Electronic Supplemental Information

A Novel Metal-Wingtip Pentalene System: The Synthesis, Structure, and Reactivity of Non-Aromatic Wingtip Osmapentalenes

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1. General information

Unless otherwise stated, all synthesis and manipulation are performed in a high-purity argon atmosphere using Schlenk technology. Tetrahydrofuran (THF) and toluene (PhMe) are refluxed onto sodium/benzophenone-based ketone for distillation and degassing prior to the reaction. Dichloromethane (DCM), chloroform ($CHCl_3$), triethylamine (Et_3N), and dimethylformamide (DMF) are distilled with CaH_2. All other reagents are purchased from commercial suppliers and can be used without further purification. Column chromatography was performed using silica gel (200-300 mesh). Thin layer chromatography was performed on a 25 mm thick thin layer chromatography silica gel plate purchased from Wuhan Geao Hengsheng Technology Development Co., Ltd. At Bruker 400 MHz NMR spectrometer (^{31}P, 162 MHz; ^{1}H, 400 MHz; ^{13}C, 101 MHz) on the recording of NMR spectra. The ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts (δ) are relative to tetramethylsilane, and the $^{31}P\{^{1}H\}$ NMR chemical shifts are relative to 85% H_3PO_4. The absolute value of the coupling constant is measured in hertz (Hz). Multiplicity is abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). EI-MS mass spectrometry data were measured by trace MS2000. High-resolution mass spectroscopy (HRMS) experiments were conducted on Bruker En Apex Ultra 7.0T FTMS. Elemental analyses (C, H) were obtained from an Elementar Vario EL III instrument. Magnetic susceptibilities of complexes **7a−b**, **8**, **9** and **10−12a−b** were carried out with Quantum Design MPMS (SQUID) XL-5 instruments between 2 and 300 K in an applied field of 1000Oe or 2500Oe. Absorption spectra were recorded on a Shimadzu UV-3600. Electrochemical measurements were conducted with a CHI660C potentiostat. The concentrations of the analytes and the supporting electrolyte (*n*-Bu_4NPF_6) in dry argon-saturated dichloromethane were 2×10^{-3} and 10^{-1} mol dm^{-3}, respectively. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was 0.1 Vs^{-1}. Single-crystal X-ray diffraction data were collected on a Diffractometer Bruker *APEX*-II CCD or Diffractometer Bruker D8 with PHOTON III 28detector with Ga *K*α or Synchrotron radiation (λ = 1.34139 Å). Single crystals for X-ray diffraction were obtained by recrystallization from a solution of DCM layered with *n*-hexane or MeOH. The crystal was kept at a steady $T \leqq 200$ K during the data collection. The programs used to parse the crystals: olex2.solve 1.5 (Bourhis

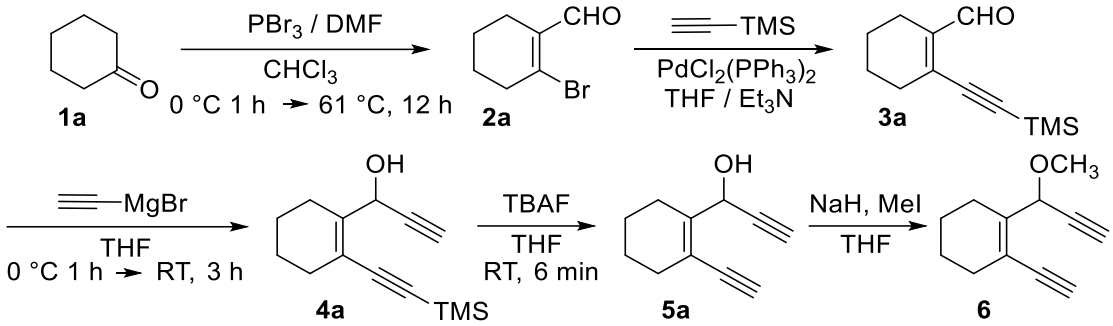
et al., 2015), *SHELXL* 2018/3 (Sheldrick, 2015), [1] Olex2 1.5 (Dolomanov *et al.*, 2009). Non-H atoms were refined anisotropically unless otherwise stated.

All calculations were conducted by using the DFT methods with Gaussian16 package. [2] Complexes **7a**, **8**, **9**, **10a**, **11a**, **12a** and **13** are simplified through the way that the PH_3 groups were used to replace the PPh_3 ligands, which are named simplified model complexes **7a′**, **8′**, **9′**, **10a′**, **11a′**, **12a′** and **13′**. In this system, B3LYP[3,4]-GD3BJ[5] was selected for the mechanistic study, [6] 6-311++G(d,p) was used for C, H and O atoms, Lanl2DZ[7] was used for Cl, Os, P atoms. Polarization functions were added for Os(ζ-(f) = 0.886), Cl(ζ(d) = 0.514) and P(ζ(d) = 0.340). Herein, we selected SMD[8] as the reaction solvent model and THF as solvent. We performed frequency calculations to confirm if the numbers of imaginary frequencies associated with the local minima and transition state are correct. Condensed Fukui Function (CFF) calculations[9] are obtained at the CAM-B3LYP/6-311++G(d,p) ~ Lanl2DZ computational level. We scanned the C-O bond lengths (scanning 7 points at 0.1 Å intervals) in the process of forming **Int3** (Figure S43), and their energies increased and then decreased, indicating the existence of a transition state in this process, but we could not find it.

