Facile syntheses of polycyclic metallaarynes

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Supporting Information

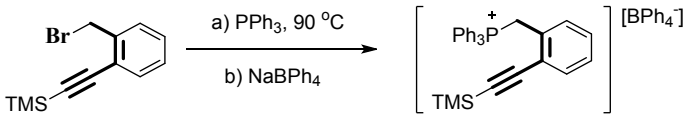
Contents

1. General and synthetic experiments

General Procedures.

All reactions were carried out in oven-dried glassware under an atmosphere of argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox under N_2 unless otherwise specified. Molecular sieves (4 Å) were dried under vacuum at 200 °C for at least 24 hours before storage inside a glovebox. Diethyl ether, *n*-hexane and tetrahydrofuran were dried over sodium benzophenone ketyl, toluene was dried over sodium, and dichloromethane was dried over calcium hydride. C_6D_6 and CD_2Cl_2 were dried over calcium hydride. All solvents were stored over 4 Å molecular sieves under an inert atmosphere. Benzyl bromide **1-1**[1], the triflate **4**[2], the aldehyde **7**[3] and $OsCl_2(PPh_3)_3$[4] were prepared according to reported procedures. All other chemicals were purchased from either Aldrich, Acros Chemical Co. or Meryer Chemical Co. and used as received unless otherwise specified. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz, 100 MHz and 162 MHz, respectively. All signals were reported in δ unit with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external 85% H_3PO_4 for phosphorus chemical shifts. Mass spectra were collected on an Agilent GC/MS 5975C system, or a MALDI Micro MX mass spectrometer, or an API QSTAR XL System. Microanalyses were performed in M-H-W Laboratories (Phoenix, AZ, USA).

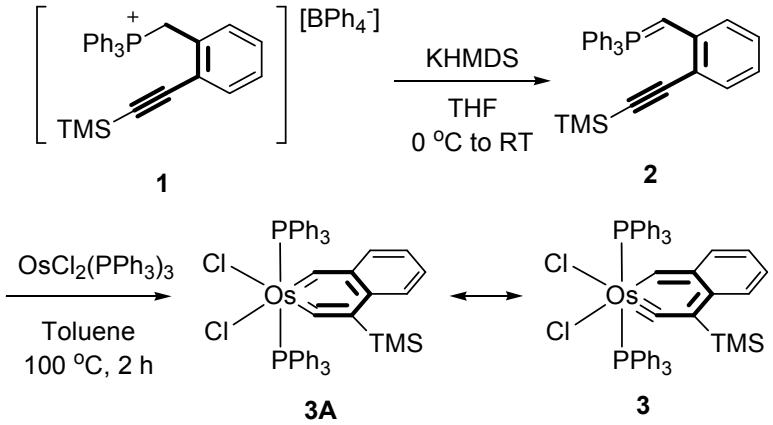
Synthesis of the phosphonium salt 1.



1-1 **1**

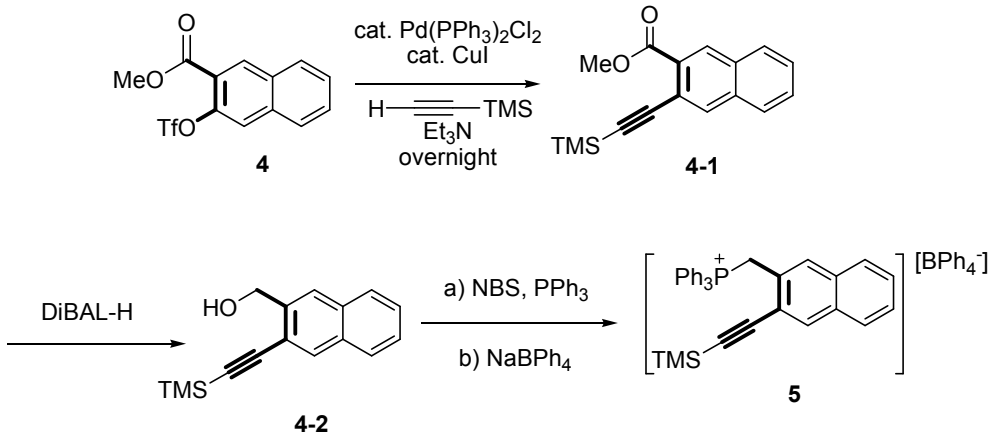
To a solution of the benzyl bromide **1-1** (4.00 g, 15.0 mmol) in toluene (60 mL) was added triphenylphosphine (3.93 g, 17.0 mmol) in one portion. The reaction mixture was heated at 90 ^{o}C overnight followed by removal of all volatiles under vacuum. The oily residue was washed with diethyl ether (20 mL × 3) to provide a grey solid which was dissolved in methanol (150 mL). The solution was treated with $NaBPh_4$ (5.80 g, 17.0 mmol) in methanol (50 mL). The white crystalline precipitate of the phosphonium salt **1** was collected on a filter frit and washed by methanol (20 mL × 3) and diethyl ether (20 mL × 2), and then vacuum dried. Yield, 8.0 g, 10.40 mmol, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (t, ^{3}J = 7.6 Hz, 3H), 7.46 (td, ^{3}J = 7.8, 3.4 Hz, 6H), 7.36 (s, 9H), 7.10 (dd, ^{3}J = 12.6, 7.9 Hz, 7H), 6.93 – 6.86 (m, 13H), 6.70 (d, ^{3}J = 7.1 Hz, 1H), 4.25 (d, $^{2}J_{PH}$ = 13.9 Hz, 2H), 0.18 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 21.3. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.2 (q, $^{1}J_{BC}$ = 49.1 Hz), 136.4, 135.6, 133.8 (d, $^{1}J_{PC}$ = 9.7 Hz), 133.3, 130.5 (d, $^{1}J_{PC}$ = 12.5 Hz), 130.2, 129.6, 129.2, 128.0, 125.6, 121.8, 116.8, 116.0, 101.7, 100.7, 29.4 (d, $^{1}J_{PC}$ = 49.6 Hz), -0.1. HRMS: m/z calcd for $[C_{30}H_{30}PSi]^{+}$: 449.1849. Found: 449.1856. Anal. Calcd. for $C_{58}H_{52}BPSi$: C, 84.36, H, 6.56. Found: C, 84.34, H, 6.36.

Synthesis of the complex 3.



To a cooled (0 °C) solution of phosphonium salt **1** (1.95 g, 2.53 mmol) in THF (40 mL) was added KHMDS (2.53 mL, 1.0 M in THF, 2.53 mmol). The reaction mixture was stirred for 1 h at room temperature. The volatiles of the mixture were removed under reduced pressure. The orange-red residue was extracted with toluene (20 mL), filtered through Celite and the filter cake was washed with toluene (10 mL × 2). The solvent of the combined filtrates was removed under vacuum to provide an orange red residue. A solution of $OsCl_2(PPh_3)_3$ (3.48 g, 2.65 mmol) in toluene (35 mL) was added to the orange red residue. The reaction mixture was heated at 110 °C for 2 h. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with *n*-hexane (20 mL × 3) and dried under vacuum. The residue was purified by column chromatography on SiO_2 using mixtures of ethyl acetate : *n*-hexane (= 1 : 6 to 1 : 3) as the eluent. The green band was collected, and the solvents were removed under reduced pressure to provide the complex **3** as a green solid. Yield, 1.67 g, 1.72 mmol, 68%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 15.76 (s, 1H), 7.68 – 7.54 (m, 12H), 7.28 – 7.12 (m, 18H), 6.99 – 6.94 (m, 1H), 6.91 – 6.85 (m, 1H), 6.66 – 6.60 (m, 1H), 6.57 – 6.51 (m, 1H), 0.26 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ -2.93. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 308.0 (t, J = 11.2 Hz, Os≡*C* (C1)), 277.6 (br s, Os*C*H (C5)), 150.5, 139.7, 136.5, 136.3, 134.9 (t, J = 5.1 Hz, *o*- or *m*-PPh_3), 131.9 (t, J = 26.8 Hz, *ipso*-PPh_3), 130.7 (*p*-PPh_3), 127.9 (t, J = 5.0 Hz, *o*- or *m*-PPh_3), 126.9, 121.4, 97.4, 0.9 (s, $SiMe_3$). Anal. Calcd. for $C_{48}H_{44}Cl_2P_2SiOs$: C, 59.31, H, 4.56. Found: C, 59.05, H, 4.60.

Synthesis of the phosphonium salt 5:



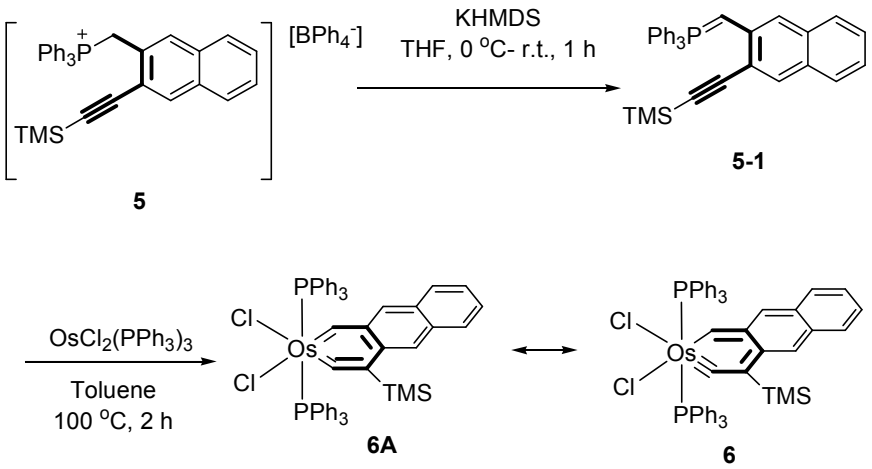
Synthesis of 4-1. To a mixture of the triflate **4** (3.42 g, 10.23 mmol), $Pd(PPh_3)_2Cl_2$ (0.351 g, 0.50 mmol) and CuI (0.195 g, 1.02 mmol) in degassed triethylamine (60 mL) was added trimethylsilylacetylene (1.70 mL, 12.27 mmol). The reaction mixture was heated to 90 ^oC and stirred at this temperature overnight. The reaction mixture was cooled to room temperature, and then diluted with diethyl ether (100 mL). The resulting mixture was filtered through a short pad of silica gel and the filter cake was washed with diethyl ether (30 mL × 2). The solvents of combined filtrate were removed under reduced pressure. The oily residue was purified by column chromatography on SiO_2 using a mixture of diethyl ether : *n*-hexane (1 : 15) as the eluent to provide the ester **4-1** as a light-yellow oil. Yield, 2.80 g, 9.91 mmol, 97%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.11 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.62 – 7.49 (m, 2H), 3.98 (s, 3H), 0.31 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.0, 135.0, 134.2, 131.8, 129.1, 128.9, 128.7, 127.6, 127.4, 119.1, 103.8, 98.4, 52.2, 0.1. HRMS: m/z calcd for $[C_{17}H_{18}O_2Si]^+$: 282.1076. Found: 282.1071.

Synthesis of 4-2. To a chilled (−78 °C) solution of the ester **4-1** (2.70 g, 9.56 mmol) in THF (60 mL) was added DiBAL-H (30 mL, 1.0 M in THF, 30.00 mmol). After the addition, the reaction mixture was stirred for another 1 h at that temperature. The reaction mixture was warmed to 0 °C and was quenched (*Caution:* a large amount of gas evolution occurred) by careful addition of water (1.20 mL) followed by 15% aqueous NaOH solution (1.20 mL) and water (3 mL). The reaction mixture was warmed to room temperature and stirred for 0.5 h before addition of anhydrous $MgSO_4$. The resulting mixture was stirred for 0.5 h followed by filtration through a frit of medium-pore size. The filter cake was washed by ethyl acetate (50 mL × 3). The solvents of combined filtrate were removed under vacuum. The sticky oily residue was purified by column chromatography on SiO_2 using a mixture of diethyl ether : *n*-hexane (= 1 : 8) as the eluent to provide the alcohol **4-2** as a light-yellow oil. Yield, 2.20 g, 8.65 mmol, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.79 (s, 1H), 7.78 – 7.71 (m, 2H), 7.50 – 7.42 (m, 2H), 4.95 (s, 2H), 2.65 (s, 1H), 0.33 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.1, 133.1, 132.8, 132.2, 127.9, 127.5, 127.2, 126.5, 125.7, 118.9, 103.0, 99.3, 64.1, 0.1. HRMS: m/z calcd for $[C_{16}H_{18}OSi]^+$: 254.1127. Found: 254.1125.

Synthesis of 5. To a cooled (0 °C) solution of the alcohol **4-2** (2.10 g, 8.27 mmol) in dichloromethane (50 mL) was added triphenylphosphine (4.80 g, 16.5 mmol) followed by N-bromosuccinimide (1.62 g, 9.10 mmol) in three portions. The reaction mixture was stirred for 1 h before water (30 mL) was added to quench the reaction. The organic layer was separated from the aqueous layer which was extracted by dichloromethane (50 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and dried under reduced pressure. The oily residue was dissolved in methanol (50 mL) and treated with a solution of $NaBPh_4$ (3.42 g, 10.00 mmol) in methanol (30 mL). The white crystalline precipitate of the phosphonium salt **5** was

collected on a filter frit and washed by methanol (20 mL × 3) and diethyl ether (20 mL × 2), and then vacuum dried. Yield, 4.74 g, 5.79 mmol, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.85 – 7.69 (m, 4H), 7.66 – 7.31 (m, 18H), 7.21 – 7.05 (m, 7H), 6.98 – 6.84 (m, 11H), 4.38 (d, *J* = 13.6 Hz, 2H), 0.24 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 20.72. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1 (q, *J* = 49.3 Hz), 136.3, 135.6, 133.9 (d, *J* = 9.7 Hz), 133.7, 132.5, 130.4 (d, *J* = 12.6 Hz), 128.0 (d, *J* = 17.1 Hz), 127.7 (d, *J* = 30.4 Hz), 125.6, 124.0 (d, *J* = 9.4 Hz), 121.9 (d, *J* = 4.0 Hz), 121.8, 116.9 116.1, 102.2, 100.1, 29.2 (d, *J* = 49.6 Hz), 0.0 (s). Anal. HRMS: m/z calcd for $[C_{34}H_{32}PSi]^{+}$: 499.2005. Found: 499.2017. Anal. Calcd. for $C_{58}H_{52}BPSi$: C, 85.07, H, 6.40. Found: C, 85.18, H, 6.28.

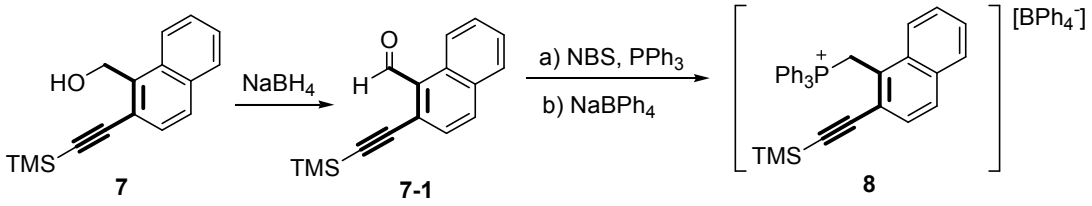
Synthesis of the complex 6.



To a cooled (0 °C) solution of the phosphonium salt **5** (0.44 g, 0.54 mmol) in THF (15 mL) was added KHMDS (0.54 mL, 1.0 M in THF, 0.54 mmol). The reaction mixture was stirred for 1 h at room temperature. The volatiles were removed under reduced pressure. The orange-red residue was extracted with toluene (10 mL), filtered through Celite and the filter cake was washed with toluene (5 mL × 2). The solvent of the combined filtrates was removed under

vacuum to provide an orange red residue. A solution of $OsCl_2(PPh_3)_3$ (0.64 g, 0.49 mmol) in toluene (15 mL) was added to the orange red residue. The reaction mixture was heated at 110 °C for 2 h. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with *n*-hexane (10 mL × 3) and dried under vacuum. The residue was purified by column chromatography on SiO_2 using mixtures of ethyl acetate : *n*-hexane (1 : 6 to 1 : 3) as the eluent. The yellow band was collected, and the solvents were removed under reduced pressure to provide the complex **6** as a yellow solid. Yield, 0.27 g, 0.26 mmol, 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.51 (s, 1H), 7.71 – 7.63 (m, 12H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 (s, 1H), 7.12 – 7.04 (m, 19H), 0.25 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -7.02. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 304.1 (t, *J* = 11.2 Hz, Os≡*C* (C1)), 288.4 (br s, Os*C*H (C5)), 141.6, 138.6, 137.4, 137.2, 134.3 (t, *J* = 5.2 Hz, *o*- or *m*-PPh_3), 132.2 (t, *J* = 26.4 Hz, *ipso*-PPh_3), 130.9, 130.7, 130.0 (*p*-PPh_3), 128.7, 127.5 (t, *J* = 4.9 Hz, *o*- or *m*-PPh_3), 126.1, 124.3, 123.9, 94.7, 0.7 (s, Si*Me*$_3$). Anal. Calcd. for $C_{52}H_{46}Cl_2P_2SiOs\cdot CH_2Cl_2$: C, 57.50, H, 4.37. Found: C, 57.41, H, 4.34.

Synthesis of the phosphonium salt 8:



Synthesis of 7-1. To a cooled (0 °C) solution of the aldehyde **7** (2.00 g, 7.92 mmol) in MeOH (40 mL) was added $NaBH_4$ (0.302 g, 8.00 mmol) in one portion. The reaction mixture was allowed to warm to room temperature and then stirred for another 1 h. The reaction was

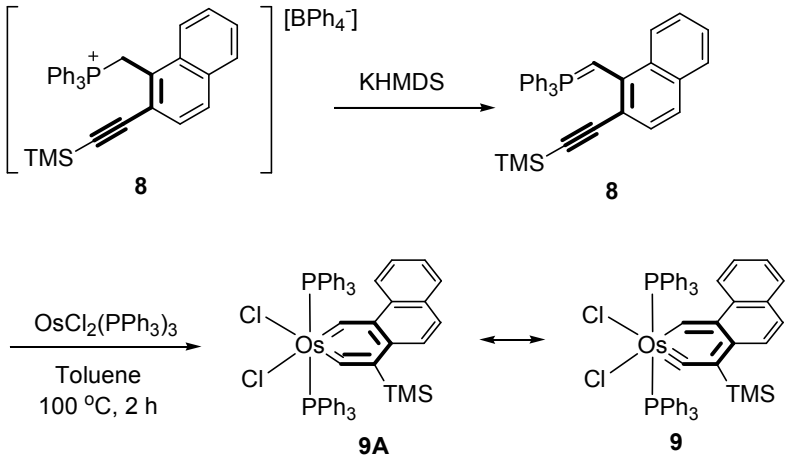
quenched by addition of a saturated NH_4Cl solution (50 mL). The volatiles of the reaction mixture were removed under reduced pressure. The aqueous layer was then extracted with ethyl acetate (50 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and dried under reduced pressure. The sticky oily residue was purified by column chromatography on SiO_2 using a mixture of diethyl ether : *n*-hexane (1 : 5) as the eluent to provide the alcohol **7-1** as a light-yellow oil. Yield, 1.71 g, 6.73 mmol, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.79 (s, 1H), 7.78 – 7.71 (m, 2H), 7.50 – 7.42 (m, 2H), 4.95 (s, 2H), 2.65 (s, 1H), 0.33 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.2, 133.6, 131.7, 128.8, 128.5, 127.1, 126.7, 124.8, 120.4, 103.8, 99.6, 60.6, 0.09. HRMS: m/z calcd for $[C_{16}H_{18}OSiH]^+$: 255.1200. Found 255.1175.

