C1 75.85(19), Os1-C4-C5 115.2(4), C4-C5-C6 115.7(4), C5-C6-C7 118.4(4), C6-C7-Os1 112.5(3), C7-Os1-C4 78.10(18), Os1-C7-C8 130.6(3), C7-C8-C9 123.7(4), C8-C9-C10 122.6(4), C9-C10-C11 123.0(5), C10-C11-Os1 138.2(4), C11-Os1-C7 81.89(19), Os1-C11-C12 79.5(6), C11-C12-Os1 61.8(5), C12-Os1-C11 38.7(3), P1-Os1-P2 171.35(4).

7. Reaction of 3 with 4-methoxyphenyl boronic acid



Reaction was performed according to common Suzuki-coupling reaction conditions. (4-methoxyphenyl) boronic acid was used for the reaction, as monitored by in situ NMR (Figure S47), obtaining product **4** and **5**. The ratio of product **4** to **5** is 39/61 by integral of the characteristic hydrogen spectrum (H1).

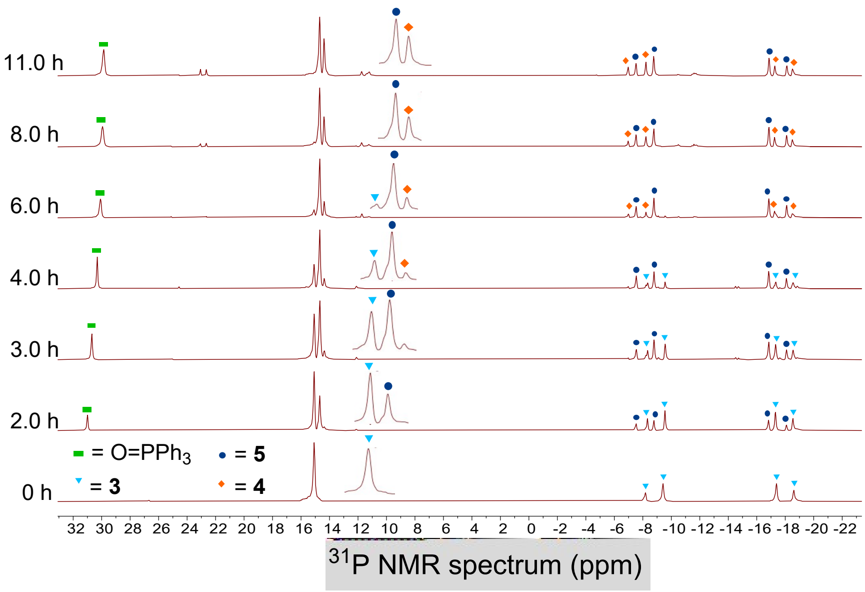
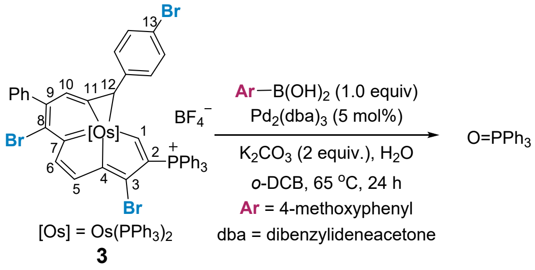


Figure S47 Overlapping ^{31}P {^{1}H} NMR Spectrums.

8. Reaction of 3 with 1 equiv. 4-methoxyphenyl boronic acid



Reaction was performed according to common Suzuki-coupling reaction conditions. (4-methoxyphenyl) boronic acid (1 equiv.) was used for the reaction, as monitored by in situ NMR (Figure S48), almost obtaining triphenylphosphine oxide.

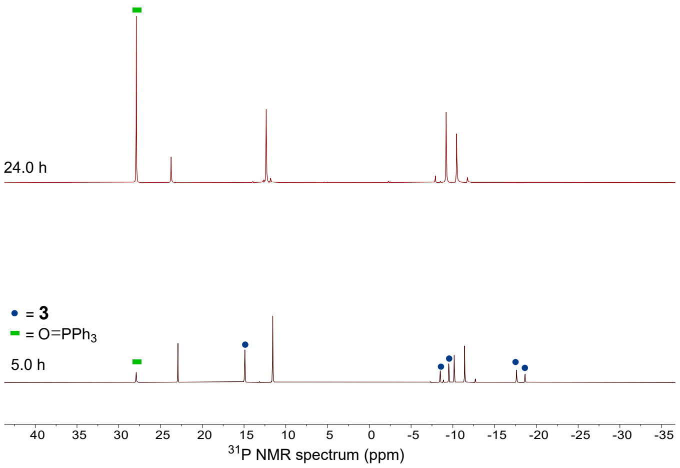
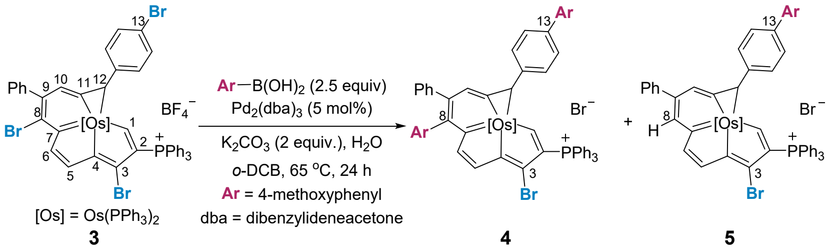