Structures were optimized using the CAM-B3LYP[10] density functional. π-contribution of electron localization function (ELF_π) [3] analyses were conducted by the Multiwfn program. [11] And for large differences between some upper and lower bifurcation values, the average values were taken. The fuzzy atom bond orders (FBO) [12] are obtained through the Multiwfn program. Since the molecular orbitals (MOs) show that the ligand Cl at the equatorial plane has a lone pair of electrons contributing to the ring, so some orbitals were selected for ELF_π calculations in **7a′**, **8′**, **9′**, **10a′**, **11a′**, **12a′** and **13′**. The relevant selected orbitals are provided in Figures S44-S52.

2. Synthesis and characterization of 7a, 8 and 9

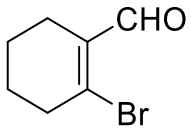
2.1 Preparation and characterization of compounds 5a and 6



Preparation and characterization of compound 2a [13]

Under Ar conditions, to a solution of DMF (3.3 equiv, 33.0 mmol, 2.5 mL) in dry chloroform (30 mL), PBr_3 (3.0 equiv, 30.0 mmol, 2.9 mL) was added dropwise at 0 °C. The mixture was stirred for 60 min, and then a solution of compound **1a** (1.0 equiv, 10.0 mmol) was added. The solution was stirred for 12 h, and the content was poured to 100 mL water, neutralized with solid $NaHCO_3$ and extracted with dichloromethane (3×200 mL). The extract was washed with a saturated NaCl solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel 300 mesh, PE: EtOAc = 100:1) to afford compound **2a** as an oil (91% yield).

2-Bromocyclohex-1-ene-1-carbaldehyde(2a)

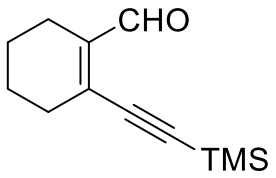


Colorless oil, 1.71 g, Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 2.75 (ddd, *J* = 8.6, 6.2, 2.3 Hz, 2H), 2.28 (ddd, *J* = 8.4, 6.0, 2.3 Hz, 2H), 1.79 – 1.74 (m, 2H), 1.72 – 1.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 143.8, 135.3, 38.8, 25.0, 24.2, 21.1. EI-MS: m/z = 187.98 $[M]^+$; Found: m/z = 187.98 $[M]^+$.

Preparation and characterization of compound 3a [14]

Under Ar conditions, a mixture of compound **2a** (1.0 equiv, 10.0 mmol), CuI (1 mol%), $PdCl_2(PPh_3)_2$ (1 mol%) and Et_3N (10 mL) as solvent were stirred at 55 °C, then ethynylbenzene (1.1 equiv) was added into the reaction system by dropwise, and the reaction system was detected by TLC. After completion of the reaction, subsequent filtration through a pad of Celite® rinsing with Et_2O. The residue was purified by flash chromatography (silica gel 300 mesh, PE: EtOAc = 40:1) to afford compound **3a** (92% yield).

2-((Trimethylsilyl)ethynyl)cyclohex-1-ene-1-carbaldehyde(3a)

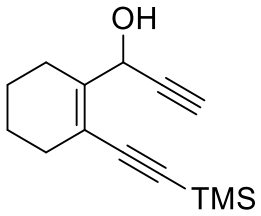


Light yellow oil, 1.90 g, Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 2.41 (t, *J* = 5.1 Hz, 2H), 2.25 (t, *J* = 5.9 Hz, 2H), 1.64 (dd, *J* = 7.3, 3.9 Hz, 4H), 0.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 143.9, 140.1, 104.9, 101.7, 32.4, 22.2, 22.0, 21.2, 0.0. EI-MS: m/z = 206.11 $[M]^+$; Found: m/z = 206.11 $[M]^+$.

Preparation and characterization of compound 4a [15]

Under Ar conditions, a solution of compound **3a** (1.0 equiv, 5.0 mmol) in THF, before addition of ethynylmagnesium bromide (1.5 equiv, 0.5 mol/L in THF, 10 mL) at 0 °C, the reaction mixture was allowed to warm up to room temperature, and the reaction system was detected by TLC. After completion of the reaction, the residue was quenched with saturated NH_4Cl solution, extracted with ethyl acetate and dried over $MgSO_4$. After removal of the solvent, to give compound **4a** as a yellow oil (96% yield).

1-(2-((Trimethylsilyl)ethynyl)cyclohex-1-en-1-yl)prop-2-yn-1-ol(4a)

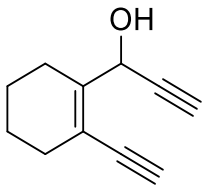


Yellow oil, 1.11 g, Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (dd, *J* = 4.7, 2.0 Hz, 1H), 2.49 (d, *J* = 2.2 Hz, 1H), 2.31 (d, *J* = 5.7 Hz, 2H), 2.25 (d, *J* = 4.9 Hz, 1H), 2.22 – 2.18 (m, 2H), 1.64 (ddd, *J* = 16.7, 10.2, 5.3 Hz, 4H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 118.7, 103.5, 98.7, 82.6, 73.3, 63.8, 30.1, 23.6, 22.0, 21.9, 0.0. EI-MS: m/z = 232.13 $[M]^+$; Found: m/z = 232.13 $[M]^+$.