Synthesis of 8. To a cooled (0 °C) solution of the alcohol **7-1** (1.60 g, 6.29 mmol) in dichloromethane (50 mL) was added triphenylphosphine (3.46 g, 13.2 mmol) followed by N-bromosuccinimide (1.12 g, 6.30 mmol) in three portions. The reaction mixture was stirred for 1 h before water (30 mL) was added to quench the reaction. The organic layer was separated from the aqueous layer which was extracted by dichloromethane (50 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and dried under reduced pressure. The oily residue was dissolved in methanol (50 mL) and treated with a solution of $NaBPh_4$ (2.74 g, 8.00 mmol) in methanol (30 mL). The white crystalline precipitate of the phosphonium salt **8** was collected on a filter frit and washed by methanol (20 mL × 3) and diethyl ether (20 mL × 2), and then vacuum dried. Yield, 3.91 g, 4.78 mmol, 76 %. ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.98 – 7.85 (m, 5H), 7.70 – 7.52 (m, 13H), 7.51 – 7.46 (m, 1H), 7.43 – 7.38 (m, 1H), 7.34 (s, 8H), 7.24 – 7.15 (m, 1H), 6.95 – 6.85 (m, 8H), 6.81 – 6.72 (m, 4H), 5.64 – 5.42 (m, 2H), 0.22 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, Acetone-d_6): δ 20.55. ^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6): δ 164.9

(dd), 137.0, 136.3 (d, J = 3.0 Hz), 135.2 (d, J = 9.9 Hz), 134.3 (d, J = 2.8 Hz), 132.1 (d, J = 4.2 Hz), 131.1 (d, J = 12.5 Hz), 130.4 (d, J = 4.0 Hz), 129.9, 129.7 (d, J = 4.1 Hz), 128.2 (d, J = 16.6 Hz), 127.7 (d, J = 10.0 Hz), 126.0 (dd, J = 5.5, 2.7 Hz), 125.1 (d, J = 7.3 Hz), 125.0 (d, J = 1.8 Hz), 118.3 (d, J = 85.3 Hz), 103.5 (d, J = 97.4 Hz), 28.8 (d, J = 49.0 Hz), -0.1.

Anal. HRMS: m/z calcd for $[C_{34}H_{32}PSi]^+$: 499.2005. Found: 499.1983.

Synthesis of the complex 9.



To a cooled (0 °C) solution of phosphonium salt **8** (0.44 g, 0.54 mmol) in THF (15 mL) was added KHMDS (0.54 mL, 1.0 M in THF, 0.54 mmol). The reaction mixture was stirred for 1 h at room temperature. The volatiles were removed under reduced pressure. The orange-red residue was extracted with toluene (10 mL), filtered through Celite and the filter cake was washed with toluene (5 mL × 2). The solvent of the combined filtrates was removed under vacuum to provide an orange red residue. A solution of $OsCl_2(PPh_3)_3$ (0.64 g, 0.49 mmol) in toluene (15 mL) was added to the orange red residue. The reaction mixture was heated at 100 °C for 2 h. All volatiles of the reaction mixture were removed under vacuum after the reaction mixture was cooled to room temperature. The residue was washed with *n*-hexane (10 mL × 3)

and dried under vacuum. The green residue was further recrystallized from DCM to provide the complex **9** as a green solid. Yield, 0.28 g, 0.27 mmol, 55%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 16.14 (s, 1H), 7.87 – 7.75 (m, 2H), 7.65 – 7.54 (m, 13H), 7.51 – 7.38 (m, 3H), 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 1H), 7.09 – 7.04 (m, 17H), 6.96 – 6.91 (m, 1H), 0.30 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ -0.37 (s). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ 308.1 (s, Os≡*C* (C1)), 250.9 (s, Os*C*H (C5)), 158.9, 139.1, 134.7 (t, *J* = 4.9 Hz, *o*- or *m*-PPh_3), 134.0, 132.5 (d, *J* = 4.5 Hz), 131.7 (t, *J* = 26.8 Hz, *ipso*-PPh_3), 130.4 (*p*-PPh_3), 129.8, 129.1, 129.0, 128.7, 127.9 (t, *J* = 4.7 Hz, *o*- or *m*-PPh_3), 126.0, 124.7, 123.8, 1.0 (s, Si*Me*$_3$). Anal. Calcd. for $C_{52}H_{46}Cl_2P_2SiOs{\cdot}3CH_2Cl_2$: C, 51.74, H, 4.10. Found: C, 51.88, H, 4.09.

2. NMR spectra

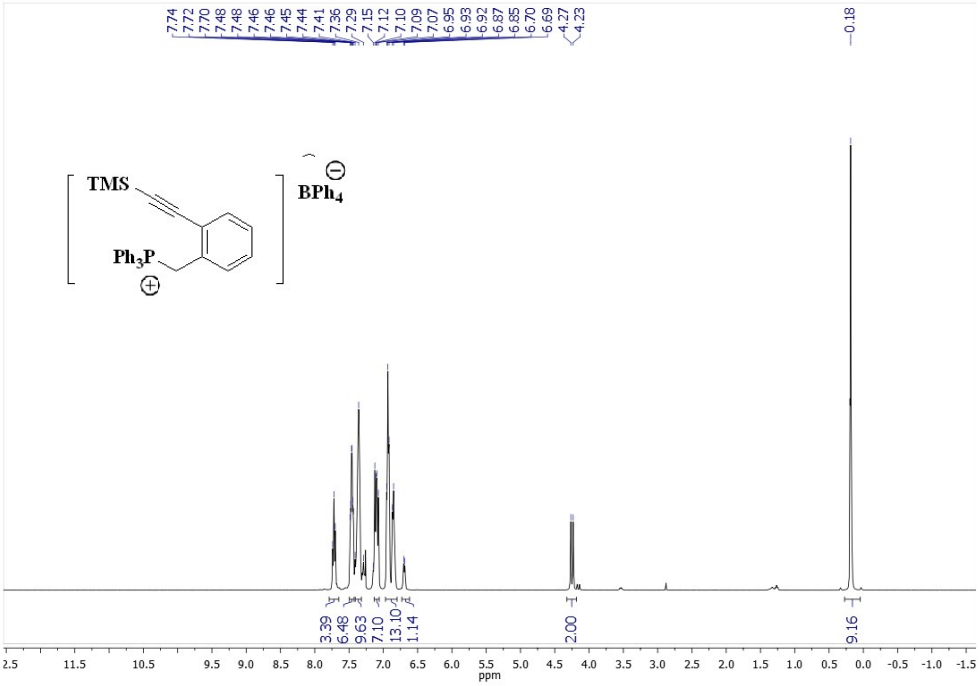


Figure S1. The ^{1}H NMR spectrum of the phosphonium salt **1** in $CDCl_3$ at 400 MHz.

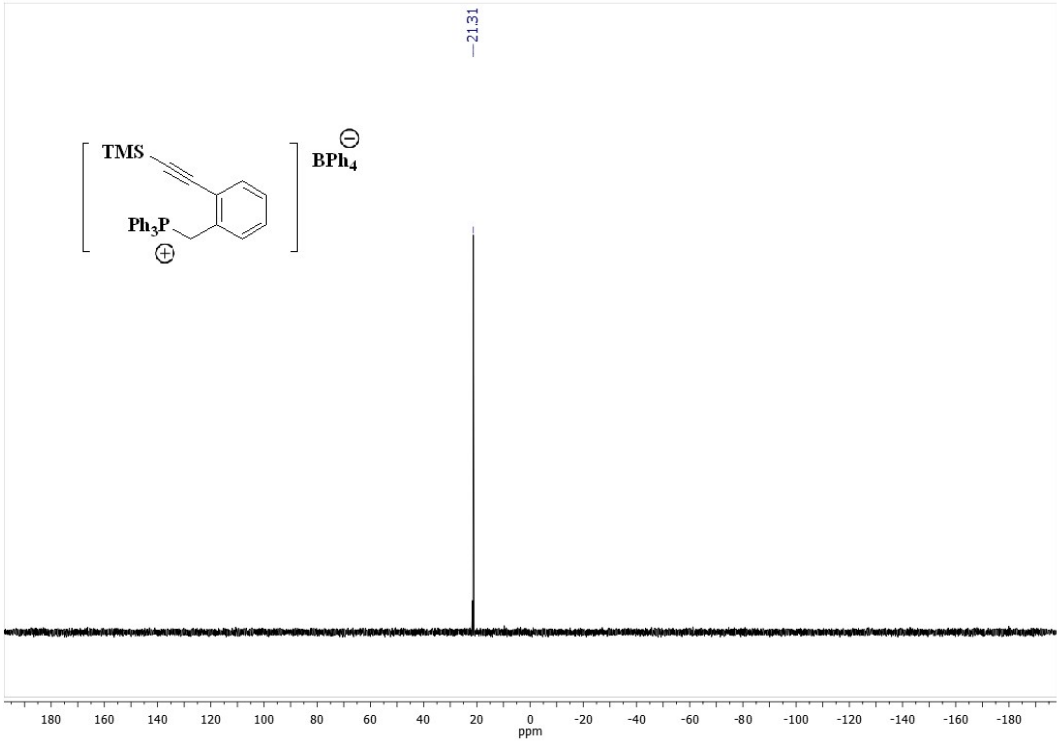


Figure S2. The $^{31}P\{^{1}H\}$ NMR spectrum of the phosphonium salt **1** in $CDCl_3$ at 162 MHz.

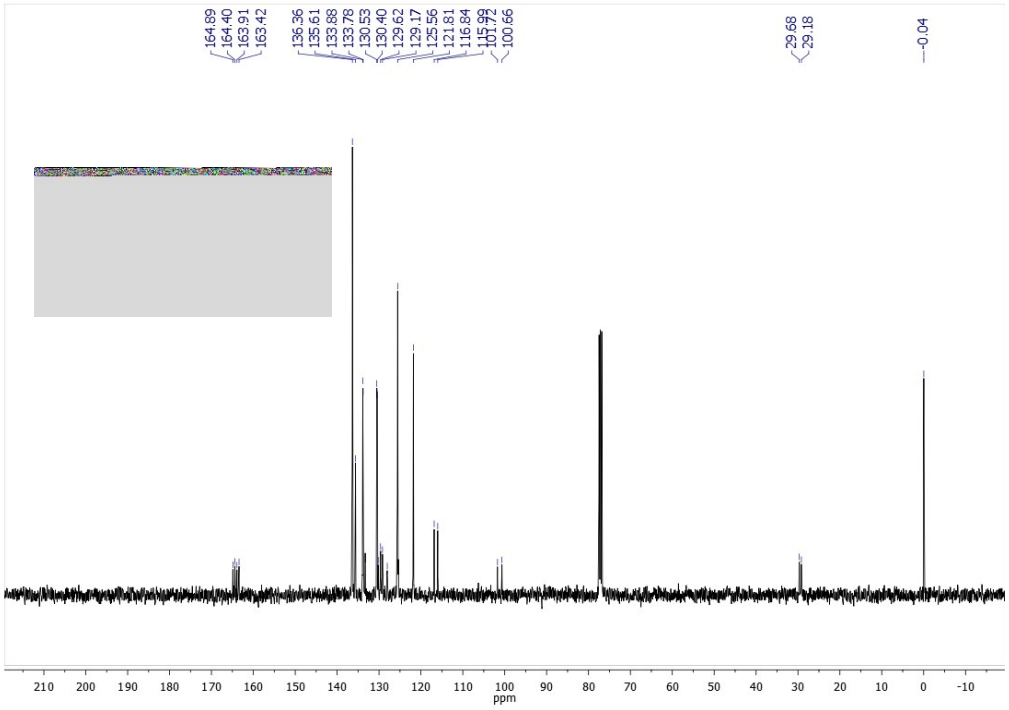


Figure S3. The $^{13}C\{^{1}H\}$ NMR spectrum of the phosphonium salt **1** in $CDCl_3$ at 100 MHz.

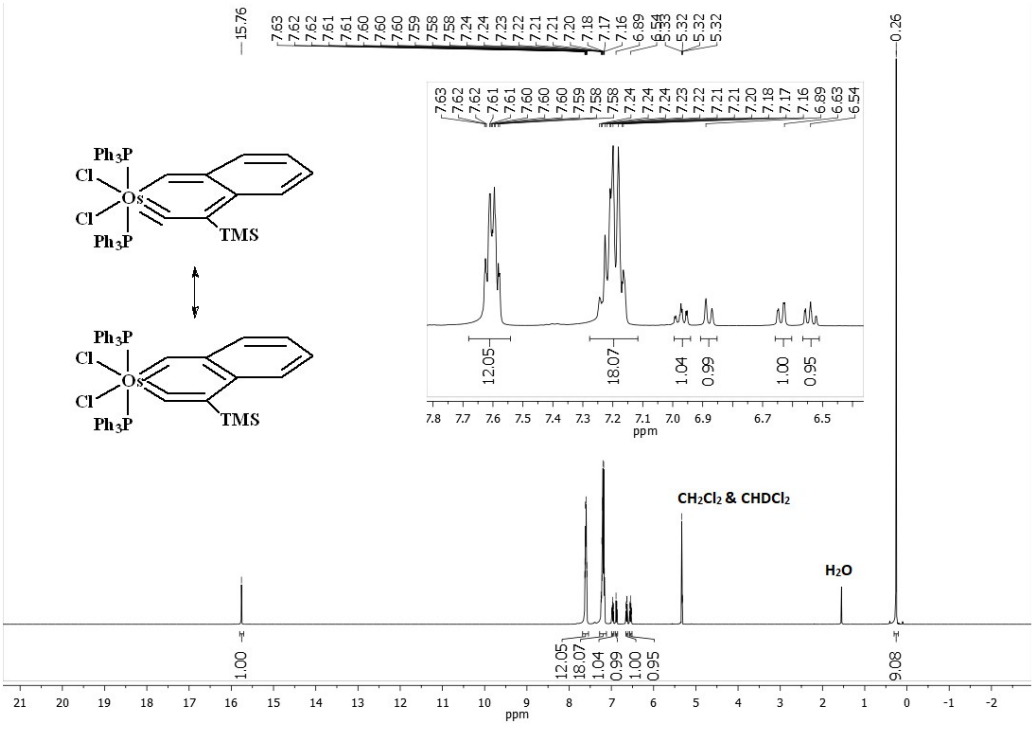


Figure S4. The ^{1}H NMR spectrum of the complex **3** in CD_2Cl_2 at 400 MHz.

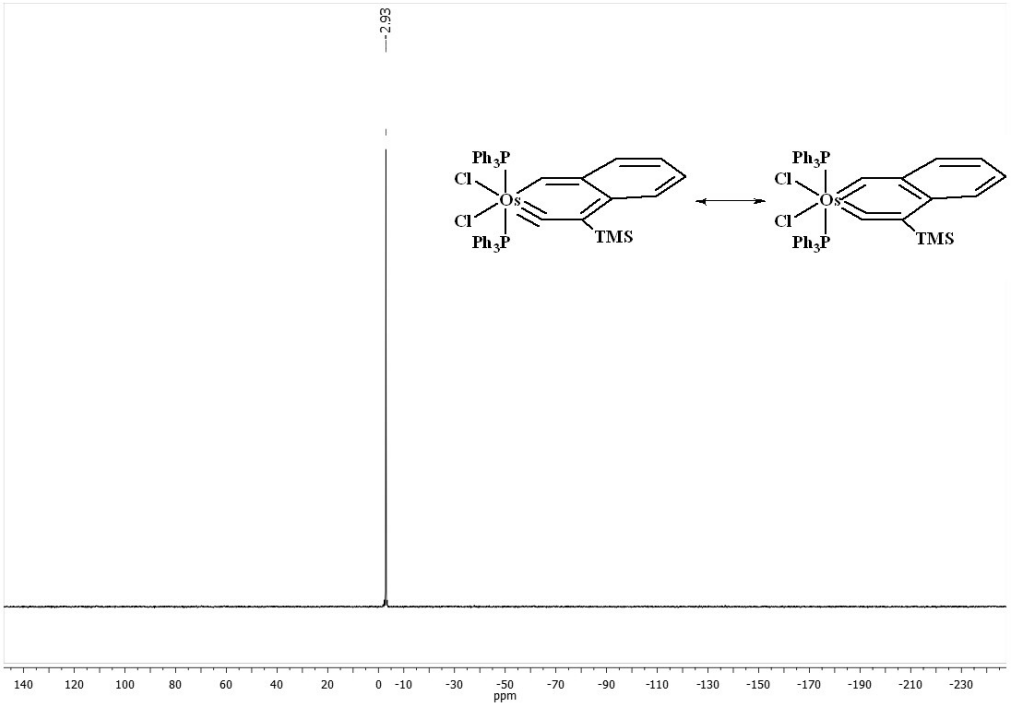


Figure S5. The ^{31}P $\{^{1}H\}$ NMR spectrum of the complex **3** in CD_2Cl_2 at 162 MHz.