Figure S48 Overlapping ^{31}P {^{1}H} NMR Spectrums.

9. Reaction of 3 with 2.5 equiv. 4-methoxyphenyl boronic acid



Reaction was performed according to common Suzuki-coupling reaction conditions. (4-methoxyphenyl) boronic acid (2.5 equiv.) was used for the reaction, as monitored by in situ NMR (Figure S49), obtaining product **4** and **5**.

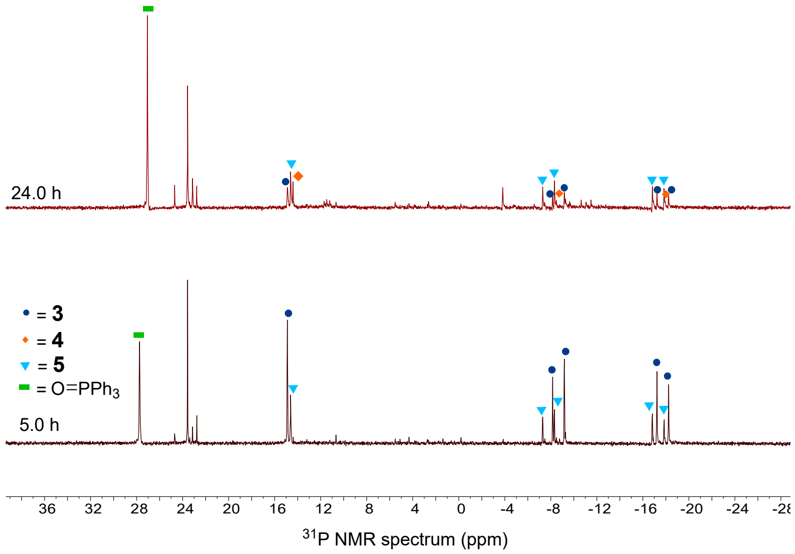
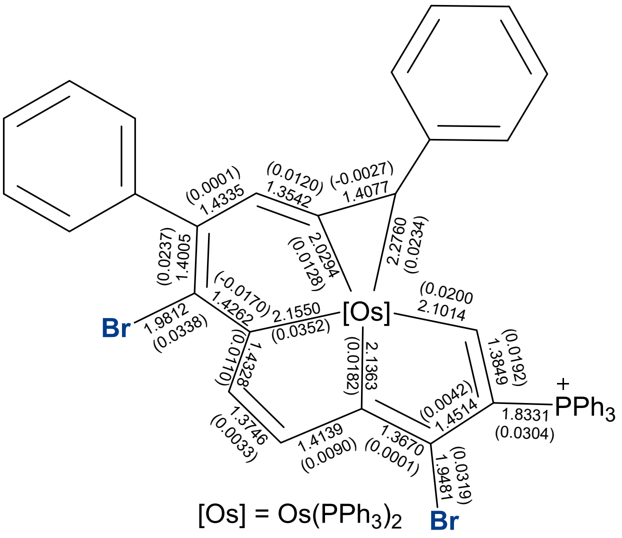


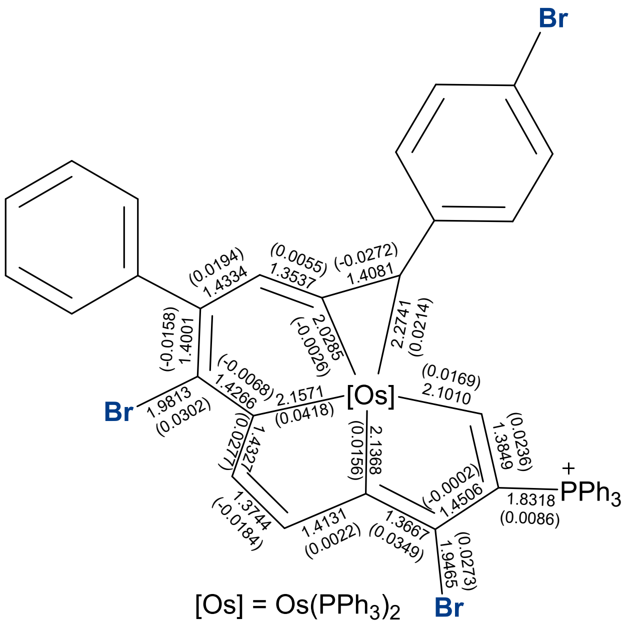
Figure S49 Overlapping ^{31}P {^{1}H} NMR Spectrums.