Preparation and characterization of compound 5a [16]

The compound **4a** (1.0 equiv, 5.0 mmol) was dissolved in TBAF (1.1 equiv, 1.0 mol/L in THF, 5.5 mL) and THF (10 mL) was added in batches. The mixture was stirred at room temperature for 6 min. The reaction mixture was quenched with water (10 mL) and then extracted with ether (3×20 mL). The combined organic phase was washed with brine (3×20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel 300 mesh, PE: EtOAc = 10:1) to give the corresponding compound **5a** as a yellow oil (91% yield).

1-(2-Ethynylcyclohex-1-en-1-yl)prop-2-yn-1-ol(5a)

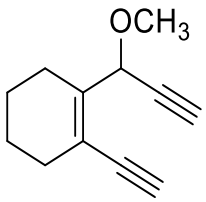


Yellow oil, 0.74 g, Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 3.17 (s, 1H), 2.50 (d, *J* = 2.1 Hz, 1H), 2.33 (t, *J* = 4.5 Hz, 2H), 2.22 (t, *J* = 4.6 Hz, 2H), 2.08 (d, *J* = 4.6 Hz, 1H), 1.65 (dt, *J* = 12.8, 6.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 117.8, 82.6, 82.1, 81.6, 73.5, 63.7, 30.0, 23.3, 22.0, 21.8. EI-MS: m/z = 160.09 $[M]^+$; Found: m/z = 160.09 $[M]^+$.

Preparation and characterization of compound 6 [17]

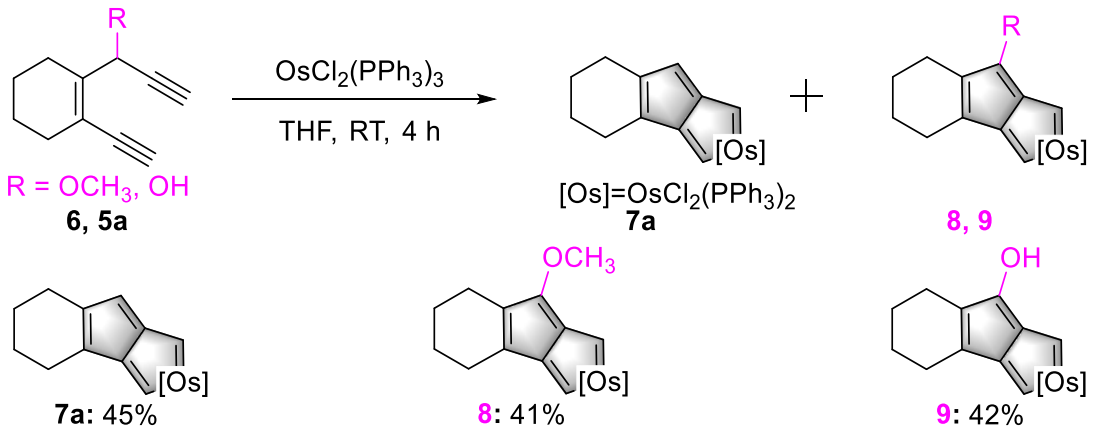
To a round-bottomed flask were added dry THF (15 mL) and NaH (60% dispersion in paraffin oil, 300 mg, 7.5 mmol, 1.5 equiv) under N_2. Compound **5a** (1.0 equiv, 5.0 mmol) was added to the solution and the mixture was stirred for 30 min. MeI (1.42 g, 10 mmol, 2 equiv) was added to the solution for 4 h. The reaction mixture was quenched with NH_4Cl solution and then extracted with DCM (3×20 mL). The combined organic phase was washed with brine (3×20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel 300 mesh, PE: EtOAc = 10:1) to give the corresponding compound **6** as a yellow oil (40% yield).

1-ethynyl-2-(1-methoxyprop-2-yn-1-yl)cyclohex-1-ene(6)



Yellow oil, 0.35 g, Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (d, *J* = 2.2 Hz, 1H), 3.36 (s, 3H), 3.16 (s, 1H), 2.48 (d, *J* = 2.2 Hz, 1H), 2.23 (p, *J* = 3.5 Hz, 4H), 1.65 (d, *J* = 4.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 119.0, 82.3, 81.4, 81.0, 73.9, 72.0, 56.3, 30.1, 23.4, 22.1, 21.8. EI-MS: m/z = 174.10 $[M]^+$; Found: m/z = 174.10 $[M]^+$.

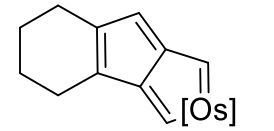
2.2 Preparation and characterization of 7a, 8 and 9



Example for the synthesis of **7a** and **9**: Under Ar conditions, 1-(2-ethynylcyclohexyl-1-en-1-yl)propyl-2-yn-1-ol (**5a**, 1.2 equiv, 1.2 mmol, 190 mg) and $OsCl_2(PPh_3)_3$ (1.0 equiv, 1.0 mmol, 1.05 g) were dissolved in 20 mL of dry THF. Stir for 4 h at room temperature. The reaction mixture was filtered, and the solids were sequentially washed with THF (3×5 mL) and ether (3×5 mL) and dried in a vacuum to obtain a solid mixture. The solid mixture was recrystallized by dichloride and *n*-hexane to obtain reddish-brown crystal **7a** and brown crystal **9**, respectively.