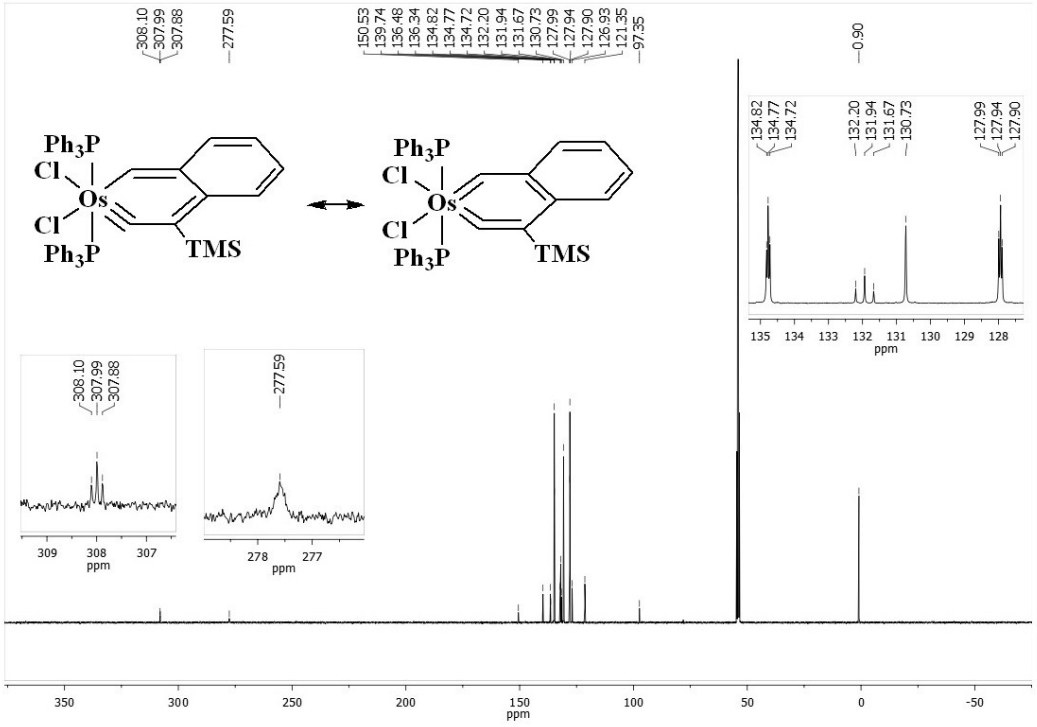


Figure S6. The $^{13}C\{^{1}H\}$ NMR spectrum of the complex **3** in CD_2Cl_2 at 100 MHz.

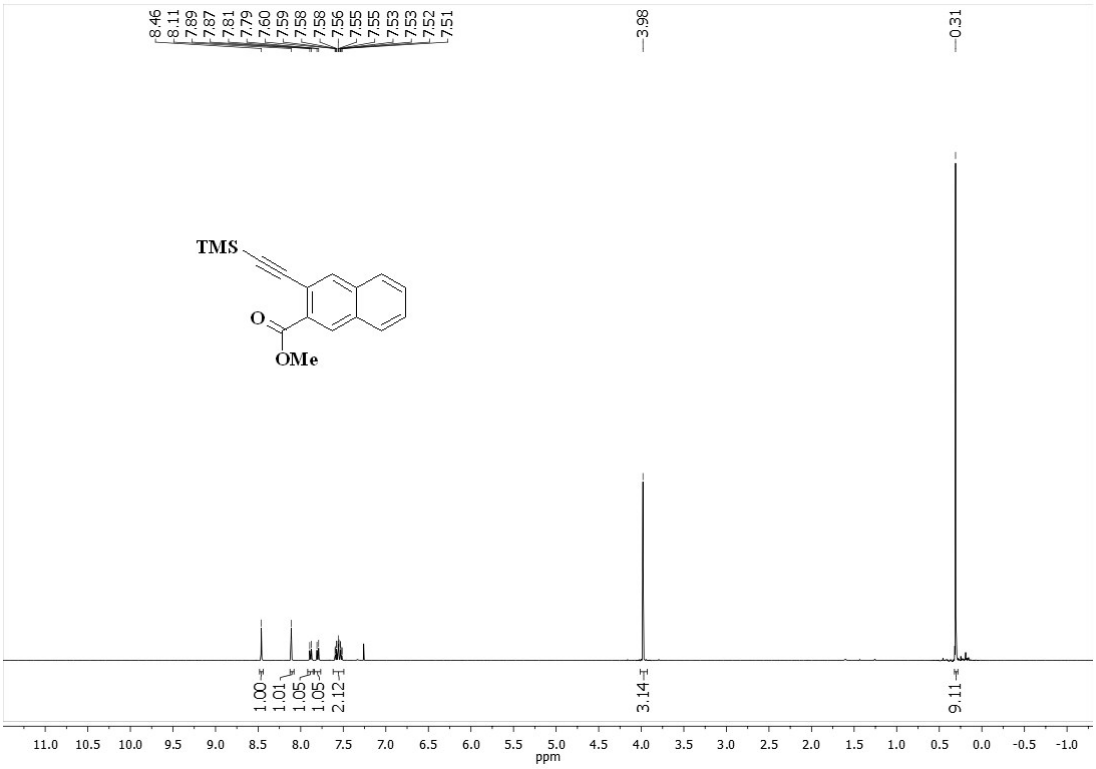


Figure S7. The ^{1}H NMR spectrum of the ester **4-1** in $CDCl_3$ at 400 MHz.

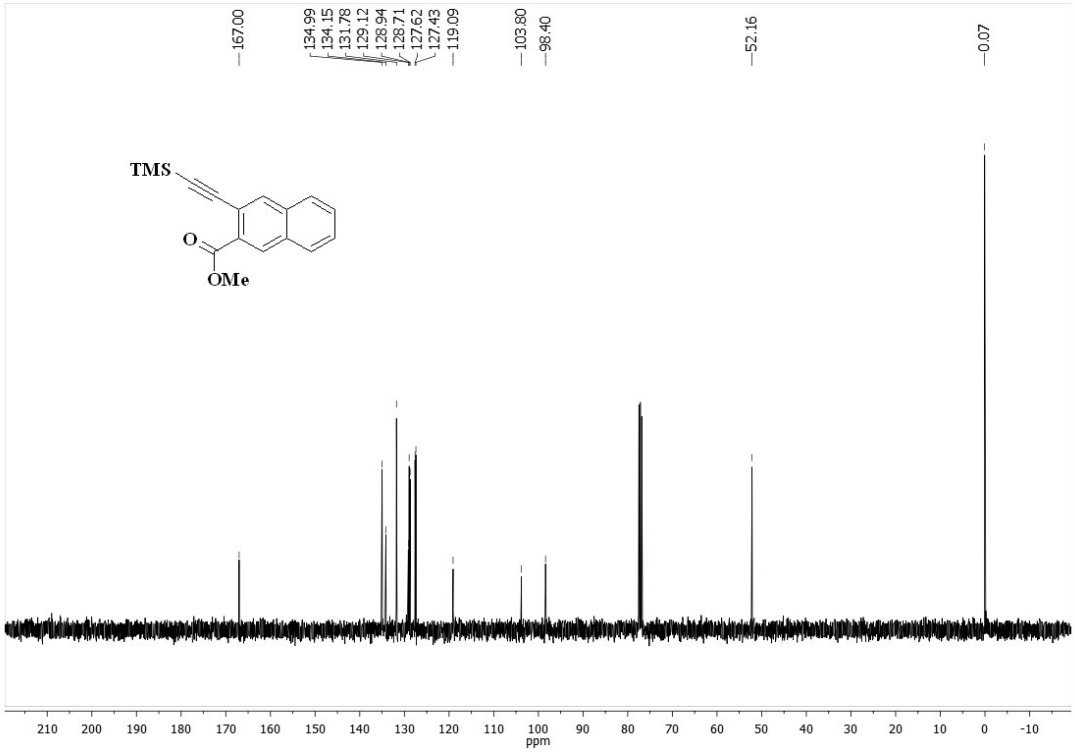


Figure S8. The $^{13}C\{^{1}H\}$ NMR spectrum of the ester **4-1** in $CDCl_3$ at 100 MHz.

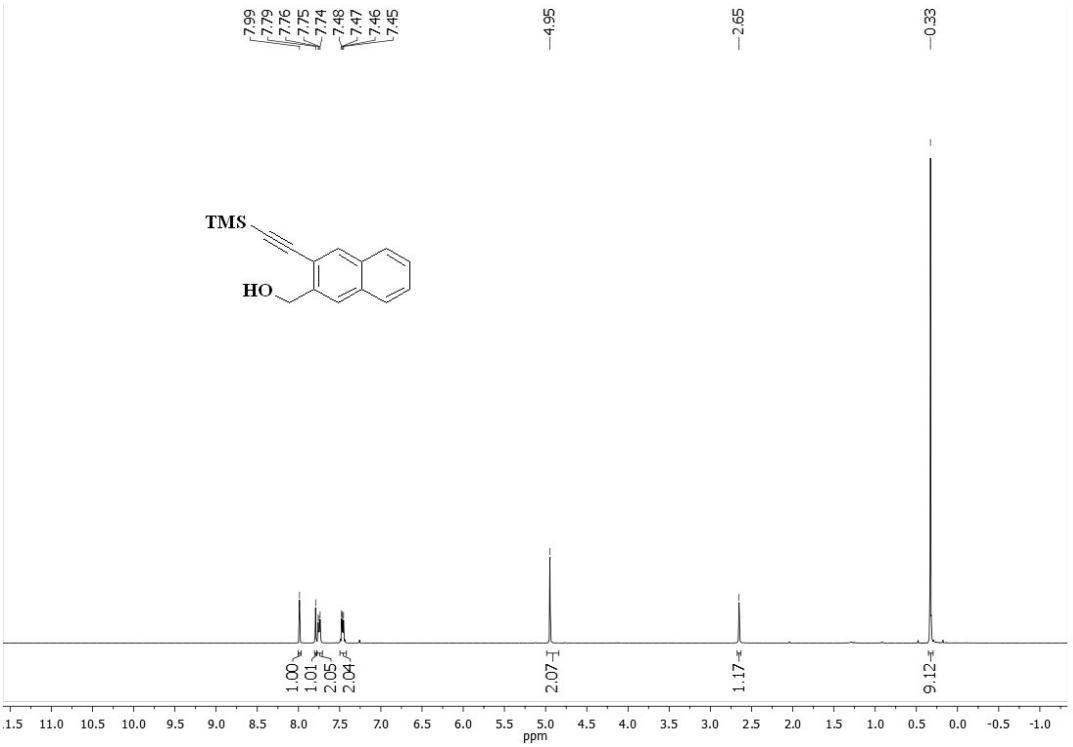


Figure S9. The ^{1}H NMR spectrum of the alcohol **4-2** in $CDCl_3$ at 400 MHz.

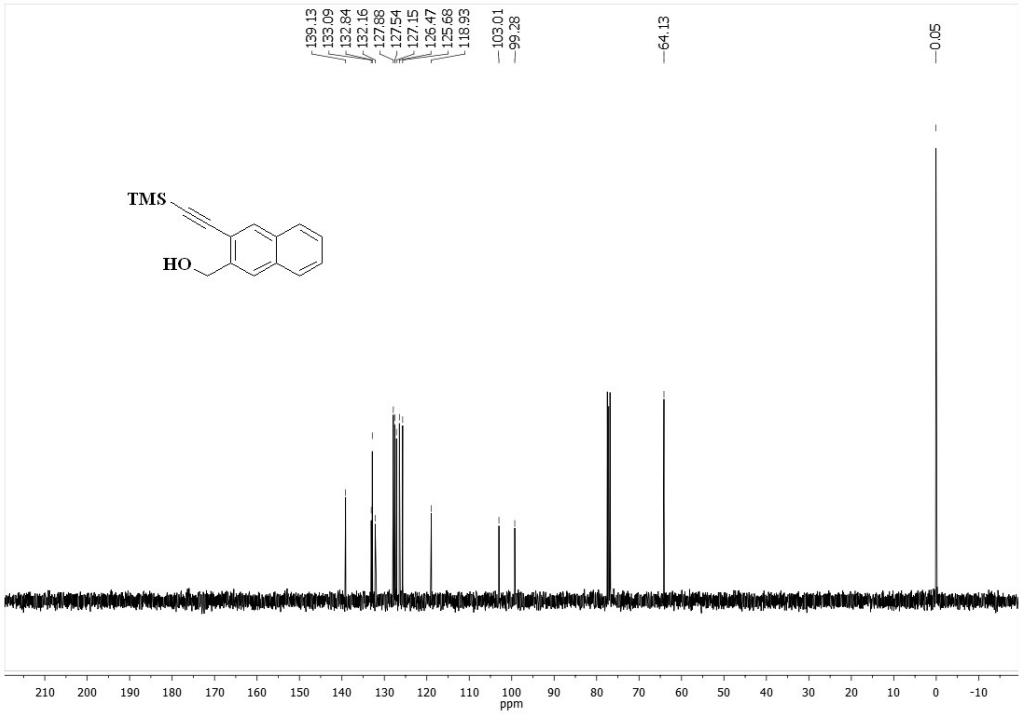


Figure S10. The $^{13}C\{^{1}H\}$ NMR spectrum of the alcohol **4-2** in $CDCl_3$ at 100 MHz.

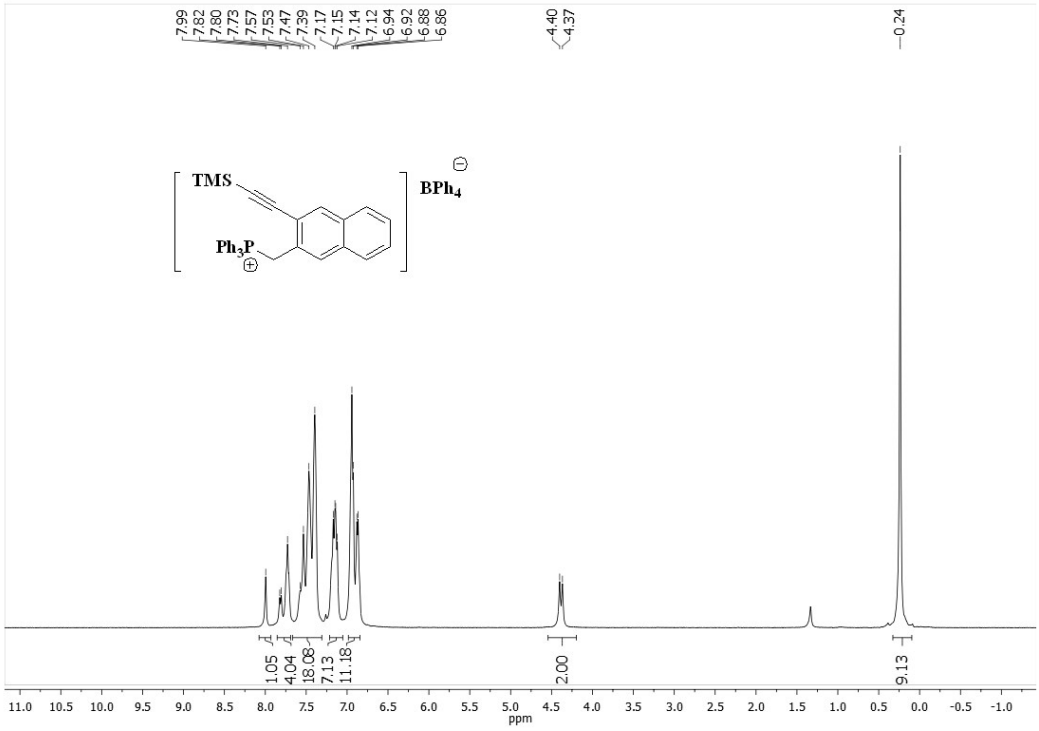


Figure S11. The ^{1}H NMR spectrum of the phosphonium salt **5** in $CDCl_3$ at 400 MHz.

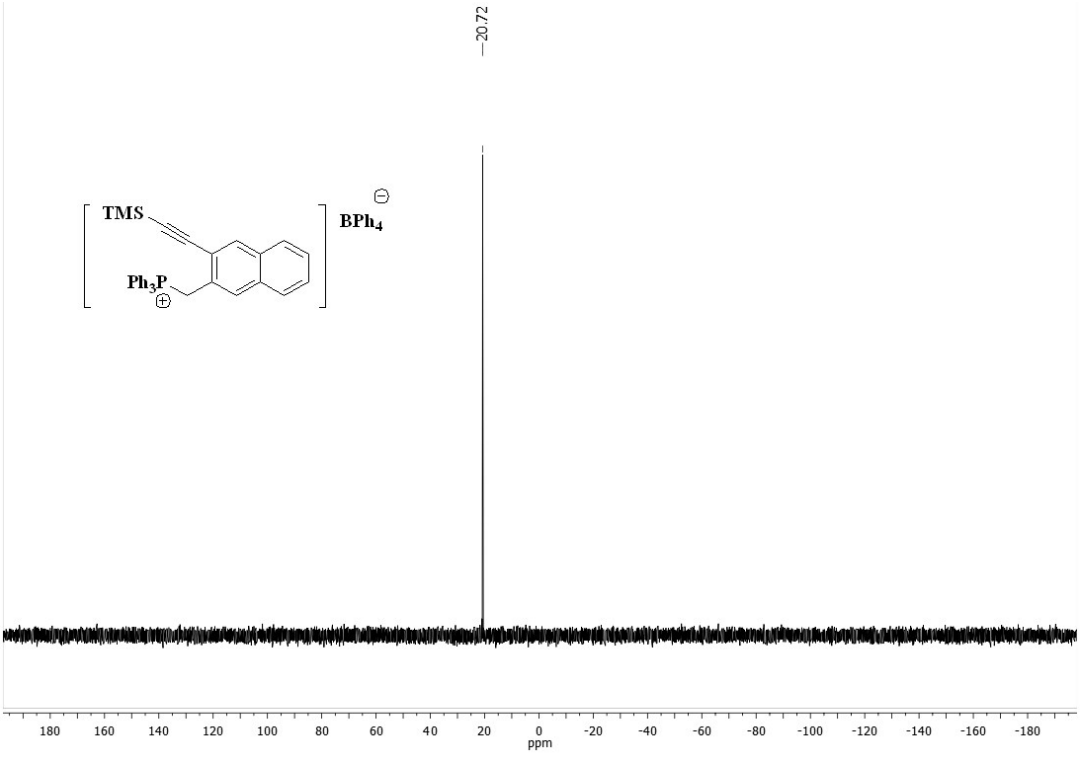


Figure S12. The $^{31}P\{^{1}H\}$ NMR spectrum of the phosphonium salt **5** in $CDCl_3$ at 162 MHz.