10. Computational Calculations

All the calculations were performed with the Gaussian 09 software package[4] except the NICS calculations were performed with the Gaussian 16 software package.[5] All the structures were first optimized at B3LYP/6-31G(d) level of destiny functional theory.[6-8] The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (SDD) were used to describe Os, P and Br atoms. Polarization functions were added for Os (ζ(f) = 0.886), P (ζ(d) = 0.340), and Br (ζ(d) = 0.389).[8-10] Frequency calculations were performed at the same level of theory as for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (no imaginary frequencies) on the potential energy surface. The NICS and BDE were calculated at B3LYP/def2-TZVP[10-11] level of destiny functional theory. The fukui value were calculated at M06L/def2-TZVP level of destiny functional theory and analysed by Multiwfn. [12-13] The AICD were calculated at B3LYP/6-311++G(dp) level of destiny functional theory with the same basis set of the structural optimization.[13-14] For the reaction mechanism study, molecular geometries were optimized using the B3LYP functional. The SDD basis set was used for Os, Pd, Br, P and the 6-31G(d) basis set was used for all other atoms. The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set for Os, Pd, Br, P are the same as above. The Frequency calculations were performed at the same level of theory as for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency) on the potential energy surface. Intrinsic reaction coordinate calculations were performed to ensure that the first-order saddle points found were true transition states (TS) connecting the reactants and the products. Single-point energies were calculated with the B3LYP/def2-tzvp functional. Solvation effects were incorporated during geometry optimizations and Single-point energies using the PCM solvation model with *o*-DiChloroBenzene. Em = GD3 were used in the Single-point energy calculations.

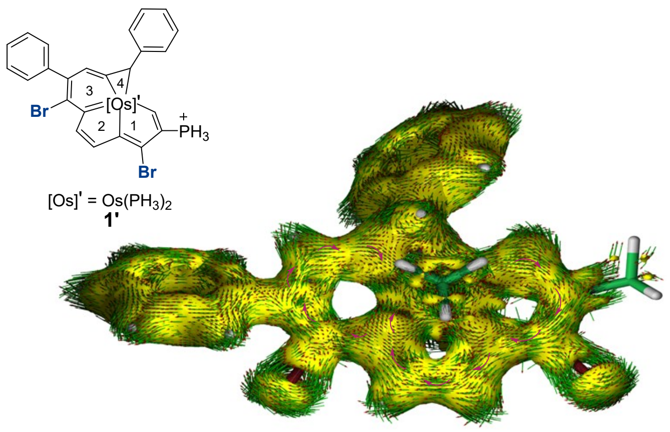


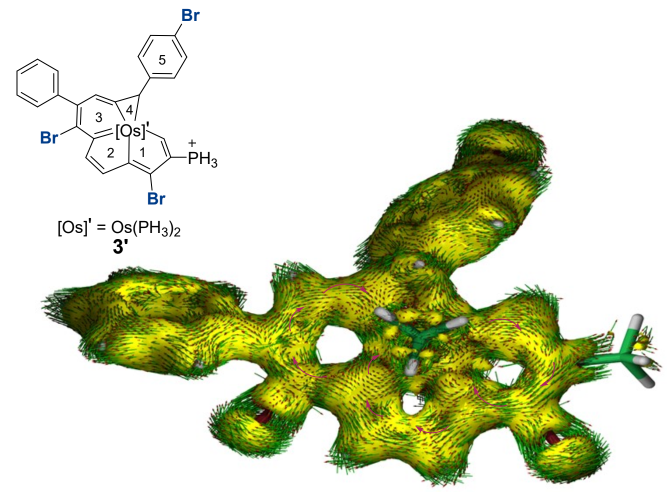
1



3

Figure S50 The bond length chang about structural optimization of **1** and **3**. Outside the brackets is the bond length of optimized structure, and in parentheses is the bond length difference of optimized structure and crystal structure.