Note: resonance structures of compounds **7a**, **8** and **9**.

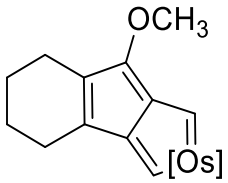
Osmapentalene(7a)



$[Os]=OsCl_2(PPh_3)_2$

Reddish-brown solid, 418 mg, Yield: 45%. Anal. Calcd (%) for $C_{47}H_{41}Cl_2OsP_2$: C 60.77, H 4.45, found: C 60.57, H 4.47. HRMS (ESI): *m/z* calcd for $[C_{47}H_{41}Cl_2OsP_2\text{-}Cl^-]^+$: 894.1981, found: 894.1947.

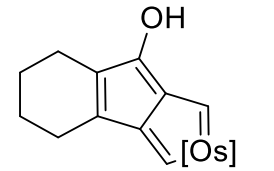
Osmapentalene(8)



$[Os]=OsCl_2(PPh_3)_2$

Reddish-brown solid, 393 mg, Yield: 41%. Anal. Calcd (%) for $C_{48}H_{43}Cl_2OOsP_2$: C 60.12, H 4.52, found: C 60.23, H 4.34. HRMS (ESI): *m/z* calcd for $[C_{48}H_{43}Cl_2OOsP_2\text{-}Cl^-]^+$: 924.2087, found: 924.2087.

Osmapentalene(9)

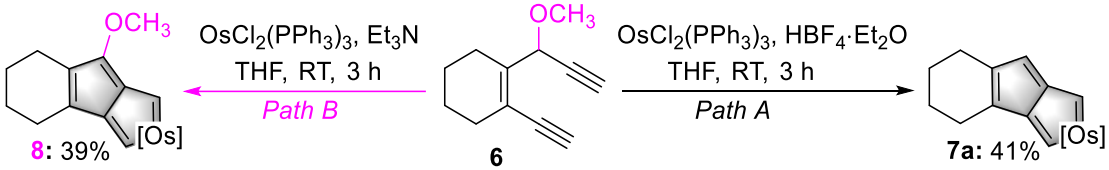


[Os]=$OsCl_2(PPh_3)_2$

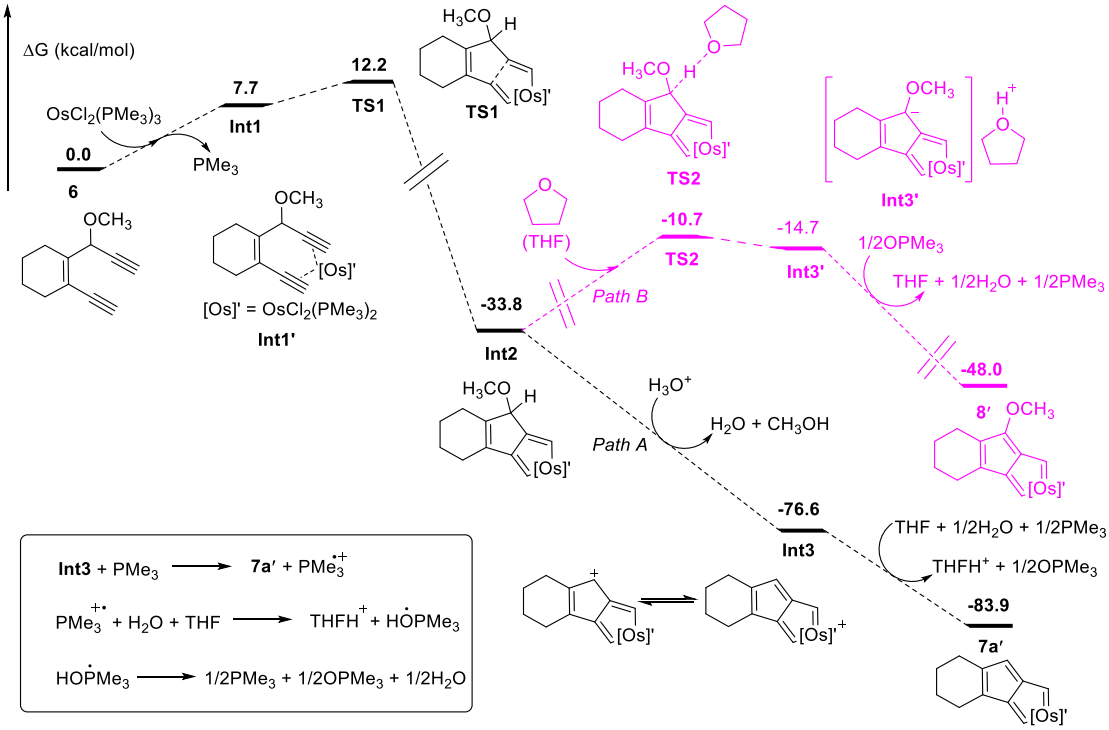
Brown solid, 397 mg, Yield: 42%. Anal. Calcd (%) for $C_{47}H_{41}Cl_2OOsP_2$: C 59.74, H 4.37, found: C 59.70, H 4.43. HRMS (ESI): *m/z* calcd for $[C_{47}H_{41}Cl_2OOsP_2\text{-}Cl^-]^+$: 910.1930, found: 910.1915.