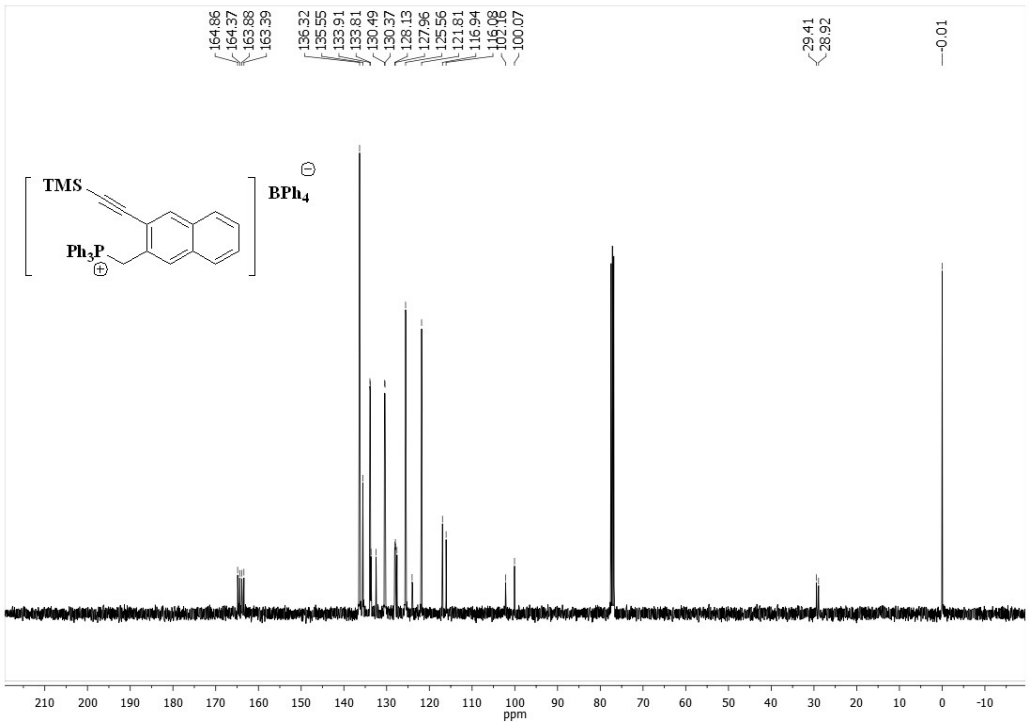


Figure S13. The ^{13}C {^{1}H} NMR spectrum of the phosphonium salt **5** in $CDCl_3$ at 100 MHz.

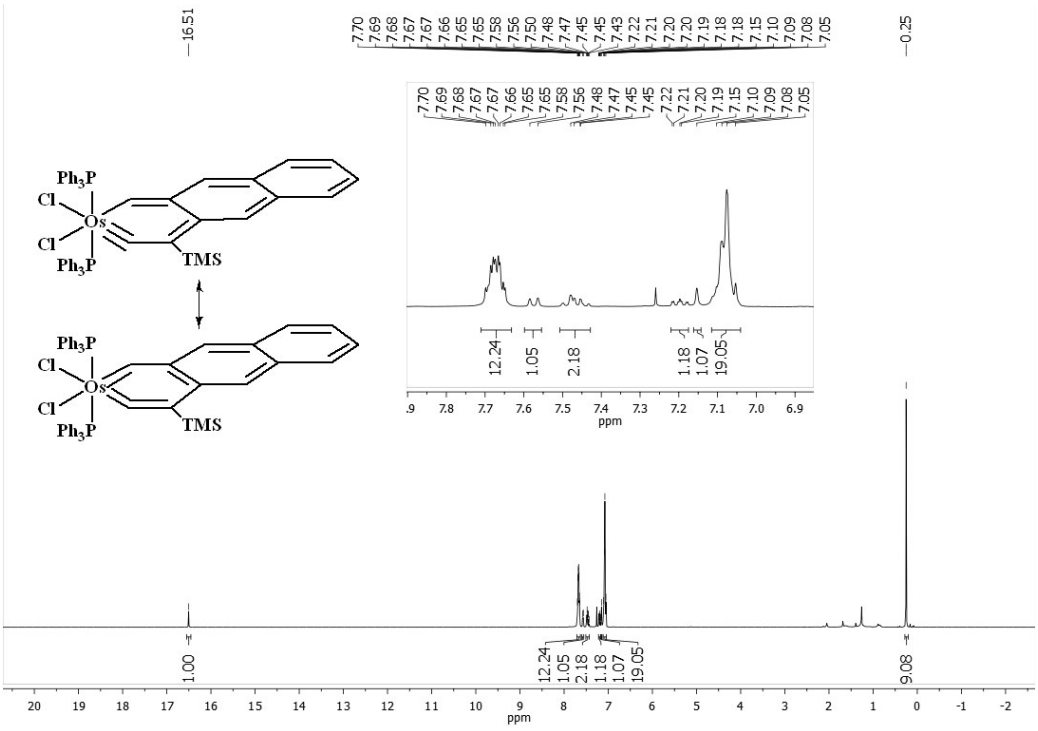


Figure S14. The ^{1}H NMR spectrum of the complex **6** in $CDCl_3$ at 400 MHz.

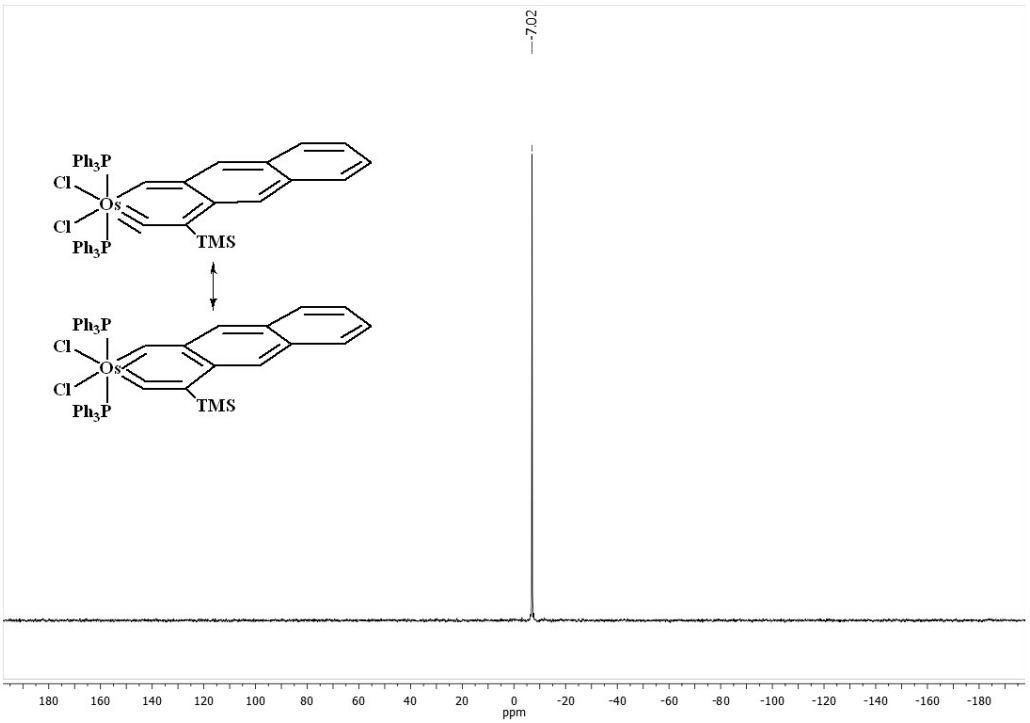


Figure S15. The $^{31}P\{^{1}H\}$ NMR spectrum of the complex **6** in $CDCl_3$ at 162 MHz.

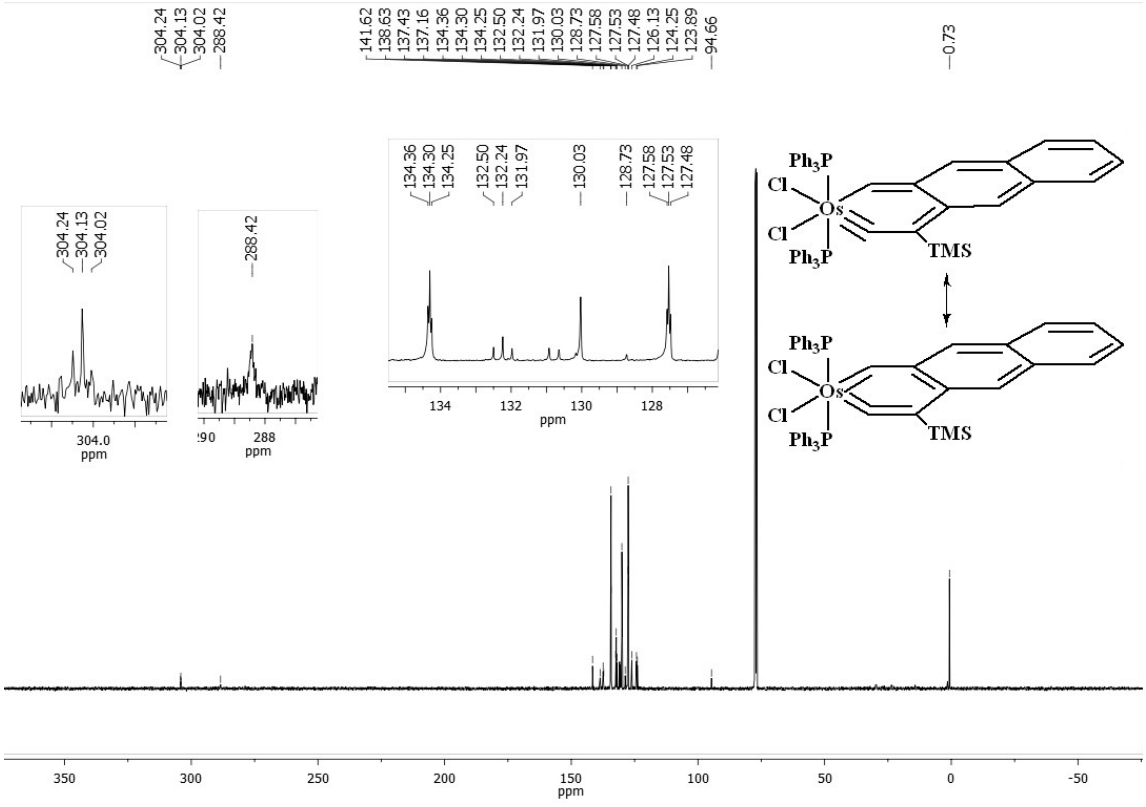


Figure S16. The $^{13}C\{^{1}H\}$ NMR spectrum of the complex **6** in $CDCl_3$ at 100 MHz.

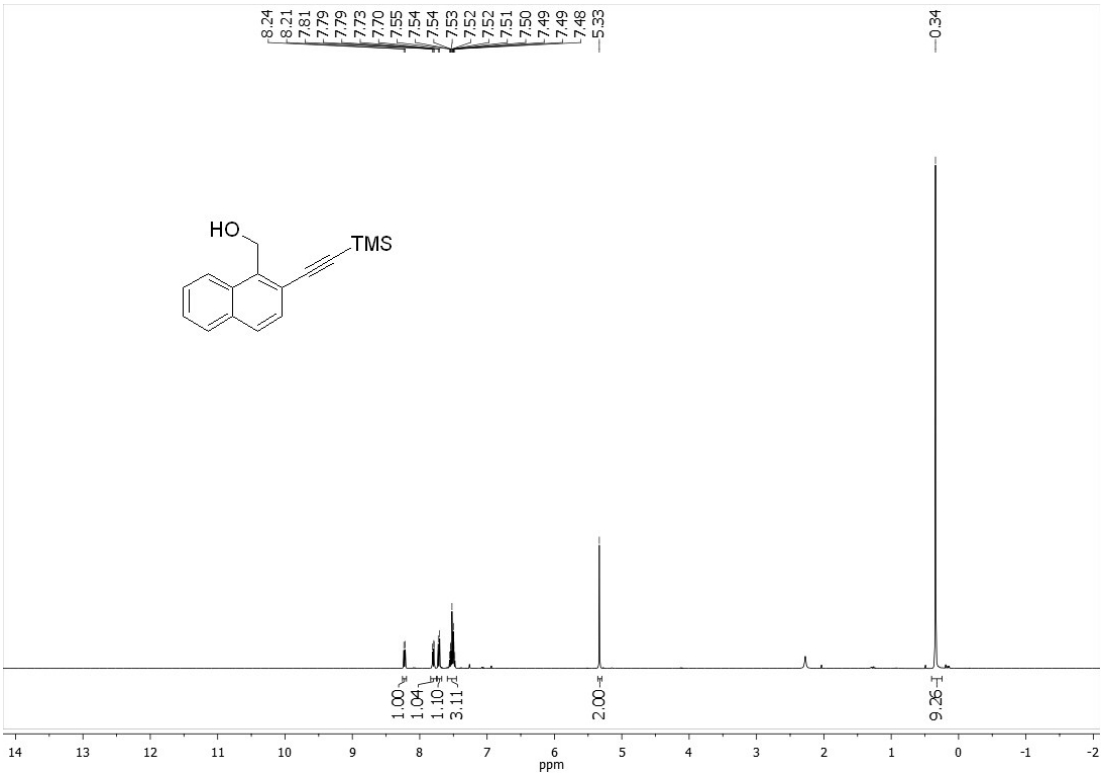


Figure S17. The ^{1}H NMR spectrum of the alcohol **7-1** in $CDCl_3$ at 400 MHz.

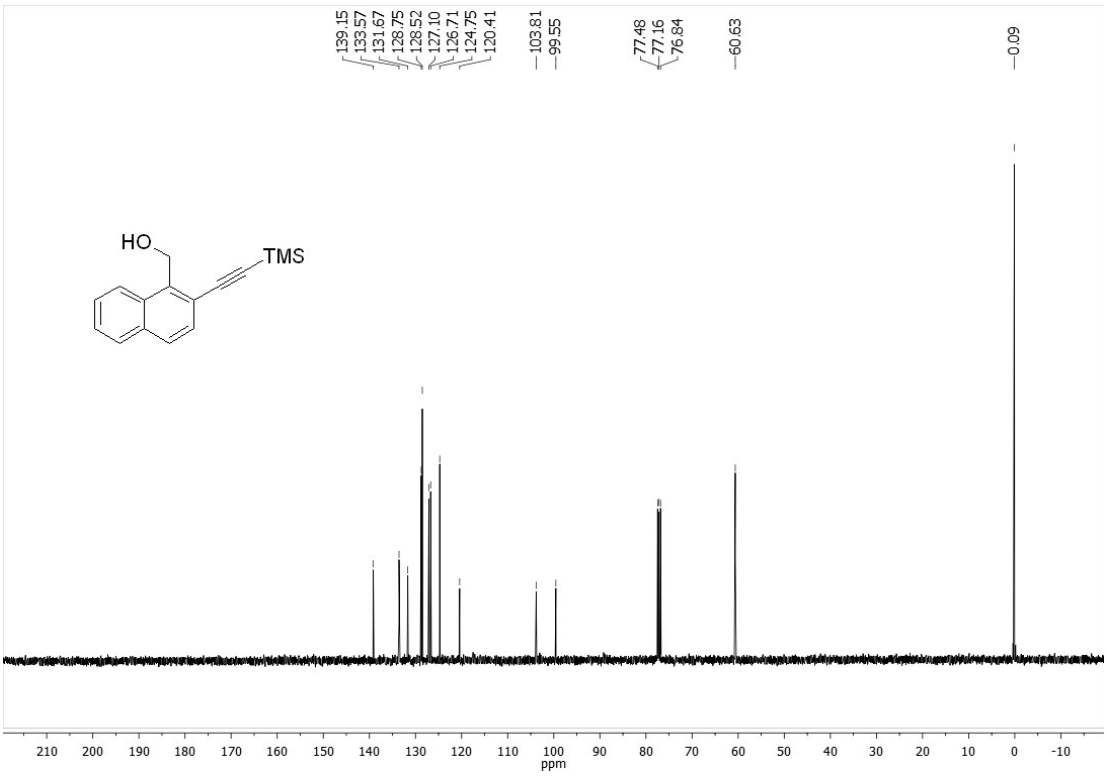


Figure S18. The $^{13}C\{^{1}H\}$ NMR spectrum of alcohol **7-1** in $CDCl_3$ at 100 MHz.

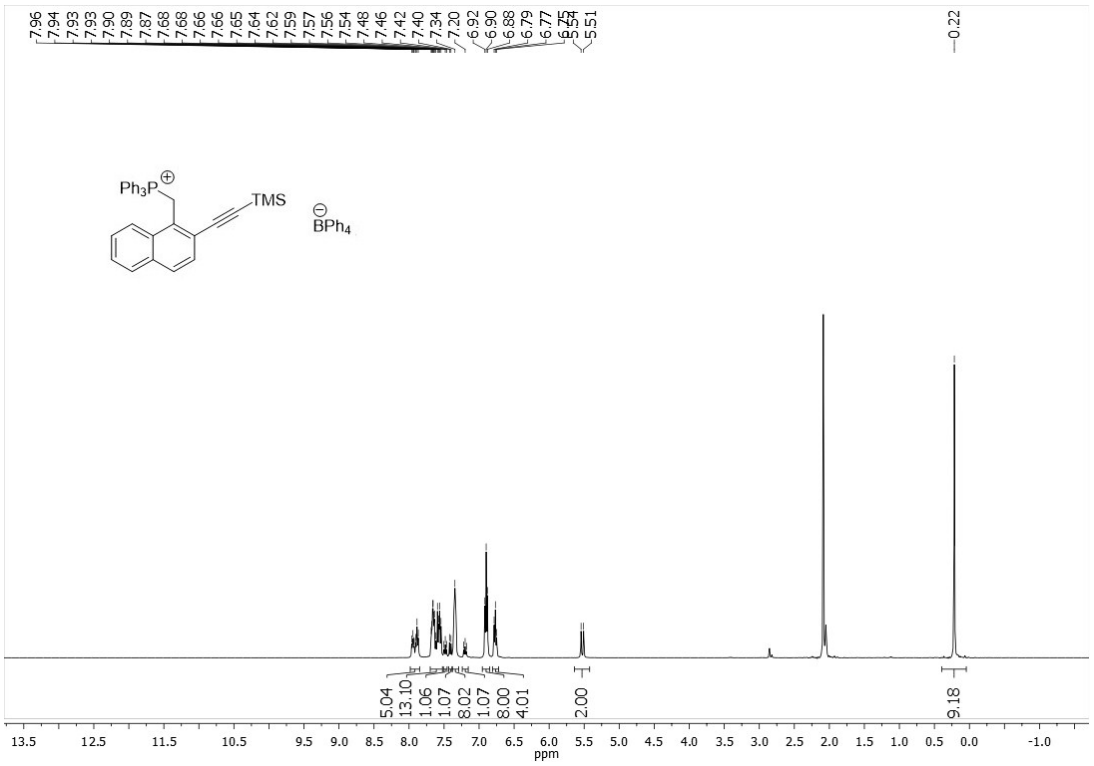


Figure S19. The ^{1}H NMR spectrum of the phosphonium salt **8** in acetone-d_6 at 400 MHz.