[Os]' = Os$(PH_3)_2$
3'

Figure S51 AICD isosurfaces of **1'** and **3'**

11. Oxidative addition of 3-8C' and PdL$_2$ at C13

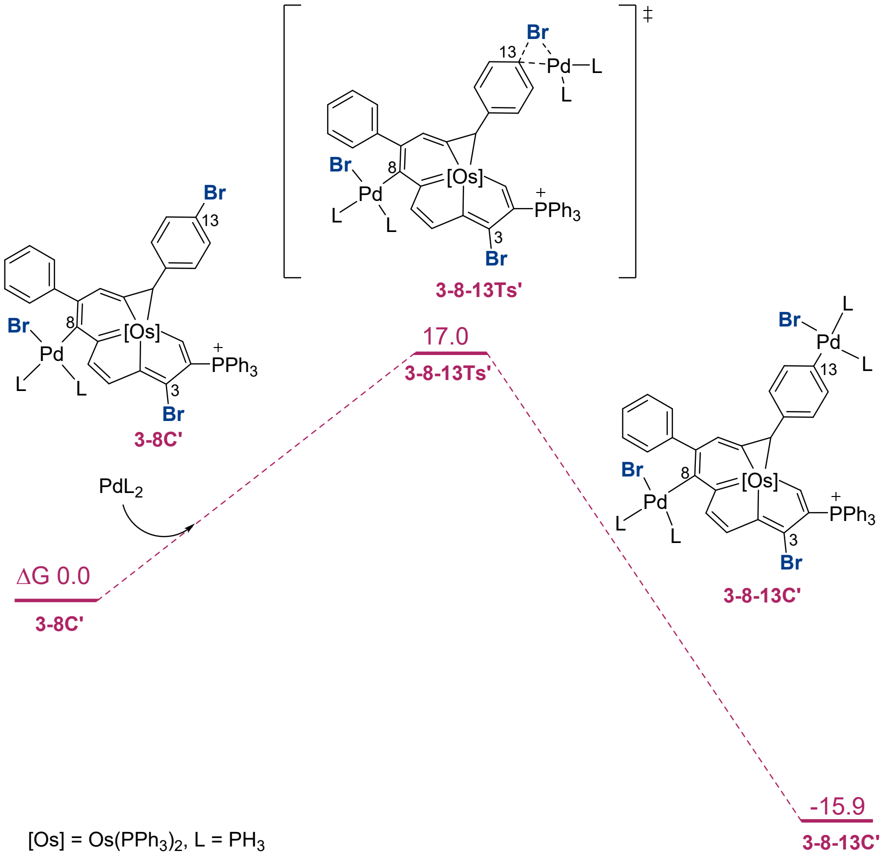
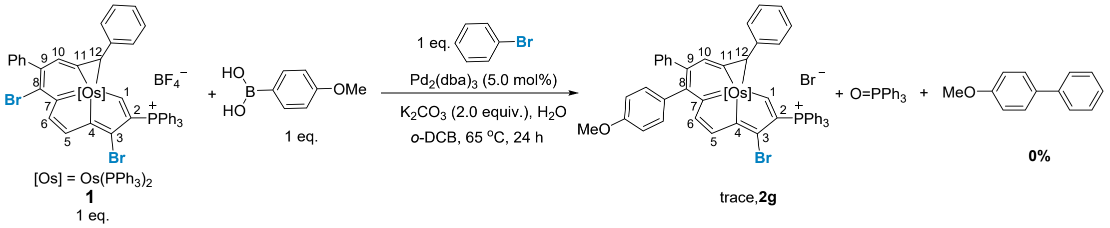


Figure S52 DFT-computed Gibbs free energy profile for the oxidative addition steps. Reaction between **3-8C'** and PdL$_2$ at C13, L = PH$_3$. All energies were computed at the level B3LYP-D3/def2-TZVP/PCM(*o*-DCB)//B3LYP/6-31G(d)(SDD for Os, Br, P), and are given in kcal/mol.