3. The reaction mechanism for forming 7a and 8

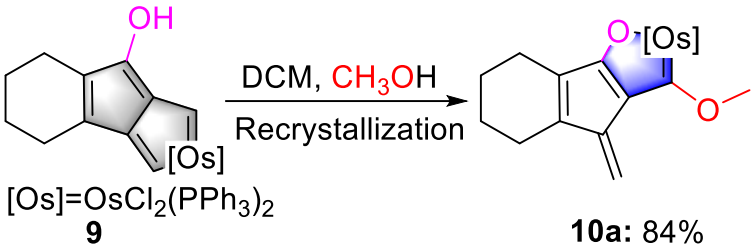
3.1 Control experiments



3.2 DFT calculations for mechanistic investigation of 7a′ and 8′ formed

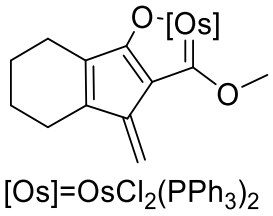


3.3 Synthesis and characterization of 10a



Osmapentalene **9** (1.0 equiv, 0.1 mmol, 95 mg) was recrystallized with DCM and MeOH to obtain a yellow-green crystal **10a** (yield 84%).

Osmafuran(10a)



Yellow-green crystal, 82 mg, Yield: 84%. Anal. Calcd (%) for $C_{48}H_{43}Cl_2O_2OsP_2$: C 59.13, H 4.45, found: C 59.10, H 4.47. HRMS (ESI): *m/z* calcd for $[C_{48}H_{43}Cl_2O_2OsP_2\text{-}Cl^-]^+$: 940.2036, found: 940.1971.

3.4 Proposed mechanism for forming 10a from 9

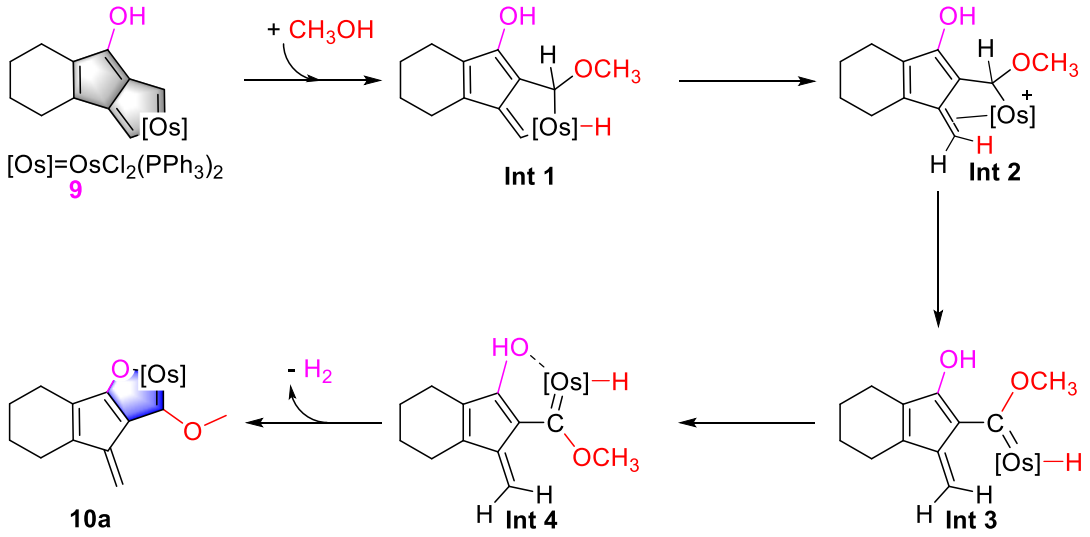


Figure S1. Proposed mechanism for forming **10a** from **9**.

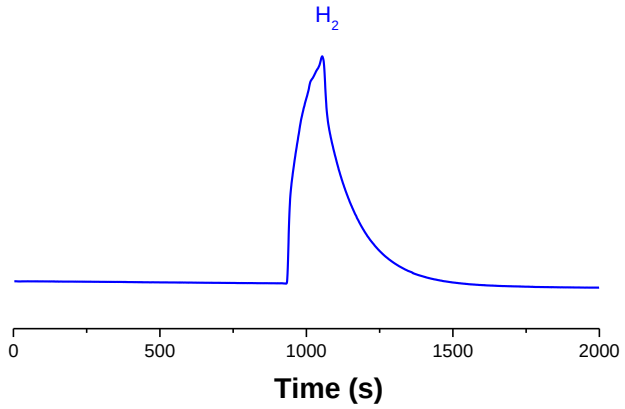
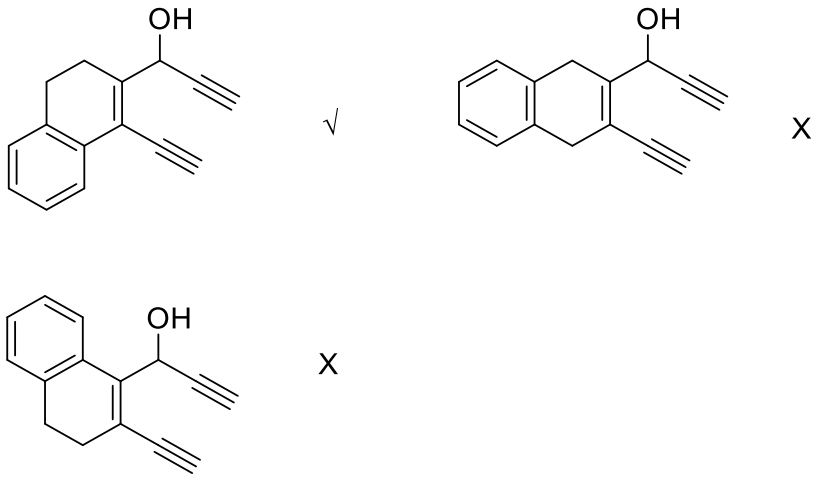