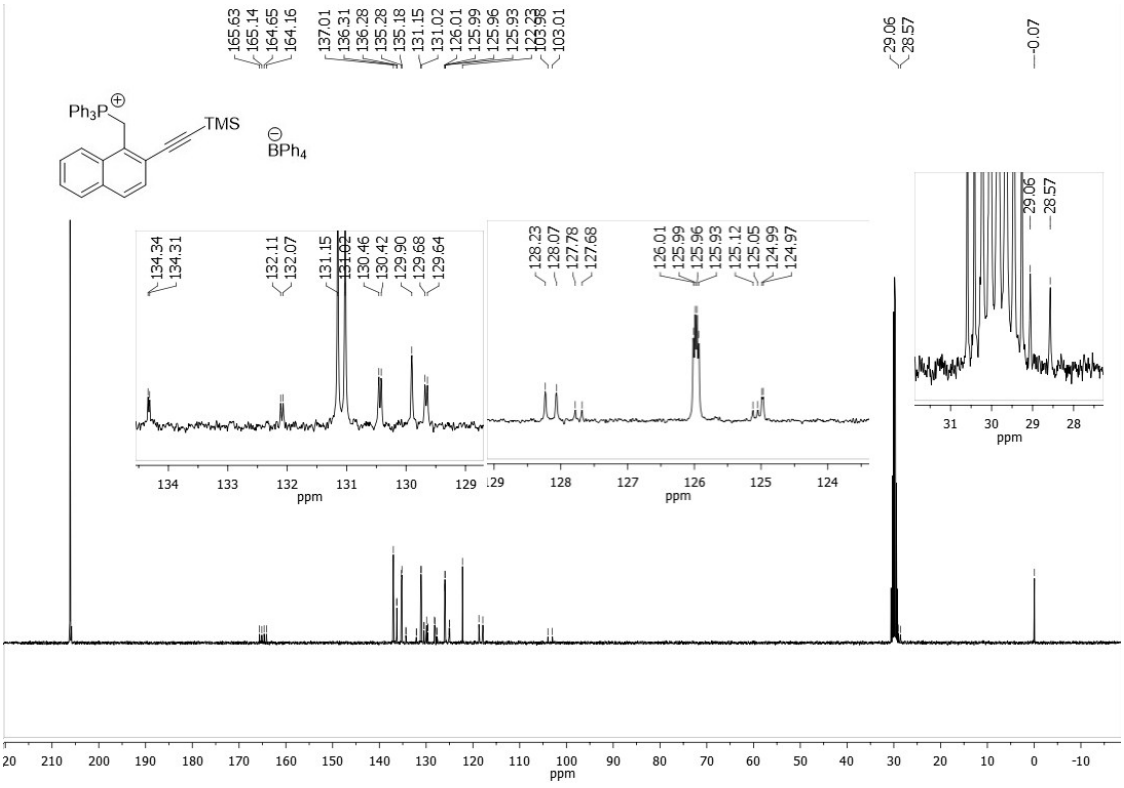


Figure S20. The $^{13}C\{^{1}H\}$ NMR spectrum of the phosphonium salt **8** in acetone-d_6 at 100 MHz.

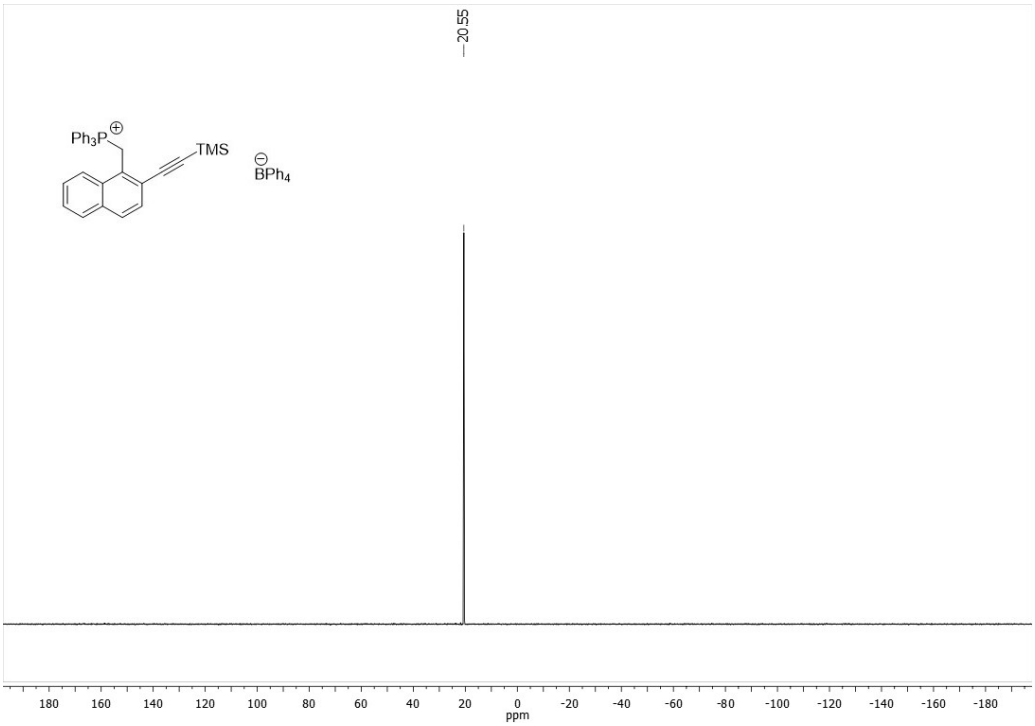


Figure S21. The ^{31}P $\{^{1}H\}$ NMR spectrum of the phosphonium salt **8** in acetone-d_6 at 162 MHz.

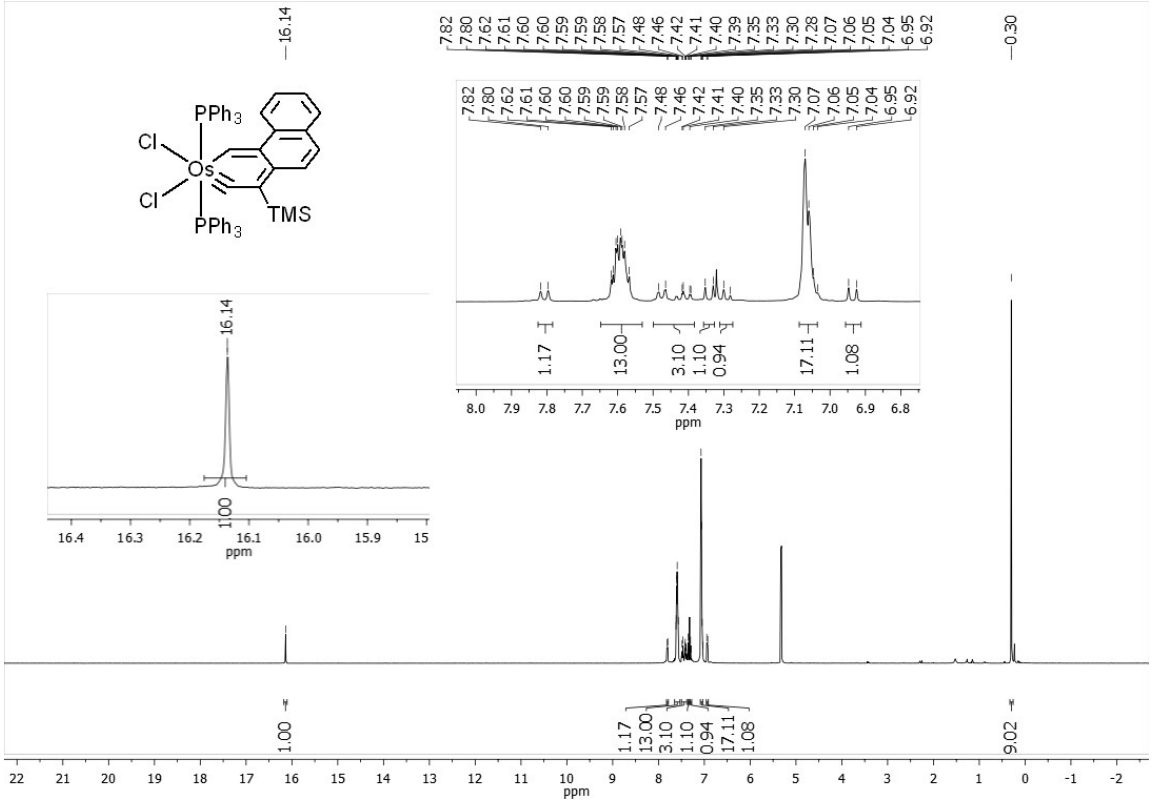


Figure S22. The ^{1}H NMR spectrum of the complex **9** in CD_2Cl_2 at 400 MHz.

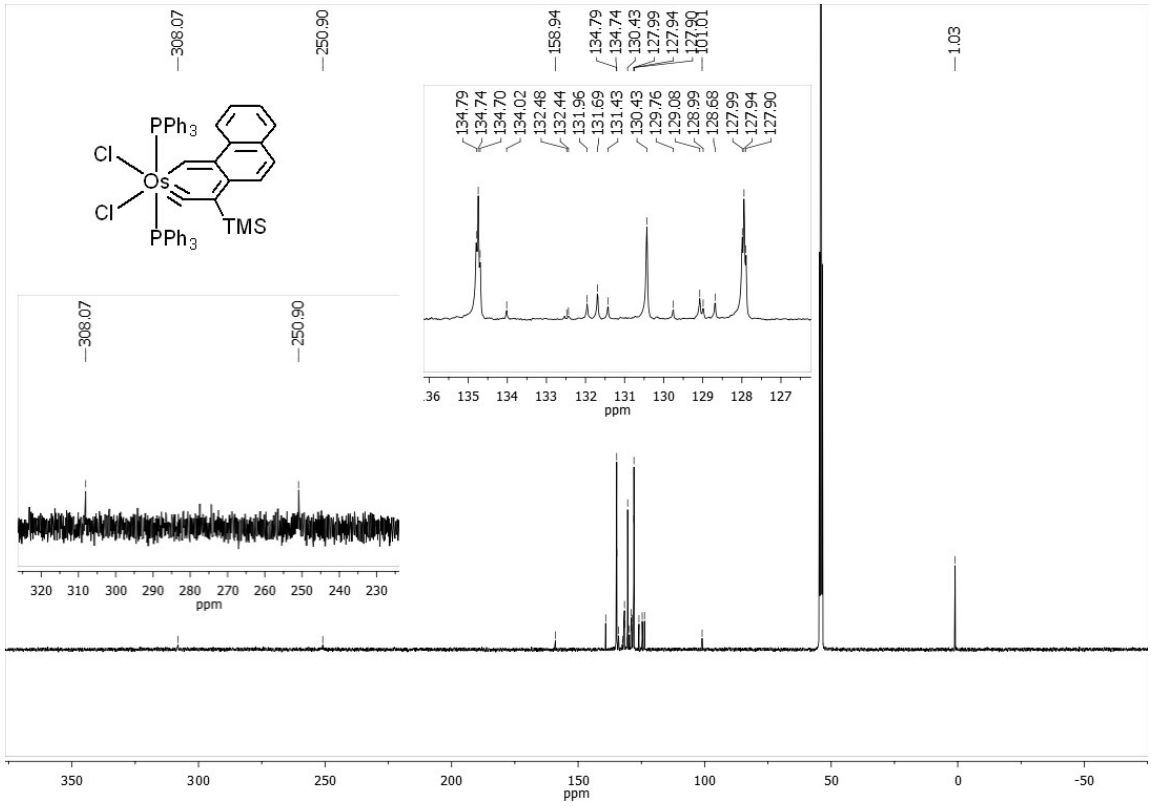


Figure S23. The ^{13}C {^{1}H} NMR spectrum of the complex **9** in CD_2Cl_2 at 100 MHz.

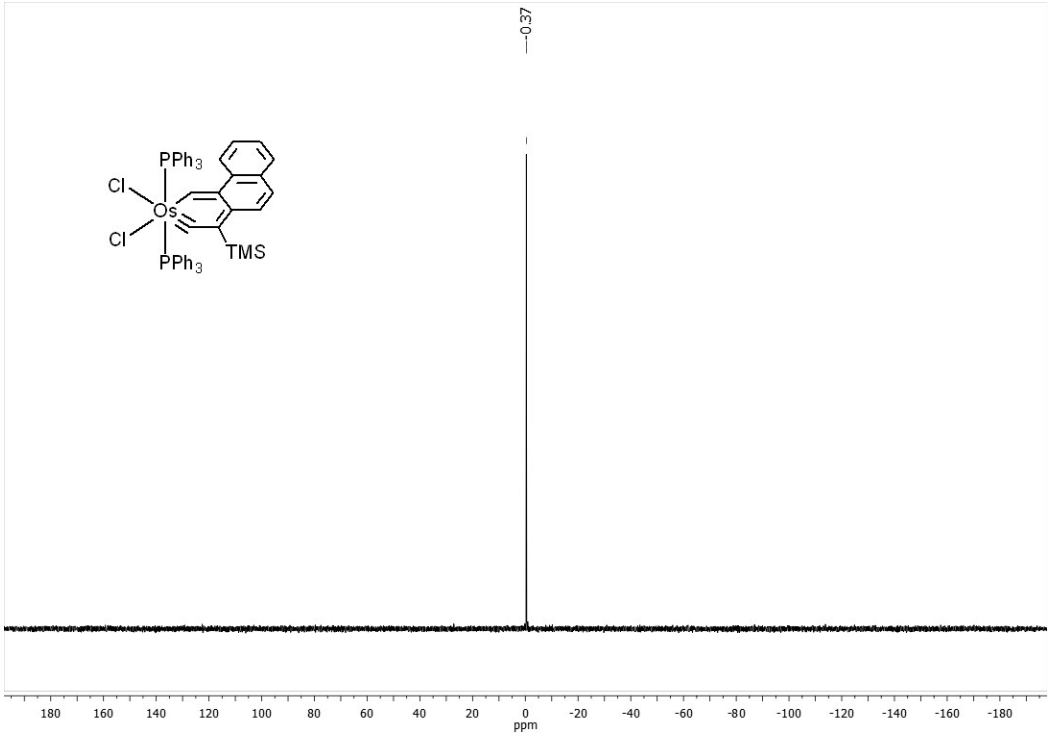


Figure S24. The ^{31}P {^{1}H} NMR spectrum of the complex **9** in CD_2Cl_2 at 162 MHz.

3. Crystallographic studies of 3, 6 and 9

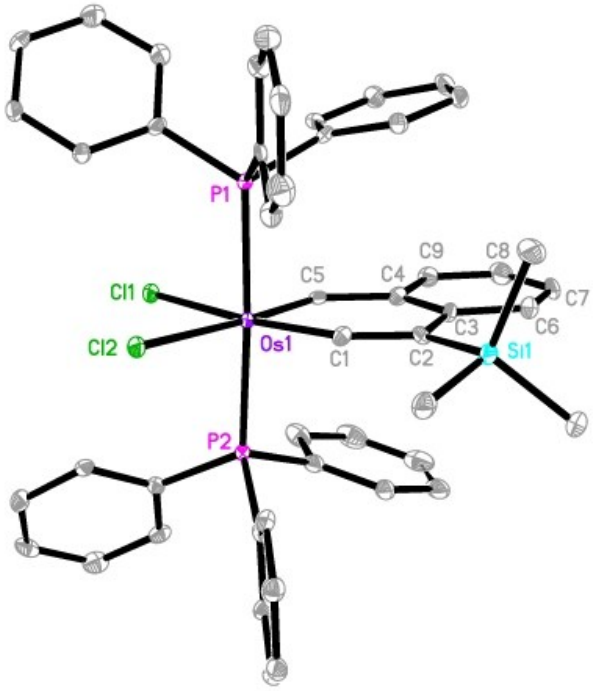


Figure S25. The X-ray crystal structure (30% probability level of the thermal ellipsoid) of the complex **3**.

Selected bond lengths (Å) and angles (deg) for complex **3**: Os1-C1: 1.826(6); Os1-C5: 1.963(6); C1-C2: 1.337(8); C2-C3: 1.463(9); C3-C4: 1.427(9); C4-C5: 1.425(8); C1-Os1-C5: 79.5(2); Os1-C1-C2: 153.1(5); C1-C2-C3: 110.7(5); C2-C3-C4: 121.6(5); C3-C4-C5: 123.2(6); C4-C5-Os1: 131.8(5) .

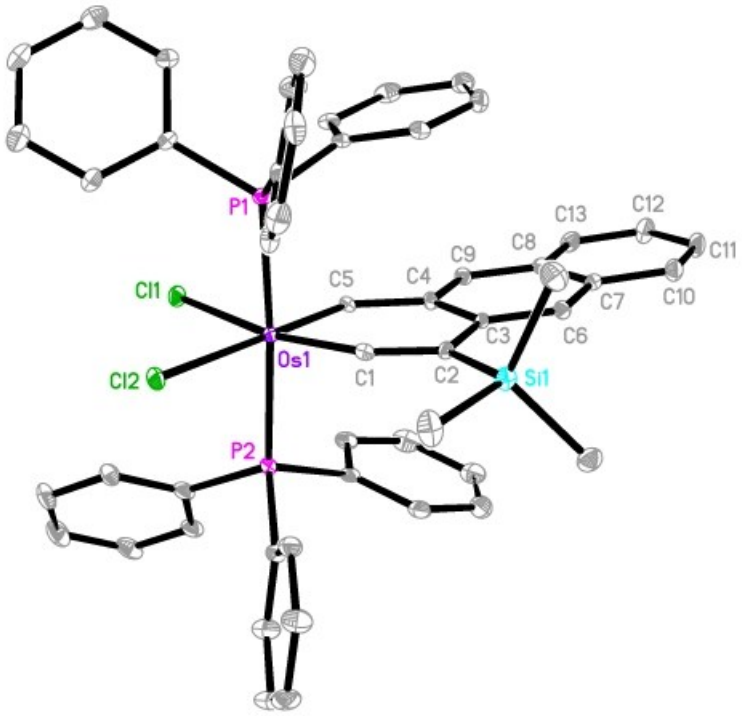


Figure S26. The X-ray crystal structure (30% probability level of the thermal ellipsoid) of the complex **6**.

Selected bond lengths (Å) and angles (deg) for complex **6**: Os1-C1: 1.816(6); Os1-C5: 1.964(6); C1-C2: 1.330(8); C2-C3: 1.438(12); C3-C4: 1.471(8); C4-C5: 1.428(8); C1-Os1-C5: 79.2(2); Os1-C1-C2: 153.7(5); C1-C2-C3: 112.6(6); C2-C3-C4: 115.5(5); C3-C4-C5: 123.1(6); C4-C5-Os1: 131.8(5).