12. Mix 1.0 equiv. compound 1 and 1.0 equiv. bromobenzene with 1.0 equiv. *p*-methoxyphenylboronic acid



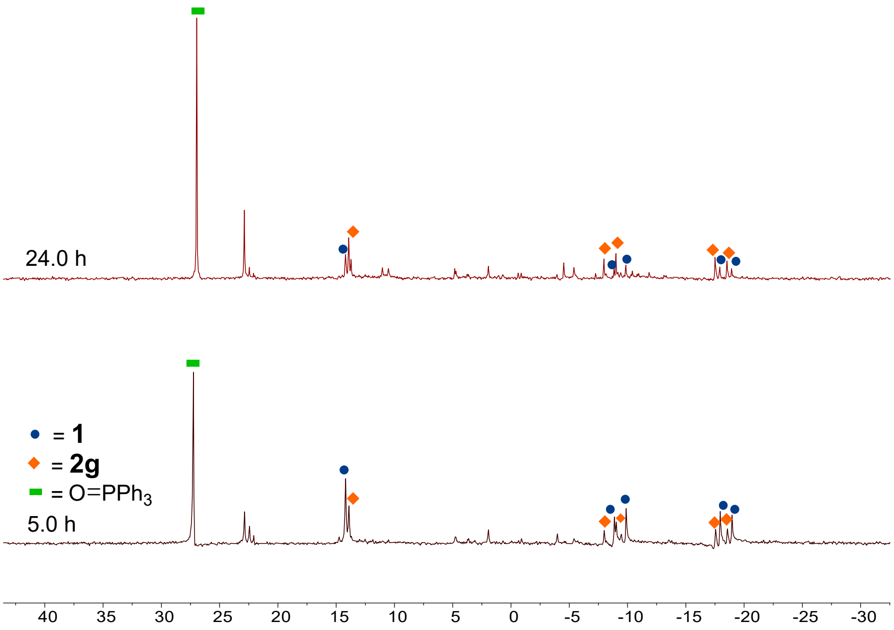


Figure S53 Overlapping ^{31}P {^{1}H} NMR Spectrums.