Figure S2. Mass spectrum showing the signal of hydrogen (H_2) at *m/z* = 2.

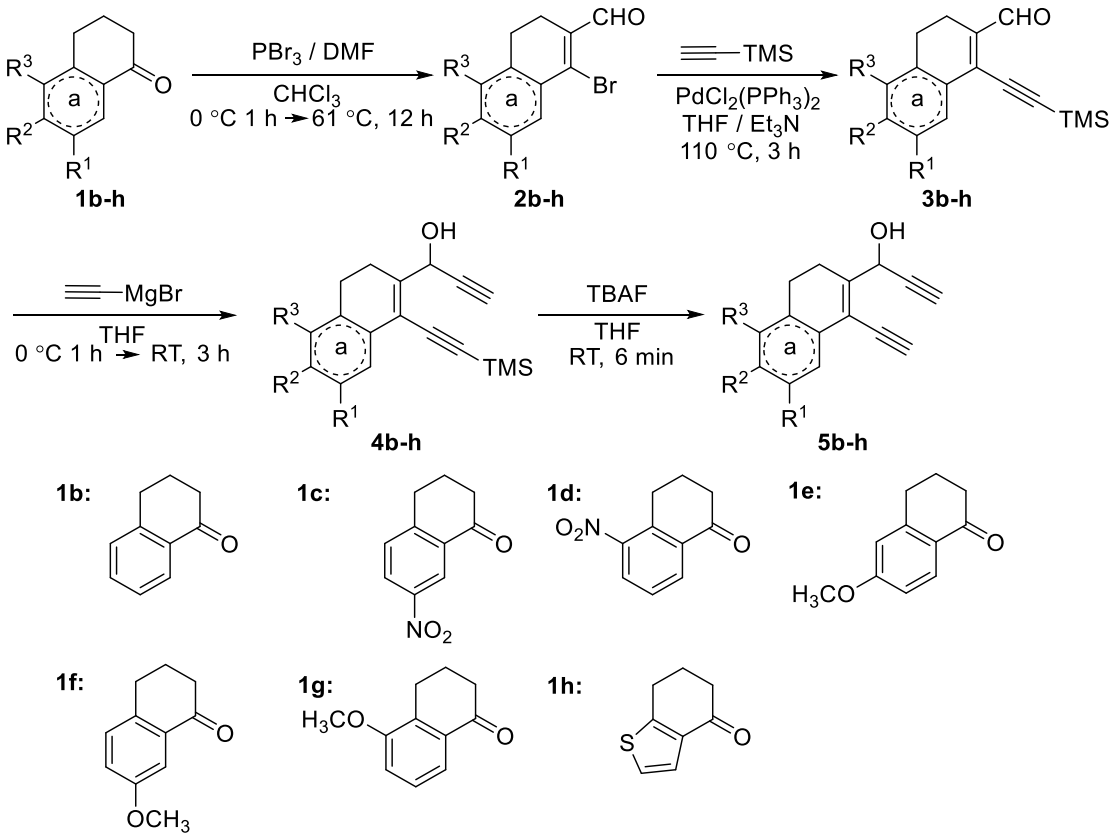
To further investigate the formation of H_2, we performed an in-line mass spectrometry analysis. The gas produced in the reaction system was first collected in a gas bag, which was then connected to the mass spectrometer inlet. By introducing air first, followed by the gas from the bag, and then switching back to air, we observed that the H_2 signal initially increased and then decreased (Figure S2). This result confirms the generation of H_2 in the reaction system and supports our proposed mechanism.

4. Synthesis and characterization of 7 and 10

4.1 Substrate expansion

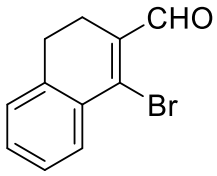


4.2 Preparation and characterization of compounds 5b−h



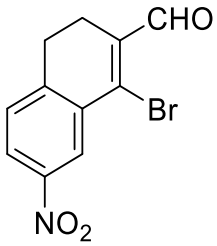
2b−h are prepared according to the basic steps of 2a.

1-Bromo-3,4-dihydronaphthalene-2-carbaldehyde(2b)



Light yellow solid, 2.22 g, Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.19 (d, *J* = 6.8 Hz, 1H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 139.1, 134.5, 133.0, 131.4, 128.8, 127.6, 127.2, 27.2, 22.9. EI-MS: m/z = 235.98 $[M]^+$; Found: m/z = 235.98 $[M]^+$.