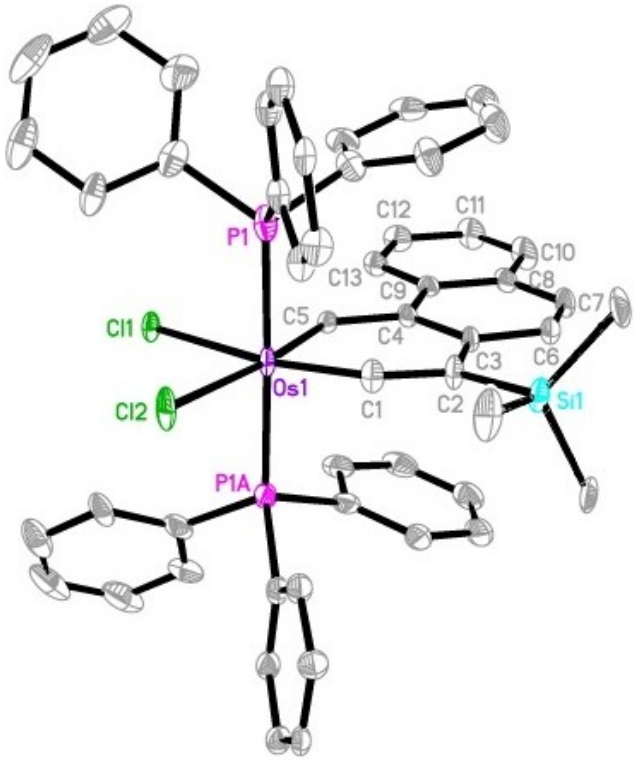


Figure S27. The X-ray crystal structure (30% probability level of the thermal ellipsoid) of the complex **9**.

Selected bond lengths (Å) and angles (deg) for complex **9**: Os1-C1: 1.791(7); Os1-C5: 2.002(6); C1-C2: 1.342(10); C2-C3: 1.445(10); C3-C4: 1.447(10); C4-C5: 1.398(9); C1-Os1-C5: 78.7(3); Os1-C1-C2: 153.7(6); C1-C2-C3: 111.4(6); C2-C3-C4: 122.1(6); C3-C4-C5: 121.2(6); C4-C5-Os1: 132.9(5).

Table S1. Crystallographic details for the complex **3**

Complex	**3·CH_2Cl_2**
CCDC No.	1589937
Empirical formula	$C_{49}H_{46}Cl_4OsP_2Si$
Formula weight	1056.89
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P21/c

a/Å	11.60758(19)
b/Å	16.9798(3)
c/Å	22.4892(4)
α/°	90
β/°	94.8290(15)
γ/°	90
Volume/Å3	4416.77(13)
Z	4
ρcalcg/cm3	1.589
μ/mm 1	8.887
F(000)	2112.0
Crystal size/mm3	0.04 × 0.04 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.532 to 134.996
Index ranges	-13 ≤ h ≤ 9, -20 ≤ k ≤ 14, -26 ≤ l ≤ 25
Reflections collected	13755
Independent reflections	7871 [Rint = 0.0500, Rsigma = 0.0752]
Data/restraints/parameters	7871/0/517
Completeness to theta = 66.5°	99.0%
Goodness-of-fit on F2	1.003
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.0906
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.0972
Largest diff. peak/hole / e Å^{-3}	1.53/-1.12

Table S2. Selected bond lengths for the complex **3**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Os1	Cl1	2.4608(13)	C31	C36	1.378(9)
Os1	Cl2	2.4731(13)	C32	C33	1.392(9)

Os1	P1	2.4180(15)	C33	C34	1.381(10)
Os1	P2	2.4114(15)	C34	C35	1.378(10)
Os1	C1	1.826(6)	C35	C36	1.397(9)
Os1	C5	1.963(6)	C41	C42	1.414(9)
P1	C21	1.821(6)	C41	C46	1.396(8)
P1	C31	1.830(6)	C42	C43	1.388(10)
P1	C41	1.824(6)	C43	C44	1.386(10)
P2	C51	1.818(6)	C44	C45	1.389(9)
P2	C61	1.828(6)	C45	C46	1.373(8)
P2	C71	1.834(6)	C51	C52	1.384(9)
Si1	C2	1.887(6)	C51	C56	1.415(9)
Si1	C10	1.858(7)	C52	C53	1.377(9)
Si1	C11	1.868(7)	C53	C54	1.395(12)
Si1	C12	1.859(7)	C54	C55	1.367(12)
C1	C2	1.337(8)	C55	C56	1.385(10)
C2	C3	1.463(9)	C61	C62	1.388(8)
C3	C4	1.427(9)	C61	C66	1.387(9)
C3	C6	1.415(8)	C62	C63	1.398(8)
C4	C5	1.425(8)	C63	C64	1.379(9)
C4	C9	1.430(8)	C64	C65	1.404(9)
C6	C7	1.380(9)	C65	C66	1.385(8)
C7	C8	1.397(10)	C71	C72	1.400(9)
C8	C9	1.353(9)	C71	C76	1.400(9)
C21	C22	1.403(8)	C72	C73	1.402(9)
C21	C26	1.390(8)	C73	C74	1.370(9)
C22	C23	1.387(9)	C74	C75	1.376(10)
C23	C24	1.397(9)	C75	C76	1.396(9)
C24	C25	1.382(9)	Cl1S	C1S	1.740(8)
C25	C26	1.408(9)	Cl2S	C1S	1.815(9)
C31	C32	1.405(9)			

Table S3. Selected bond angles for the complex **3**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Cl1	Os1	Cl2	88.51(5)	C26	C21	P1	120.1(5)
P1	Os1	Cl1	89.07(5)	C26	C21	C22	119.9(5)
P1	Os1	Cl2	89.23(5)	C23	C22	C21	120.6(6)
P2	Os1	Cl1	87.85(5)	C22	C23	C24	119.4(6)
P2	Os1	Cl2	89.86(5)	C25	C24	C23	120.3(6)
P2	Os1	P1	176.82(5)	C24	C25	C26	120.4(6)
C1	Os1	Cl1	163.74(18)	C21	C26	C25	119.3(6)

C1	Os1	Cl2	107.75(18)	C32	C31	P1	119.1(5)
C1	Os1	P1	91.54(18)	C36	C31	P1	120.6(5)
C1	Os1	P2	91.65(18)	C36	C31	C32	120.2(6)
C1	Os1	C5	79.5(2)	C33	C32	C31	119.8(7)
C5	Os1	Cl1	84.19(17)	C34	C33	C32	119.3(7)
C5	Os1	Cl2	172.70(17)	C35	C34	C33	121.0(7)
C5	Os1	P1	90.45(17)	C34	C35	C36	120.2(7)
C5	Os1	P2	90.06(17)	C31	C36	C35	119.5(6)
C21	P1	Os1	109.01(19)	C42	C41	P1	123.2(5)
C21	P1	C31	104.1(3)	C46	C41	P1	119.2(5)
C21	P1	C41	105.9(3)	C46	C41	C42	117.5(6)
C31	P1	Os1	116.5(2)	C43	C42	C41	120.4(6)
C41	P1	Os1	118.0(2)	C44	C43	C42	120.3(6)
C41	P1	C31	102.0(3)	C43	C44	C45	119.6(6)
C51	P2	Os1	108.6(2)	C46	C45	C44	120.1(6)
C51	P2	C61	105.2(3)	C45	C46	C41	121.8(6)
C51	P2	C71	104.3(3)	C52	C51	P2	121.8(5)
C61	P2	Os1	118.1(2)	C52	C51	C56	118.5(6)
C61	P2	C71	100.4(3)	C56	C51	P2	119.1(5)
C71	P2	Os1	118.6(2)	C53	C52	C51	121.9(7)
C10	Si1	C2	108.7(3)	C52	C53	C54	119.2(8)
C10	Si1	C11	108.7(3)	C55	C54	C53	119.6(7)
C10	Si1	C12	109.6(4)	C54	C55	C56	121.9(8)
C11	Si1	C2	112.3(3)	C55	C56	C51	118.7(7)
C12	Si1	C2	109.5(3)	C62	C61	P2	121.1(5)
C12	Si1	C11	108.0(3)	C66	C61	P2	119.7(5)
C2	C1	Os1	153.1(5)	C66	C61	C62	119.1(6)
C1	C2	Si1	123.2(5)	C61	C62	C63	120.8(6)
C1	C2	C3	110.7(5)	C64	C63	C62	119.7(6)
C3	C2	Si1	125.9(4)	C63	C64	C65	119.8(6)
C4	C3	C2	121.6(5)	C66	C65	C64	119.8(6)
C6	C3	C2	120.8(6)	C65	C66	C61	120.8(6)
C6	C3	C4	117.6(6)	C72	C71	P2	118.4(5)
C3	C4	C9	118.8(6)	C72	C71	C76	119.4(6)
C5	C4	C3	123.2(6)	C76	C71	P2	121.7(5)
C5	C4	C9	118.0(6)	C71	C72	C73	119.0(6)
C4	C5	Os1	131.8(5)	C74	C73	C72	121.2(6)
C7	C6	C3	121.3(6)	C73	C74	C75	120.0(6)
C6	C7	C8	121.1(6)	C74	C75	C76	120.3(6)
C9	C8	C7	119.2(6)	C75	C76	C71	120.0(6)
C8	C9	C4	122.0(6)	Cl1S	C1S	Cl2S	110.6(5)
C22	C21	P1	119.3(4)				

Table S4. Crystallographic details for the complex **6**

Complex	**6·CH_2Cl_2**
CCDC No.	1589938
Empirical formula	$C_{53}H_{48}Cl_4OsP_2Si$
Formula weight	1106.94
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	I2
a/Å	13.9889(2)
b/Å	16.4530(2)
c/Å	21.3301(3)
α/°	90
β/°	97.2730(10)
γ/°	90
Volume/Å3	4869.82(11)
Z	4
ρcalcg/cm3	1.510
μ/mm 1	8.090
F(000)	2216.0
Crystal size/mm3	0.15 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.806 to 134.976
Index ranges	$-16 \leq h \leq 15$, $-19 \leq k \leq 13$, $-14 \leq l \leq 25$
Reflections collected	7646
Independent reflections	5484 [R_{int} = 0.0214, R_{sigma} = 0.0381]
Data/restraints/parameters	5484/3/580
Completeness to theta = 66.5°	98.7%

Goodness-of-fit on F2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0276, wR_2 = 0.0695
Final R indexes [all data]	R_1 = 0.0284, wR_2 = 0.0700
Largest diff. peak/hole / e Å^{-3}	2.48/-0.85

Table S5. Selected bond lengths for the complex **6**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Os1	Cl1	2.4663(14)	C31	C32	1.406(10)
Os1	Cl2	2.4640(15)	C31	C36	1.389(10)
Os1	P1	2.4081(11)	C32	C33	1.382(10)
Os1	P2	2.3985(11)	C33	C34	1.388(11)
Os1	C1	1.816(6)	C34	C35	1.395(11)
Os1	C5	1.964(6)	C35	C36	1.390(10)
P1	C21	1.821(8)	C41	C42	1.398(9)
P1	C31	1.820(8)	C41	C46	1.395(10)
P1	C41	1.833(5)	C42	C43	1.384(9)
P2	C51	1.832(8)	C43	C44	1.397(11)
P2	C61	1.831(6)	C44	C45	1.375(11)
P2	C71	1.820(8)	C45	C46	1.388(9)
Si1	C2	1.889(8)	C51	C52	1.389(9)
Si1	C14	1.866(7)	C51	C56	1.381(11)
Si1	C15	1.871(6)	C52	C53	1.364(10)
Si1	C16	1.867(7)	C53	C54	1.390(12)
C1	C2	1.330(8)	C54	C55	1.390(11)
C2	C3	1.438(12)	C55	C56	1.404(11)
C3	C4	1.471(8)	C61	C62	1.399(9)
C3	C6	1.370(9)	C61	C66	1.381(9)
C4	C5	1.428(8)	C62	C63	1.394(9)
C4	C9	1.380(8)	C63	C64	1.374(11)
C6	C7	1.422(9)	C64	C65	1.393(11)
C7	C8	1.434(9)	C65	C66	1.385(9)
C7	C10	1.436(9)	C71	C72	1.409(10)
C8	C9	1.413(9)	C71	C76	1.380(11)
C8	C13	1.391(9)	C72	C73	1.387(10)
C10	C11	1.343(9)	C73	C74	1.385(12)
C11	C12	1.406(10)	C74	C75	1.408(12)
C12	C13	1.377(10)	C75	C76	1.386(11)
C21	C22	1.401(10)	C1S	Cl1S	1.778(13)

C21	C26	1.389(10)	C1S	Cl2S	1.754(12)
C22	C23	1.395(10)	C1SA	Cl1A	1.743(13)
C23	C24	1.372(11)	C1SA	Cl2A	1.711(15)
C24	C25	1.386(11)	Cl2A	Cl2A[1]	1.886(11)
C25	C26	1.394(10)			

Table S6. Selected bond angles for the complex **6**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Cl2	Os1	Cl1	91.48(5)	C13	C12	C11	119.1(7)
P1	Os1	Cl1	87.70(5)	C12	C13	C8	121.3(6)
P1	Os1	Cl2	90.76(7)	C22	C21	P1	118.9(6)
P2	Os1	Cl1	89.14(5)	C26	C21	P1	121.4(5)
P2	Os1	Cl2	87.22(7)	C26	C21	C22	119.5(7)
P2	Os1	P1	176.21(4)	C23	C22	C21	120.1(7)
C1	Os1	Cl1	162.75(17)	C24	C23	C22	120.4(6)
C1	Os1	Cl2	105.70(17)	C23	C24	C25	119.5(6)
C1	Os1	P1	90.45(17)	C24	C25	C26	121.2(7)
C1	Os1	P2	93.18(17)	C21	C26	C25	119.3(7)
C1	Os1	C5	79.2(2)	C32	C31	P1	120.6(6)
C5	Os1	Cl1	83.68(18)	C36	C31	P1	119.4(5)
C5	Os1	Cl2	174.65(18)	C36	C31	C32	119.1(7)
C5	Os1	P1	91.33(17)	C33	C32	C31	119.1(7)
C5	Os1	P2	90.41(17)	C32	C33	C34	121.8(6)
C21	P1	Os1	117.6(3)	C33	C34	C35	119.2(6)
C21	P1	C41	101.5(4)	C36	C35	C34	119.2(6)
C31	P1	Os1	108.3(2)	C31	C36	C35	121.5(6)
C31	P1	C21	104.8(3)	C42	C41	P1	122.5(5)
C31	P1	C41	105.6(4)	C46	C41	P1	118.3(5)
C41	P1	Os1	117.69(16)	C46	C41	C42	118.9(5)
C51	P2	Os1	117.5(3)	C43	C42	C41	120.3(6)
C61	P2	Os1	116.80(19)	C42	C43	C44	120.0(6)
C61	P2	C51	101.7(3)	C45	C44	C43	120.2(6)
C71	P2	Os1	109.0(2)	C44	C45	C46	120.0(7)
C71	P2	C51	105.0(3)	C45	C46	C41	120.7(6)
C71	P2	C61	105.6(3)	C52	C51	P2	119.3(6)
C14	Si1	C2	108.4(3)	C56	C51	P2	121.5(5)
C14	Si1	C15	111.9(3)	C56	C51	C52	119.2(7)
C14	Si1	C16	108.1(4)	C53	C52	C51	121.3(7)
C15	Si1	C2	110.6(3)	C52	C53	C54	120.0(7)
C16	Si1	C2	110.5(3)	C53	C54	C55	119.9(7)

C16	Si1	C15	107.3(3)	C54	C55	C56	119.4(7)
C2	C1	Os1	153.7(5)	C51	C56	C55	120.2(7)
C1	C2	Si1	121.5(7)	C62	C61	P2	122.2(5)
C1	C2	C3	112.6(6)	C66	C61	P2	118.4(5)
C3	C2	Si1	125.7(4)	C66	C61	C62	119.3(6)
C2	C3	C4	119.5(5)	C63	C62	C61	119.8(7)
C6	C3	C2	123.5(6)	C64	C63	C62	120.5(7)
C6	C3	C4	117.0(6)	C63	C64	C65	119.7(6)
C5	C4	C3	123.1(6)	C66	C65	C64	120.1(7)
C9	C4	C3	119.8(6)	C61	C66	C65	120.6(7)
C9	C4	C5	117.0(6)	C72	C71	P2	119.8(6)
C4	C5	Os1	131.8(5)	C76	C71	P2	120.2(5)
C3	C6	C7	123.2(6)	C76	C71	C72	119.5(7)
C6	C7	C8	119.8(6)	C73	C72	C71	119.5(7)
C6	C7	C10	123.3(6)	C74	C73	C72	120.8(7)
C8	C7	C10	116.9(6)	C73	C74	C75	119.7(7)
C9	C8	C7	116.9(6)	C76	C75	C74	119.3(7)
C13	C8	C7	120.0(6)	C71	C76	C75	121.2(7)
C13	C8	C9	123.1(6)	Cl2S	C1S	Cl1S	111.8(10)
C4	C9	C8	123.2(6)	Cl2A	C1SA	Cl1A	115.1(11)
C11	C10	C7	121.2(6)	C1SA	Cl2A	Cl2A[1]	155.4(7)
C10	C11	C12	121.5(7)				

Table S7. Crystallographic details for the complex **9**

Complex	**9·3CH$_2$Cl$_2$**
CCDC No.	1831065
Empirical formula	$C_{49}H_{46}Cl_4OsP_2Si$
Formula weight	1276.79
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	11.4227(2)
b/Å	17.2735(3)
c/Å	13.9125(3)

α/°	90
β/°	102.8377(19)
γ/°	90
Volume/Å3	2676.46(9)
Z	2
ρcalcg/cm3	1.586
μ/mm 1	9.239
F(000)	1277.0
Crystal size/mm3	0.12 × 0.06 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.938 to 134.996
Index ranges	-13 ≤ h ≤ 10, -20 ≤ k ≤ 20, -16 ≤ l ≤ 16
Reflections collected	15170
Independent reflections	4986 [R_{int} = 0.0386, R_{sigma} = 0.0363]
Data/restraints/parameters	4986/114/416
Completeness to theta = 66.5°	99.7%
Goodness-of-fit on F2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1023
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.1045
Largest diff. peak/hole / e $Å^{-3}$	1.82/-1.30

Table S8. Selected bond lengths for the complex **9**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Os1	Cl1	2.4651(14)	C1	C2	1.342(10)
Os1	Cl2	2.4645(16)	C2	Si1[1]	1.909(8)
Os1	P1[1]	2.4099(14)	C2	C3	1.445(10)
Os1	P1	2.4099(14)	C3	C4	1.447(10)
Os1	C1	1.791(7)	C3	C6	1.424(9)
Os1	C5	2.002(6)	C4	C5	1.398(9)
P1	C21	1.828(6)	C4	C9	1.451(9)

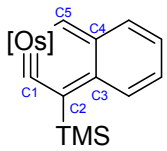
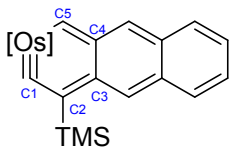
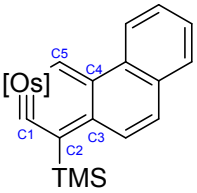
P1	C31	1.800(12)	C6	C7	1.339(11)
P1	C31A	1.895(14)	C7	C8	1.416(11)
P1	C41	1.827(6)	C8	C9	1.414(10)
Si1	Si1[1]	0.456(16)	C8	C10	1.422(11)
Si1	C2	1.909(8)	C9	C13	1.412(11)
Si1	C14	1.861(10)	C10	C11	1.363(13)
Si1	C15	1.863(13)	C11	C12	1.389(12)
Si1	C16	1.857(14)	C12	C13	1.388(10)