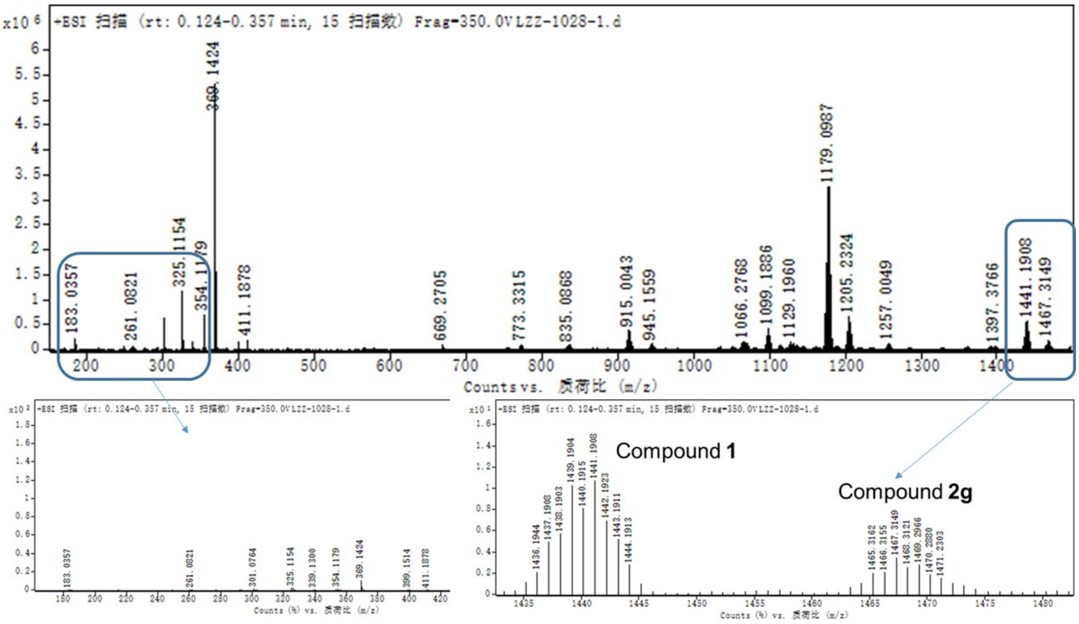


Figure S54 In situ Positive-ion ESI-MS spectrum

13. Oxidative addition of 3 and PdL (L = PH_3)

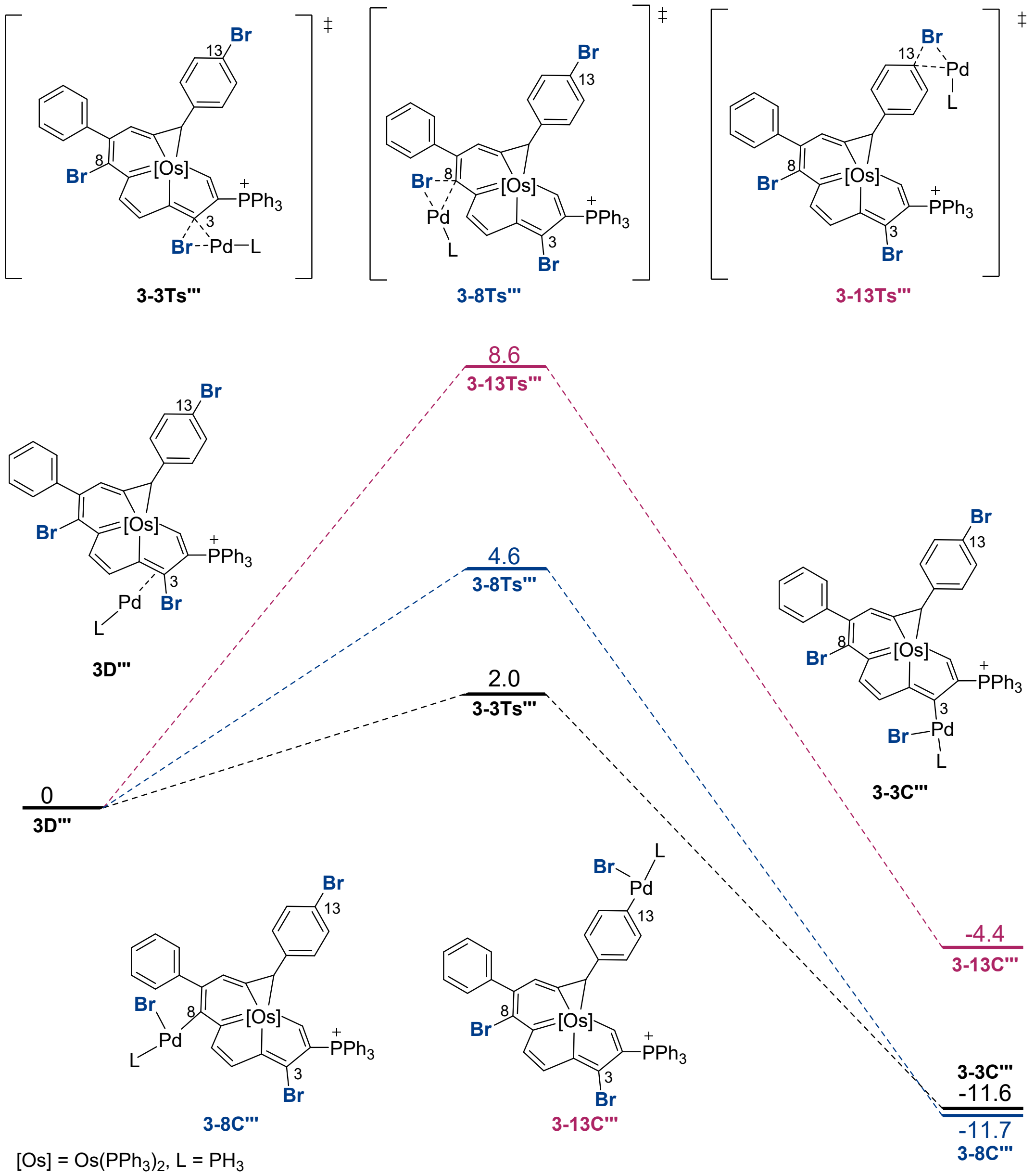


Figure S55 DFT-computed Gibbs free energy profile for the oxidative addition steps. Reaction between **3** and PdL at C3 or C8 or C13, L = PH_3. All energies were computed at the level B3LYP-D3/def2-TZVP/PCM(*o*-DCB)//B3LYP/6-31G(d)(SDD for Os, Br, P), and are given in kcal/mol.