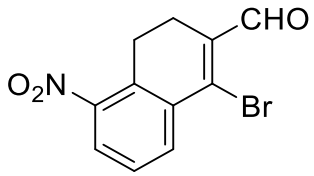
1-bromo-7-nitro-3,4-dihydronaphthalene-2-carbaldehyde(2c)



White solid, 2.58 g, Yield: 92%.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.75 (d,

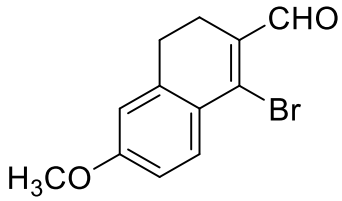
J = 2.3 Hz, 1H), 8.22 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 3.00 – 2.95 (m, 2H), 2.69 (dd, *J* = 9.2, 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 147.4, 145.7, 136.2, 135.7, 134.5, 128.8, 125.7, 123.5, 27.3, 22.4. EI-MS: m/z = 280.97 $[M]^+$; Found: m/z = 280.97 $[M]^+$.

1-bromo-5-nitro-3,4-dihydronaphthalene-2-carbaldehyde(2d)



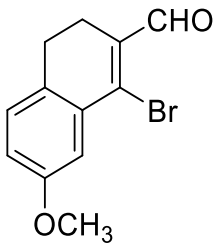
White solid, 2.53 g, Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 3.11 – 3.05 (m, 2H), 2.65 – 2.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 149.0, 136.0, 135.5, 135.3, 133.6, 132.7, 127.4, 126.5, 23.0, 21.9. EI-MS: m/z = 280.97 $[M]^+$; Found: m/z = 280.97 $[M]^+$.

1-Bromo-6-methoxy-3,4-dihydronaphthalene-2-carbaldehyde(2e)



Light yellow solid, 2.50 g, Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 6.72 (s, 1H), 3.85 (s, 3H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.63 – 2.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 162.1, 141.3, 139.3, 132.2, 130.9, 126.0, 113.4, 112.1, 55.5, 27.7, 22.8. EI-MS: m/z = 265.99 $[M]^+$; Found: m/z = 265.99 $[M]^+$.

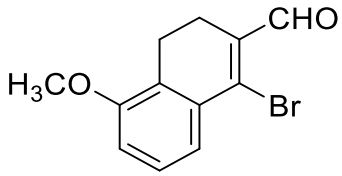
1-Bromo-7-methoxy-3,4-dihydronaphthalene-2-carbaldehyde(2f)



Light yellow solid, 2.53 g, Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.45 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.64 – 2.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 158.6, 139.0,

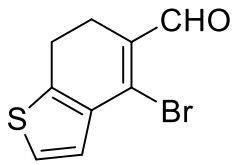
134.9, 134.0, 131.2, 128.5, 116.7, 114.4, 55.6, 26.3, 23.4. EI-MS: m/z = 265.99 $[M]^+$; Found: m/z = 265.99 $[M]^+$.

1-Bromo-5-methoxy-3,4-dihydronaphthalene-2-carbaldehyde(2g)



Light yellow solid, 2.47 g, Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 2.83 (t, *J* = 8.2 Hz, 2H), 2.57 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 155.7, 138.9, 134.6, 133.9, 127.4, 127.1, 121.2, 113.6, 55.8, 22.4, 19.2. EI-MS: m/z = 265.99 $[M]^+$; Found: m/z = 265.99 $[M]^+$.

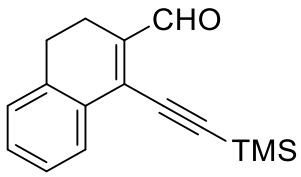
4-bromo-6,7-dihydrobenzo[b]thiophene-5-carbaldehyde(2h)



Light yellow solid, 2.18 g, Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.32 (d, *J* = 5.3 Hz, 1H), 7.13 (d, *J* = 5.3 Hz, 1H), 2.94 (dd, *J* = 9.8, 7.4 Hz, 2H), 2.81 – 2.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 143.7, 135.7, 133.5, 129.7, 127.1, 122.6, 24.1, 22.6. EI-MS: m/z = 241.94 $[M]^+$; Found: m/z = 241.94 $[M]^+$.

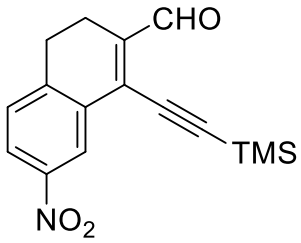
3b−h are prepared according to the basic steps of 3a.

1-((Trimethylsilyl)ethynyl)-3,4-dihydronaphthalene-2-carbaldehyde(3b)



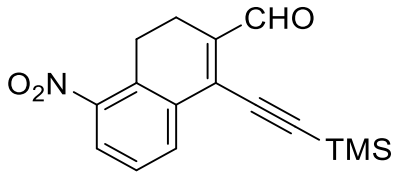
Yellow solid, 2.36 g, Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.83 (d, *J* = 6.3 Hz, 1H), 7.33 (t, *J* = 3.6 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.59 (t, *J* = 8.1 Hz, 2H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 141.5, 137.8, 136.2, 132.2, 131.0, 128.0, 127.5, 127.2, 108.1, 98.1, 26.9, 20.0, 0.0. EI-MS: m/z = 254.11 $[M]^+$; Found: m/z = 254.11 $[M]^+$.