Table S9. Selected bond angles for the complex **9**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Cl2	Os1	Cl1	87.73(5)	C4	C5	Os1	132.9(5)
P1	Os1	Cl1	90.02(3)	C7	C6	C3	121.9(7)
P1[1]	Os1	Cl1	90.02(3)	C6	C7	C8	122.4(7)
P1	Os1	Cl2	88.80(3)	C7	C8	C10	120.6(7)
P1[1]	Os1	Cl2	88.80(3)	C9	C8	C7	118.9(7)
P1	Os1	P1[1]	177.59(6)	C9	C8	C10	120.5(8)
C1	Os1	Cl1	161.7(2)	C8	C9	C4	119.6(7)
C1	Os1	Cl2	110.6(2)	C13	C9	C4	123.9(6)
C1	Os1	P1[1]	90.36(3)	C13	C9	C8	116.5(6)
C1	Os1	P1	90.36(3)	C11	C10	C8	121.0(7)
C1	Os1	C5	78.7(3)	C10	C11	C12	119.6(7)
C5	Os1	Cl1	83.01(18)	C13	C12	C11	120.4(8)
C5	Os1	Cl2	170.74(18)	C12	C13	C9	122.1(7)
C5	Os1	P1[1]	91.20(3)	C22	C21	P1	118.5(5)
C5	Os1	P1	91.20(3)	C26	C21	P1	122.0(5)
C21	P1	Os1	119.2(2)	C26	C21	C22	119.3(6)
C21	P1	C31A	107.8(4)	C21	C22	C23	118.9(7)
C31	P1	Os1	124.4(4)	C24	C23	C22	120.4(8)
C31	P1	C21	95.6(4)	C25	C24	C23	120.2(7)
C31	P1	C41	100.7(4)	C24	C25	C26	120.4(9)
C31A	P1	Os1	108.5(4)	C25	C26	C21	120.6(8)
C41	P1	Os1	109.07(17)	C32	C31	P1	117.7(8)
C41	P1	C21	105.0(3)	C32	C31	C36	119.1(10)
C41	P1	C31A	106.6(4)	C36	C31	P1	123.2(8)
Si1[1]	Si1	C2	83.1(2)	C32A	C31A	P1	125.4(8)
Si1[1]	Si1	C14	101.1(5)	C32A	C31A	C36A	119.9(12)
Si1[1]	Si1	C15	138.2(7)	C36A	C31A	P1	114.7(9)
Si1[1]	Si1	C16	27.5(6)	C31	C32	C33	121.3(11)
C14	Si1	C2	109.8(4)	C31A	C32A	C33A	120.3(12)

C14	Si1	C15	106.7(8)	C34	C33	C32	118.8(11)
C15	Si1	C2	114.7(9)	C34A	C33A	C32A	118.8(12)
C16	Si1	C2	104.9(8)	C33	C34	C35	121.0(11)
C16	Si1	C14	108.5(8)	C33A	C34A	C35A	122.5(11)
C16	Si1	C15	112.2(6)	C34	C35	C36	119.7(11)
C2	C1	Os1	153.7(6)	C34A	C35A	C36A	117.3(11)
Si1	C2	Si1[1]	13.7(5)	C35	C36	C31	120.0(11)
C1	C2	Si1[1]	123.0(6)	C35A	C36A	C31A	121.2(12)
C1	C2	Si1	123.0(6)	C42	C41	P1	119.4(5)
C1	C2	C3	111.4(6)	C42	C41	C46	119.5(5)
C3	C2	Si1	125.1(5)	C46	C41	P1	120.5(5)
C3	C2	Si1[1]	125.1(5)	C41	C42	C43	119.1(6)
C2	C3	C4	122.1(6)	C44	C43	C42	120.8(6)
C6	C3	C2	119.9(7)	C45	C44	C43	120.1(6)
C6	C3	C4	118.1(6)	C44	C45	C46	120.6(7)
C3	C4	C9	119.0(6)	C45	C46	C41	120.0(7)
C5	C4	C3	121.2(6)	Cl1S	C1S	Cl2S	116.1(4)
C5	C4	C9	119.7(6)	Cl3S	C2S	Cl4S	111.9(9)

Table S10. Selected bond distances (Å) and angles (deg) for the complexes **3**, **6** and **9**. [Os] = $OsCl_2(PPh_3)_2$

Complexes / **Bond length (Å) and bond angel (°)**	 **3**	 **6**	 **9**
Os1-C1	1.826(6)	1.816(6)	1.791(7)
Os1-C5	1.963(6)	1.964(6)	2.002(6)
C1-C2	1.337(8)	1.330(8)	1.342(10)
C2-C3	1.463(9)	1.438(12)	1.445(10)
C3-C4	1.427(9)	1.471(8)	1.447(10)
C4-C5	1.425(8)	1.428(8)	1.398(9)
C1-Os1-C5	79.5(2)	79.2(2)	78.7(3)
Os1-C1-C2	153.1(5)	153.7(5)	153.7(6)
C1-C2-C3	110.7(5)	112.6(6)	111.4(6)
C2-C3-C4	121.6(5)	115.5(5)	122.1(6)

C3-C4-C5	123.2(6)	123.1(6)	121.2(6)
C4-C5-Os1	131.8(5)	131.8(5)	132.9(5)

4. Computational studies

All structures were optimized at the B3LYP level of density functional theory.[5] Frequency calculations were also performed to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe Os, P, Cl, and Si atom, while the standard 6-31G(d) basis set was used for C, O, and H.[6] Polarization functions were added for Os (ζ(f) = 0.886), P (ζ(d) = 0.387), Cl (ζ(d) = 0.640), and Si (ζ(d) = 0.284).[7] NICS values were calculated at the B3LYP/6-311++G** level.[8] All the calculations were performed with the Gaussian 03 software package.[9]

5. Selected structural parameters of polycyclic metallaarynes and their organic analogs

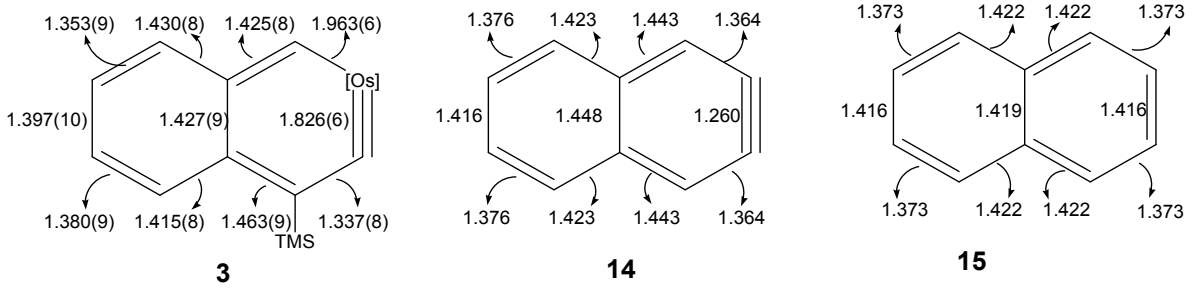


Figure S28. Selected bond distances (Å) of the β-osmanaphthalyne complex **3** (from X-ray diffraction), β-naphthalyne (**14**) (calculated) and naphthalene (**15**) (calculated). [Os] = $OsCl_2(PPh_3)_2$. It is noted that the **3** and **14** have the same bond alternating pattern and similar corresponding C-C bond distances when the C-Os-C fragment in **3** and the C-C≡C fragment in **14** are excluded. These structural parameters are also similar to those in naphthalene (**15**).

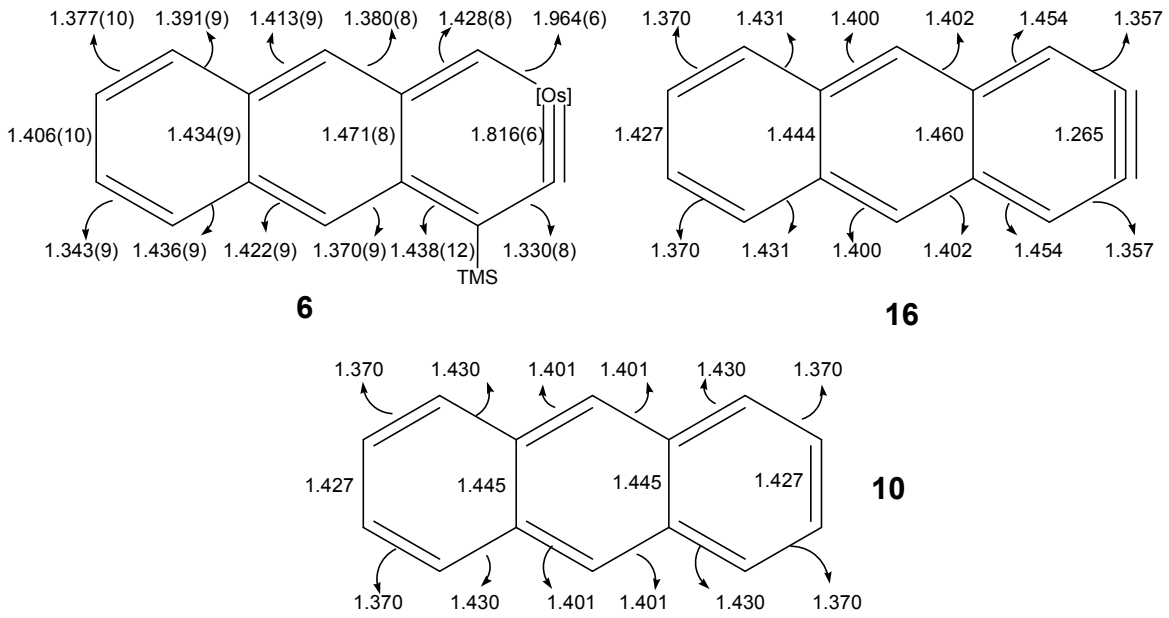


Figure S29. Selected bond distances (Å) of the osmaanthracyne complex **6** (from X-ray diffraction), β-anthracyne (**16**) (calculated) and anthracene (**10**) (calculated). [Os] = $OsCl_2(PPh_3)_2$. Whe the C-Os≡C unit in **6** and the C-C≡C unit in **16** are excluded, **6** and **16** have similar structural features (in term of bond alternation pattern and structural parameters) as indicated by the C-C bond distances. It is also noted that the structural feature of the naphthalene fragment of **6** and **16** is similar to that of anthracene (**10**).

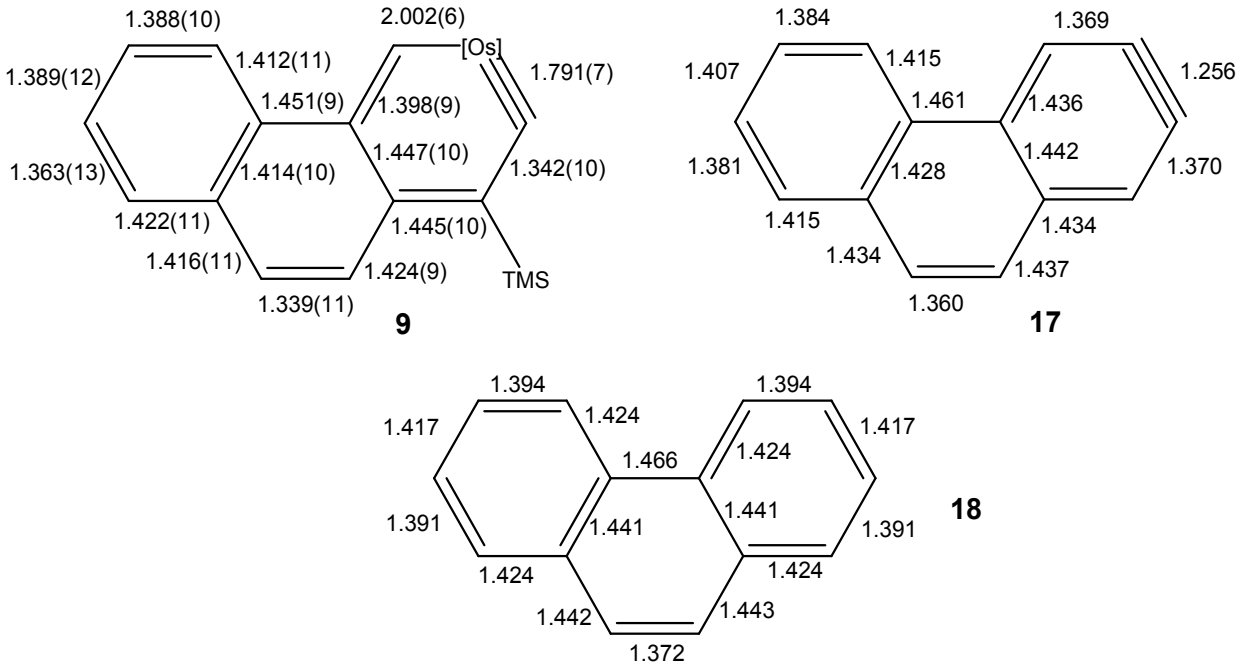
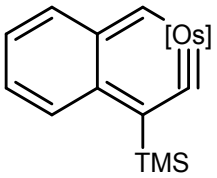
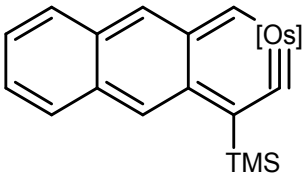


Figure S30. Selected bond distances (Å) of the osmaphenanthryne complex **9** (from X-ray diffraction), β–phenanthryne (**17**) (calculated) and phenanthrene (**18**) (calculated). [Os] = $OsCl_2(PPh_3)_2$. Whe the C-Os≡C unit in **9** and the C-C≡C unit in **17** are excluded, **9** and **17** have similar structural features (in term of bond alternation pattern and structural parameters) as indicated by the C-C bond distances. It is also noted that the structural feature of the naphthalene fragment of **9** and **17** is similar to that of phenanthrene (**18**).

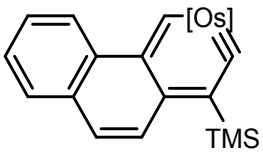
6. Calculated NICS values of polycyclic metallaarynes and their organic analogs



3

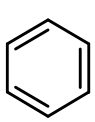


6

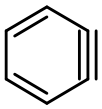


9

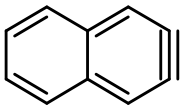
NICS(1)	-5.7	-6.4	-6.5	-7.2	-5.3	-8.5	-3.5	-5.3
NICS(1)	-8.6	-6.5	-8.9	-9.5	-5.1	-10.6	-7.1	-6.3



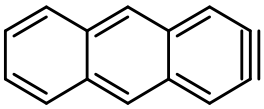
19



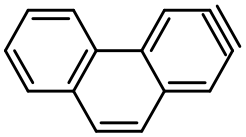
20



14



16

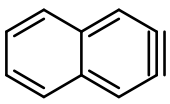


17

NICS(0)	-8.2	-19.1	-9.4	-19.2	-7.5	-11.5	-18.7	-10.1	-7.0	-20.0
NICS(1)	-10.2	-13.0	-11.4	-13.3	-9.5	-13.1	-13.0	-11.7	-9.4	-14.3

Figure S31. NICS(0) and NICS(1) values in ppm for complexes **3**, **6** and **9** and compounds **19, 20, 14, 16** and **17**. [Os] = $OsCl_2(PPh_3)_2$. It is noted that all the rings of the metallacycles have negative NICS(1) values, indicating that they are aromatic. In general, the calculated NICS values of the rings of the metallacycles are slightly less negative than those of their organic counterparts. Fusion of metallabenzyne and benzene rings also causes the NICS values of both rings to be slightly less negative.

7. Cartesian coordinates and electronic energies for all the species calculated in this study



14

E = -384.54356173 a.u.

C 2.31075900 -0.70812500 -0.00022900

C 2.31076800 0.70813200 -0.00023100

C 1.12261200 -1.40265100 -0.00004600

C 1.12262700 1.40263900 -0.00004400

C -0.12840200 -0.72410000 0.00034400

C -0.12838600 0.72408600 0.00034700

H 1.12217700 -2.48993500 0.00001600

H 1.12218600 2.48992400 0.00001900

C -1.36486200 -1.46713500 0.00059200

C -1.36483000 1.46714900 0.00059000

C -2.44183500 -0.63012600 -0.00064600

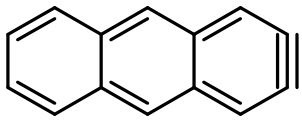
C -2.44180900 0.63015100 -0.00064800

H -1.36656500 -2.55307700 0.00012300

H -1.36651300 2.55309100 0.00011800

H 3.25438900 -1.24692700 -0.00022500

H 3.25447200 1.24680400 -0.00022600



16

E = -538.17758970 a.u.

C 0.00000000 0.71366700 3.54569400

C 0.00000000 1.40794800 2.36504700

C 0.00000000 0.72199000 1.10919200

C 0.00000000 -0.72199000 1.10919200

C 0.00000000 -1.40794800 2.36504700

C 0.00000000 -0.71366700 3.54569400

H 0.00000000 1.24681300 4.49250600

H 0.00000000 2.49541300 2.36202900

H 0.00000000 -2.49541300 2.36202900

H 0.00000000 -1.24681300 4.49250600

C 0.00000000 1.40325500 -0.11381600

C 0.00000000 -1.40325500 -0.11381600

C 0.00000000 0.72999600 -1.34396800

C 0.00000000 -0.72999600 -1.34396800

H 0.00000000 2.49131000 -0.11110400

H 0.00000000 -2.49131000 -0.11110400

C 0.00000000 1.47248200 -2.59385600

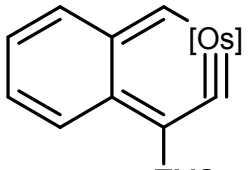
C 0.00000000 -1.47248200 -2.59385600

C 0.00000000 0.63226300 -3.65936000

C 0.00000000 -0.63226300 -3.65936000

H 0.00000000 2.55830000 -2.59702600

H 0.00000000 -2.55830000 -2.59702600



3

[Os] = $OsCl_2(PPh_3)_2$

E = -1993.60829944 a.u.