14. Oxidative addition of 3 and PdL (L = PPh$_3$)

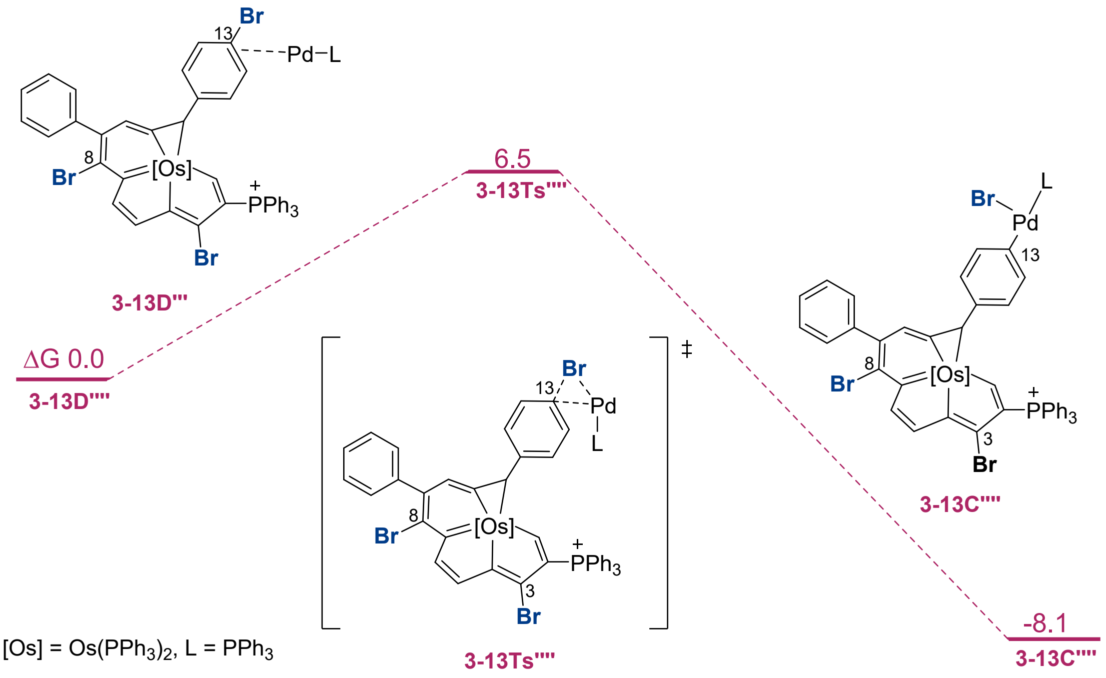
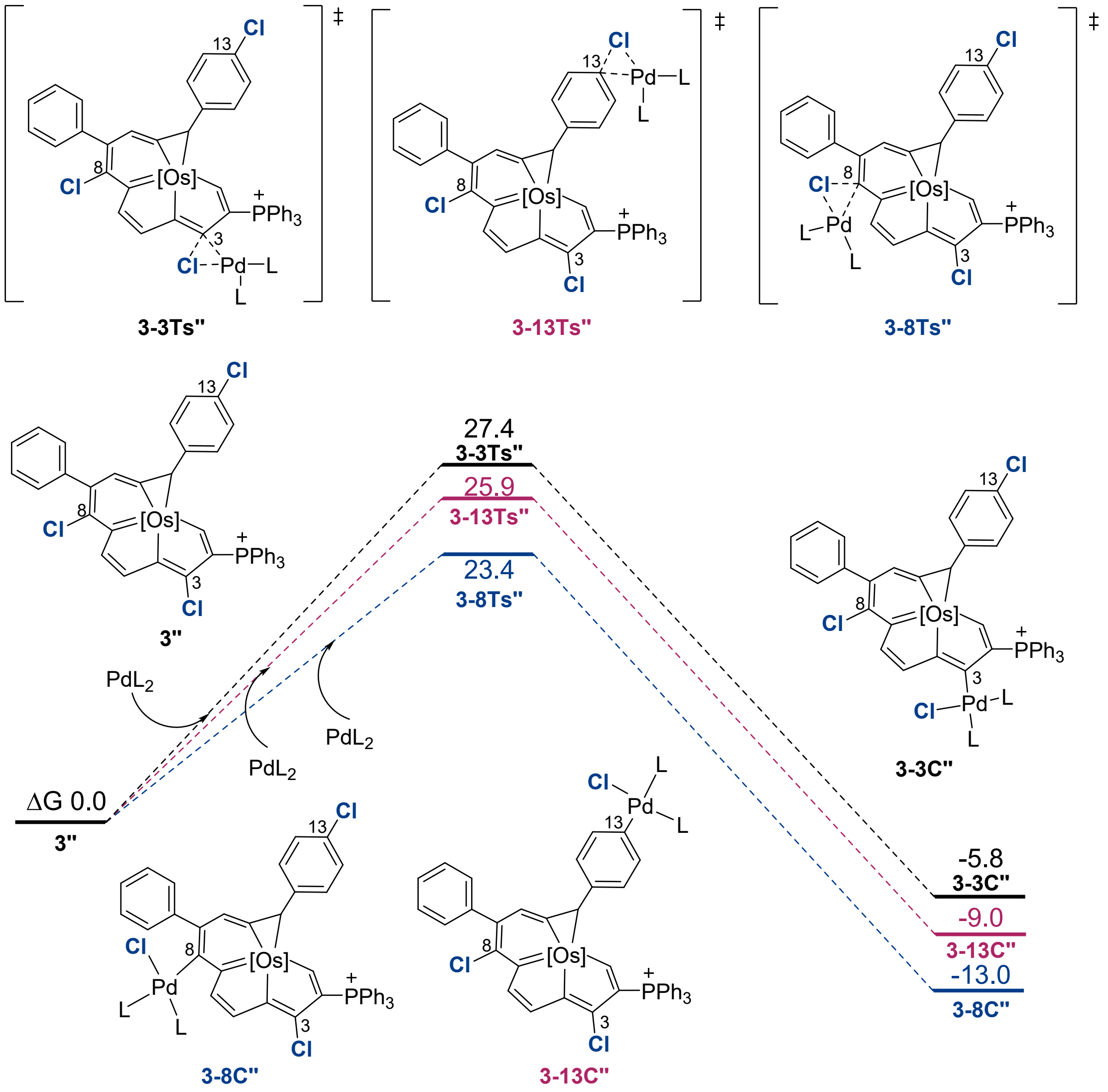


Figure S56 DFT-computed Gibbs free energy profile for the oxidative addition steps. Reaction between **3** and PdL at C13, L = PPh$_3$. All energies were computed at the level B3LYP-D3/def2-TZVP/PCM(*o*-DCB)//B3LYP/6-31G(d)(SDD for Os, Br, P), and are given in kcal/mol.

15. The oxidative addition processes with the model chloro-substituted compounds (3'')



[Os] = Os(PPh$_3$)$_2$, L = PH$_3$

Figure S57 DFT-computed Gibbs free energy profile for the oxidative addition steps. Reaction between **3''** and PdL$_2$ at C3 or C8 or C13, L = PH$_3$. All energies were computed at the level B3LYP-D3/def2-TZVP/PCM(*o*-DCB)//B3LYP/6-31G(d)(SDD for Os, Cl, P), and are given in kcal/mol.

16. Proposed Mechanism

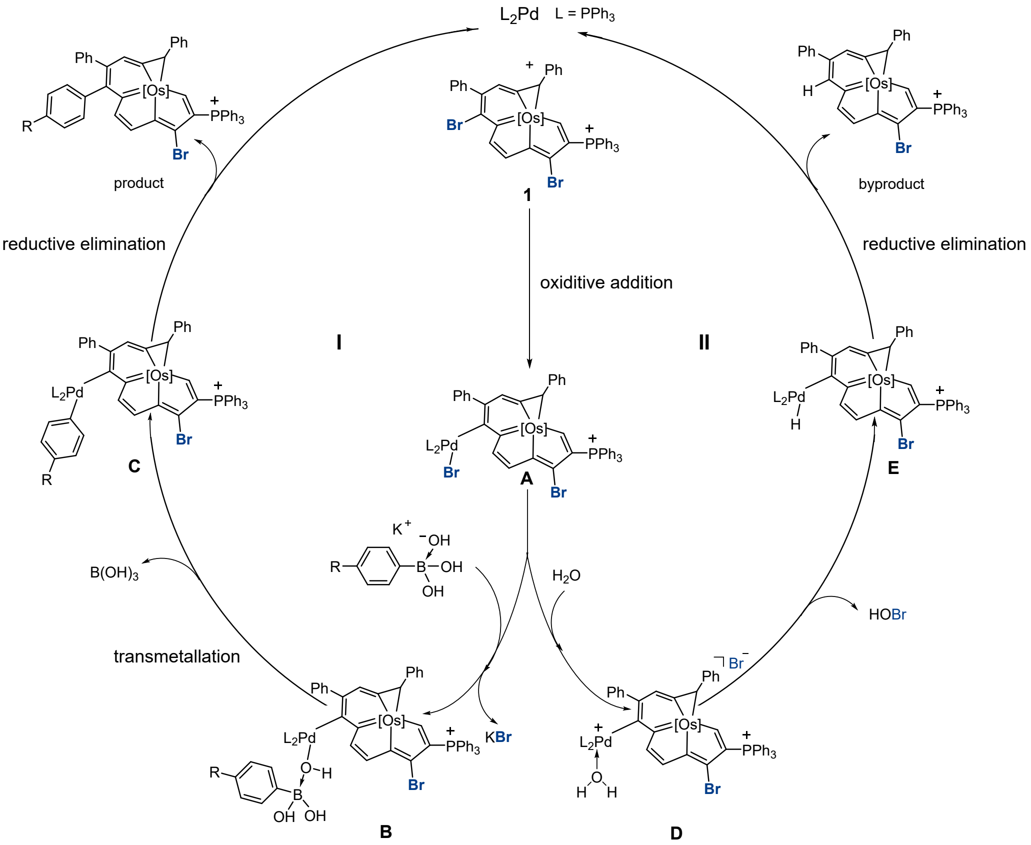


Figure S58 Proposed mechanism for the formation of product and byproduct.

17. References

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