Os -0.02113300 -0.50802900 -0.02567800

Cl -0.02759200 -2.51124100 -1.57244300

Cl -0.15549600 -2.00348500 2.01033800

P -2.50144600 -0.63086100 0.00541800

P 2.45159900 -0.75419900 0.03261900

Si 0.16684900 3.72039900 1.90292100

C 0.04642000 1.18284600 0.60104900

C 0.11906500 2.51819100 0.44065100

C 0.14176000 2.88159900 -0.97614400

C 0.09941000 1.86896200 -2.00721700

C 0.02762500 0.47119000 -1.72779900

H -0.00577400 -0.14610600 -2.62847800

C 0.19587800 4.23310100 -1.39465800

H 0.22326000 5.01865800 -0.64857900

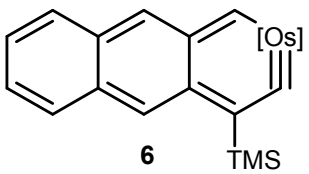
C 0.21141500 4.58310100 -2.73480000

H 0.25175100 5.63508500 -3.00780600

C 0.17401900 3.60051800 -3.74281100

H	0.18780000	3.88566400	-4.79053100
C	0.11929100	2.27307100	-3.37183600
H	0.08752000	1.49454100	-4.12936700
C	-1.35143100	4.84823800	1.87030400
H	-1.42783500	5.44060400	0.95204100
H	-1.32216400	5.54981900	2.71384400
H	-2.27040000	4.25762000	1.96116100
C	1.74811900	4.75978500	1.84748800
H	2.63296000	4.11611500	1.91739000
H	1.77560900	5.45066500	2.69982200
H	1.84528800	5.35877700	0.93585500
C	0.16456200	2.75485000	3.51674500
H	-0.70763300	2.09908600	3.59384400
H	0.13755200	3.45006800	4.36531500
H	1.06406600	2.14019600	3.61761000
C	-3.25977500	-0.15600800	-1.61771700
C	-3.81376600	-1.13044200	-2.45999400
H	-3.84626800	-2.16688600	-2.14344600
C	-4.31960200	-0.77578000	-3.71254600
H	-4.74196500	-1.54349800	-4.35516000
C	-4.28515200	0.55300800	-4.13594300
H	-4.68498200	0.82724000	-5.10860400
C	-3.72884000	1.52920400	-3.30599400
H	-3.68822500	2.56571400	-3.62943200
C	-3.21018200	1.17709200	-2.05990300
H	-2.76505500	1.94322500	-1.43316000
C	-3.27681800	0.49980900	1.26239400
C	-4.35267800	1.35325700	0.97995600
H	-4.74561100	1.42540500	-0.02820700
C	-4.93764800	2.11516900	1.99611200
H	-5.76830100	2.77508000	1.75983500
C	-4.46661200	2.01987000	3.30541700
H	-4.92773300	2.60552900	4.09629100
C	-3.40299100	1.16093000	3.59545700
H	-3.03580900	1.07290500	4.61452600
C	-2.80427200	0.41045200	2.58329500
H	-1.97776200	-0.25575800	2.81512800
C	-3.34048600	-2.24294100	0.40576400
C	-4.70009400	-2.21485300	0.76306500
H	-5.22773400	-1.26956600	0.83925300
C	-5.38586000	-3.39867800	1.03014200
H	-6.43618500	-3.36020900	1.30683300
C	-4.72254200	-4.62508700	0.94716500
H	-5.25545400	-5.54852300	1.15920700
C	-3.37406900	-4.65796300	0.59380300
H	-2.84905600	-5.60711500	0.52894100
C	-2.67976900	-3.47558300	0.32401500
H	-1.63561700	-3.51130300	0.04426800
C	3.18627800	0.10737100	-1.43324200
C	3.53184300	1.46627200	-1.38399700
H	3.44667700	2.01774600	-0.45331300
C	3.98145000	2.12277400	-2.53134200
H	4.24799400	3.17474700	-2.47656400
C	4.08108500	1.43497400	-3.74134200
H	4.43371400	1.94693100	-4.63276100
C	3.71716000	0.08792400	-3.80303000
H	3.78192800	-0.45340500	-4.74313900
C	3.26896200	-0.57373200	-2.65919500

H	2.97493500	-1.61659200	-2.72023300
C	3.32189600	-0.02787500	1.50659900
C	2.66699700	-0.00851400	2.74657700
H	1.64087400	-0.35283100	2.81851000
C	3.34349700	0.41849000	3.89256500
H	2.82616200	0.41722400	4.84824500
C	4.67139700	0.83910100	3.81458500
H	5.19312100	1.17318500	4.70755800
C	5.32959500	0.82216000	2.58306700
H	6.36502600	1.14464400	2.51140100
C	4.66344500	0.38452200	1.43829700
H	5.19387400	0.37238100	0.49188300
C	3.20200700	-2.45406100	-0.03643100
C	2.49441700	-3.57770200	0.40985600
H	1.47004900	-3.47405000	0.74217800
C	3.11366500	-4.82949500	0.43065700
H	2.55262400	-5.69322800	0.77687000
C	4.43434600	-4.97488100	0.00708400
H	4.90949900	-5.95243000	0.02165000
C	5.14490300	-3.85782700	-0.43757900
H	6.17435600	-3.95927400	-0.77112700
C	4.53448800	-2.60452700	-0.45713400
H	5.09890600	-1.74846400	-0.81241300



6

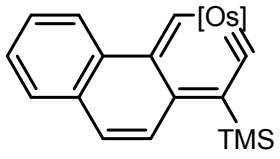
[Os] = $OsCl_2(PPh_3)_2$

E = --2147.24746645 a.u.

Os	-0.00001500	0.77157100	-0.18932600
Cl	-0.00003400	1.90556300	-2.46196900
Cl	0.00000200	2.99688700	0.99496600
P	2.47732000	0.98561100	-0.19084500
P	-2.47730300	0.98555800	-0.19086900
Si	-0.00015500	-2.19537900	3.39474500
C	-0.00001300	-0.48639600	1.11653700
C	-0.00004100	-1.75123200	1.55567800
C	-0.00000900	-2.71023600	0.43613200
C	-0.00001900	-2.23059000	-0.94216100
C	-0.00003000	-0.83590300	-1.29533700
H	-0.00003200	-0.67436800	-2.37601000
C	0.00005400	-4.08758700	0.64038500
H	0.00009600	-4.47944500	1.65172800
C	0.00009200	-5.02203400	-0.41959100
C	0.00006500	-4.54975900	-1.77651200
C	0.00001300	-3.16093200	-1.98941000
H	0.00000200	-2.78679000	-3.01063700
C	0.00016400	-6.42797600	-0.19380500
H	0.00018800	-6.79408300	0.83003600
C	0.00020400	-7.31073800	-1.24922400
H	0.00025900	-8.38081700	-1.05887000
C	0.00017400	-6.84178800	-2.59098000
H	0.00020800	-7.55555600	-3.40979200
C	0.00010600	-5.49137900	-2.84595900
H	0.00008300	-5.11925000	-3.86781100
C	1.55259100	-3.18682500	3.82720500
H	1.63839600	-4.12719300	3.27238700
H	1.55800400	-3.43328000	4.89669800

H	2.45200200	-2.59570000	3.61879200	C	3.77628400	0.29081500	-2.61594300
C	-1.55316700	-3.18648700	3.82699400	H	3.75621700	1.35131800	-2.84067100
H	-2.45234200	-2.59453500	3.61990500	C	3.27079100	2.61893900	-0.59700700
H	-1.55807600	-3.43437400	4.89615700	C	4.65176000	2.75586600	-0.36769500
H	-1.63989300	-4.12604700	3.27094900	H	5.22077100	1.93494600	0.05739900
C	-0.00001000	-0.62498200	4.42850600	C	5.30529200	3.94746500	-0.67518900
H	0.88582100	-0.01375100	4.23295200	H	6.37275100	4.03774500	-0.49195000
H	0.00052600	-0.88436000	5.49494000	C	4.58770000	5.02052100	-1.20988600
H	-0.88626600	-0.01411100	4.23374800	H	5.09567200	5.95210400	-1.44606600
C	3.27233700	0.61534700	1.45017300	C	3.21820100	4.89089800	-1.43557100
C	4.38960600	-0.21893100	1.59941500	H	2.65129900	5.72082400	-1.84852200
H	4.79906300	-0.74570400	0.74453500	C	2.55653200	3.69754200	-1.13239600
C	4.99411200	-0.37588800	2.85025200	H	1.49609100	3.60357600	-1.31748400
H	5.85682500	-1.02946900	2.94966800	C	-3.27237300	0.61534500	1.45012900
C	4.50111000	0.31061600	3.95976000	C	-4.38974400	-0.21880400	1.59933500
H	4.97701600	0.19494100	4.92993800	H	-4.79923300	-0.74553200	0.74444200
C	3.39528300	1.15244900	3.81486400	C	-4.99430200	-0.37570600	2.85015100
H	3.00880500	1.69735900	4.67205300	H	-5.85708700	-1.02919500	2.94953900
C	2.77706600	1.30061000	2.57287600	C	-4.50125300	0.31073400	3.95968000
H	1.91667000	1.95568800	2.46761800	H	-4.97720200	0.19510800	4.92984200
C	3.26985300	-0.17831900	-1.39541100	C	-3.39533100	1.15244800	3.81482000
C	3.28690900	-1.55946900	-1.13694100	H	-3.00882200	1.69731600	4.67202300
H	2.87771000	-1.94471400	-0.20823800	C	-2.77705900	1.30054800	2.57285100
C	3.82732100	-2.44711800	-2.06756200	H	-1.91659000	1.95553500	2.46762500
H	3.84005800	-3.51131900	-1.84860500	C	-3.27082800	2.61883600	-0.59713500
C	4.33818600	-1.97045900	-3.27713500	C	-4.65185300	2.75565500	-0.36810700
H	4.75600300	-2.66280100	-4.00324300	H	-5.22090700	1.93467800	0.05681800
C	4.30372300	-0.60280100	-3.55077600	C	-5.30540800	3.94721600	-0.67569700
H	4.68964500	-0.22397100	-4.49328500	H	-6.37291300	4.03740700	-0.49268500

C	-4.58778600	5.02034600	-1.21020800
H	-5.09578000	5.95189800	-1.44646200
C	-3.21823000	4.89083000	-1.43561200
H	-2.65130200	5.72080900	-1.84842000
C	-2.55654100	3.69751000	-1.13234000
H	-1.49605500	3.60362500	-1.31721000
C	-3.26972900	-0.17843000	-1.39544000
C	-3.28696500	-1.55955600	-1.13686600
H	-2.87796800	-1.94476900	-0.20806100
C	-3.82727000	-2.44722500	-2.06753300
H	-3.84016000	-3.51140800	-1.84849700
C	-4.33784100	-1.97061000	-3.27724700
H	-4.75557600	-2.66296800	-4.00338600
C	-4.30318200	-0.60297600	-3.55099100
H	-4.68886700	-0.22418300	-4.49361200
C	-3.77585200	0.29066000	-2.61611800
H	-3.75563600	1.35114400	-2.84092300



9

[Os] = $OsCl_2(PPh_3)_2$

E = -2147.24831371 a.u.

Os	-0.06800900	-0.66618000	-0.15246600
Cl	-0.15547900	-1.39676700	-2.57653200
Cl	-0.29634500	-3.05856600	0.62820700
P	-2.55246100	-0.68139100	-0.18697800
Si	0.33872300	1.67845800	3.82270700
C	0.08331300	0.35156500	1.31332300
C	0.24609300	1.54520100	1.93290200
C	0.31110200	2.64043600	0.98374000
C	0.19762200	2.43243400	-0.44083000
C	0.04174800	1.13581500	-0.98059500
H	-0.03070300	1.09644900	-2.06335700
C	0.48686700	3.97551900	1.46686400
H	0.57546800	4.13914900	2.53366400
C	0.54832900	5.04757500	0.62550300
H	0.68593100	6.04695900	1.03350900
C	0.42849000	4.90435800	-0.78914700
C	0.24506000	3.59806200	-1.33618900
C	0.48183300	6.04101200	-1.63042600
H	0.62550000	7.01802600	-1.17428800
C	0.35112800	5.91682100	-2.99824600
H	0.39131300	6.79206800	-3.64049300
C	0.15918100	4.63635800	-3.54997700
H	0.04690500	4.52303400	-4.62509900
C	0.10721900	3.51195600	-2.74384100
H	-0.05050700	2.55271700	-3.22122000
C	-3.45527600	-2.21907000	-0.71830200
C	-2.85824200	-3.19260200	-1.53036600
H	-1.82710000	-3.08046000	-1.83737100
C	-3.59760400	-4.30195300	-1.94807700
H	-3.12111300	-5.05069700	-2.57504800
C	-4.92891300	-4.45462100	-1.56167500
H	-5.49709500	-5.32258000	-1.88650700
C	-5.52868600	-3.48737500	-0.75239700
H	-6.56493100	-3.59596500	-0.44313600
C	-4.79767200	-2.37686900	-0.33228700

H	-5.27706200	-1.63752800	0.30089100
C	-3.29625000	-0.39011100	1.49222200
C	-2.85580100	-1.21837200	2.53909200
H	-2.07167400	-1.94759000	2.35384500
C	-3.43313900	-1.11653600	3.80483100
H	-3.09256700	-1.77117700	4.60265300
C	-4.44254100	-0.18083300	4.04890500
H	-4.88709900	-0.10197100	5.03748500
C	-4.88173700	0.64521000	3.01445900
H	-5.67071600	1.37149100	3.19140500
C	-4.31855500	0.53636200	1.73908300
H	-4.68633800	1.17153600	0.94077300
C	-3.27515400	0.62890600	-1.28037600
C	-3.88936300	0.29260700	-2.49491700
H	-3.99082400	-0.74753500	-2.78319900
C	-4.36729200	1.29274700	-3.34478200
H	-4.83689800	1.01549500	-4.28468600
C	-4.24364700	2.63630400	-2.99143400
H	-4.61885400	3.41253000	-3.65302900
C	-3.62890200	2.98075000	-1.78516800
H	-3.51852000	4.02457200	-1.50511600
C	-3.14073700	1.98555200	-0.93878500
H	-2.65153900	2.26794600	-0.01239700
P	2.38587200	-1.01987400	-0.27814600
C	3.04840600	-2.31987500	-1.42938500
C	2.32667900	-3.50133200	-1.65103600
H	1.34307800	-3.62415900	-1.21530800
C	2.87582500	-4.51939400	-2.43229500
H	2.30402300	-5.42846000	-2.59780600
C	4.14050100	-4.37254200	-3.00292200
H	4.56084600	-5.16692600	-3.61432100
C	4.86315100	-3.19824600	-2.78656400
H	5.84834900	-3.07091500	-3.22769000
C	4.32271400	-2.17822200	-2.00297700
H	4.89598700	-1.26931900	-1.85335000
C	3.25081000	-1.45890400	1.30852300
C	2.53463700	-2.02948900	2.36907200
H	1.46463300	-2.17611900	2.27737300
C	3.20298300	-2.45011800	3.52311200
H	2.63557400	-2.90136300	4.33266900
C	4.58482200	-2.29976900	3.63434600
H	5.10032000	-2.62634200	4.53371800
C	5.30580200	-1.73589700	2.57876400
H	6.38395200	-1.62033200	2.65233600
C	4.64588500	-1.32637900	1.42109900
H	5.22291300	-0.90073000	0.60650900
C	3.20987000	0.53803800	-0.84647200
C	3.19733100	0.85293200	-2.21650200
H	2.77203700	0.15236100	-2.92894200
C	3.72182900	2.06447300	-2.66513100
H	3.71042600	2.29271400	-3.72738000
C	4.25326500	2.98239700	-1.75571000
H	4.65886200	3.92689400	-2.10795100
C	4.25085900	2.68459400	-0.39330800
H	4.65164700	3.39688500	0.32289900
C	3.73094800	1.47004700	0.06144700
H	3.73310300	1.25415100	1.12459400
C	-1.10213200	2.71194800	4.48187100

H -1.12682200 3.73037700 4.07941500

H -2.05831900 2.23565700 4.23595500

H -1.04175400 2.79047400 5.57495600

C 1.98750900 2.43709800 4.36339900

H 2.15045200 3.45385200 3.99090500

H 2.03881900 2.47690900 5.45901900

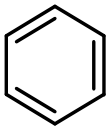
H 2.82532700 1.81951500 4.01841800

C 0.22965100 -0.04031900 4.57801100

H -0.67950800 -0.56180500 4.26515300

H 1.09028800 -0.65670000 4.30239000

H 0.21169600 0.03836800 5.67236500



19

E = -232.24382268 a.u.

C -1.06513600 -0.90376500 0.00000500

C 0.25025600 -1.37418300 0.00006900

C 1.31529400 -0.47052600 -0.00005600

C 1.06506000 0.90385300 0.00000800

C -0.25014000 1.37420100 0.00006200

C -1.31533500 0.47042100 -0.00005800

H -1.89357900 -1.60700300 -0.00006600

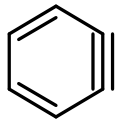
H 0.44474200 -2.44333400 0.00007800

H 2.33850200 -0.83643800 -0.00015500

H 1.89367400 1.60687800 0.00000700

H -0.44487300 2.44330100 0.00001800

H -2.33846000 0.83658800 -0.00006400



20

E = -230.90485409 a.u.

C 0.70375800 1.05887200 -0.00002100

C -0.70373800 1.05888200 -0.00002000

C 1.46181400 -0.13373300 -0.00001000

C -1.46181400 -0.13371100 -0.00001000

C 0.62555000 -1.23787400 0.00000800

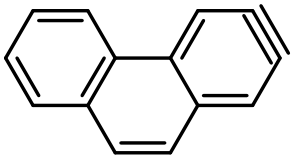
C -0.62557400 -1.23787500 0.00000800

H 2.54701100 -0.13490000 0.00004600

H -2.54701100 -0.13485700 0.00004600

H 1.22982700 2.01119200 0.00009100

H -1.22980600 2.01120300 0.00009300



17

E = -538.18558562 a.u.

C -1.28044500 0.89028400 0.00005600

C -0.47975300 2.08002900 -0.00007200

C -0.64760000 -0.38980300 0.00018800

C 0.87779300 2.01646100 -0.00010600

C 0.81147600 -0.46809900 0.00025500

C 1.57099300 0.75769700 0.00010200

H 1.47203800 2.92673500 -0.00022200

C 1.48971500 -1.73331600 0.00031100

C	3.00483700	0.75887800	0.00002100
C	2.84994100	-1.58013900	-0.00076600
C	3.51223700	-0.51326900	-0.00090900
H	0.95846400	-2.67668300	0.00003400
H	3.56210900	1.69103800	-0.00042100
H	-0.98550900	3.04251100	-0.00014100
C	-2.69255600	0.97369500	0.00007700
C	-3.47592200	-0.16338300	0.00018800
H	-4.55939900	-0.08407200	0.00019000
C	-2.85899200	-1.42823700	0.00030500
H	-3.46721200	-2.32851000	0.00040200
C	-1.47957400	-1.53474100	0.00031000
H	-1.03994800	-2.52605300	0.00041800
H	-3.15344600	1.95869000	-0.00002300

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