7-nitro-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalene-2-carbaldehyde(3c)



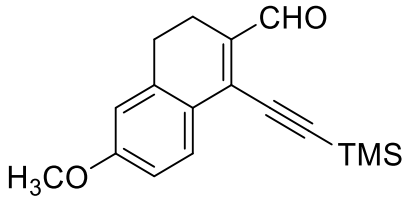
White solid, 2.78 g, Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.69 (d, *J* = 2.4 Hz, 1H), 8.20 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.38 (d, *J* = 9.3 Hz, 1H), 2.94 (t, *J* = 8.1 Hz, 2H), 2.66 (t, *J* = 8.1 Hz, 2H), 0.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 147.6, 144.8, 142.5, 134.0, 133.7, 129.0, 125.4, 122.4, 110.1, 97.0, 27.1, 19.7, 0.0. EI-MS: m/z = 299.10 $[M]^+$; Found: m/z = 299.10 $[M]^+$.

5-nitro-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalene-2-carbaldehyde(3d)



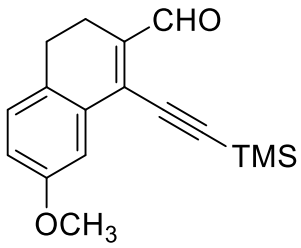
White solid, 2.72 g, Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.11 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 3.11 – 3.02 (m, 2H), 2.64 – 2.54 (m, 2H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 149.4, 142.5, 134.7, 134.0, 132.6, 131.7, 127.6, 126.3, 109.4, 97.3, 22.8, 19.3, 0.0. EI-MS: m/z = 299.10 $[M]^+$; Found: m/z = 299.10 $[M]^+$.

6-Methoxy-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalene-2-carbaldehyde(3e)



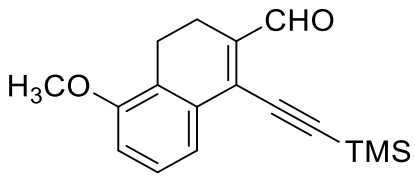
Yellow solid, 2.61 g, Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 10.2 Hz, 1H), 6.73 (s, 1H), 3.85 (s, 3H), 2.78 (t, *J* = 8.1 Hz, 2H), 2.58 (t, *J* = 8.1 Hz, 2H), 0.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 161.9, 140.0, 139.3, 136.1, 129.4, 125.3, 113.8, 112.3, 107.6, 98.3, 55.7, 27.4, 19.9, 0.0. EI-MS: m/z = 284.12 $[M]^+$; Found: m/z = 284.12 $[M]^+$.

7-Methoxy-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalene-2-carbaldehyde(3f)



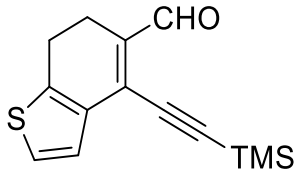
Yellow solid, 2.70 g, Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.41 (s, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 2.74 (t, *J* = 8.1 Hz, 2H), 2.57 (t, *J* = 8.1 Hz, 2H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 158.7, 141.8, 136.1, 133.1, 129.9, 128.8, 116.6, 112.7, 108.1, 98.1, 55.6, 26.0, 20.4, 0.0. EI-MS: m/z = 284.12 $[M]^+$; Found: m/z = 284.12 $[M]^+$.

5-Methoxy-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalene-2-carbaldehyde(3g)



Yellow oil, 2.73 g, Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.81 (t, *J* = 8.4 Hz, 2H), 2.55 (t, *J* = 8.3 Hz, 2H), 0.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 156.2, 141.6, 136.1, 133.2, 127.3, 126.0, 120.0, 113.3, 107.8, 98.4, 55.9, 19.5, 19.0, 0.0. EI-MS: m/z = 284.12 $[M]^+$; Found: m/z = 284.12 $[M]^+$.

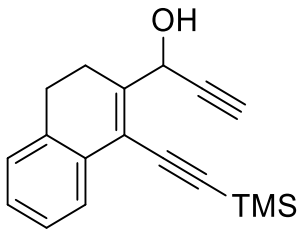
4-((trimethylsilyl)ethynyl)-6,7-dihydrobenzo[b]thiophene-5-carbaldehyde(3h)



Yellow oil, 2.37 g, Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (d, *J* = 2.3 Hz, 1H), 7.12 (dd, *J* = 9.9, 5.2 Hz, 1H), 6.99 (d, *J* = 5.2 Hz, 1H), 2.80 – 2.74 (m, 2H), 2.63 – 2.59 (m, 2H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 191.7, 142.5, 142.4, 138.3, 137.4, 134.5, 134.3, 132.5, 131.5, 126.0, 125.9, 123.4, 123.2, 106.9, 98.6, 87.9, 77.8, 22.5, 22.4, 21.2, 21.1, 0.0. EI-MS: m/z = 260.07 $[M]^+$; Found: m/z = 260.07 $[M]^+$.

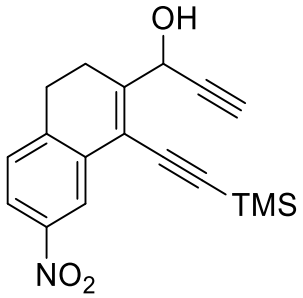
4b−h are prepared according to the basic steps of 4a.

1-(1-((Trimethylsilyl)ethynyl)-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(4b)



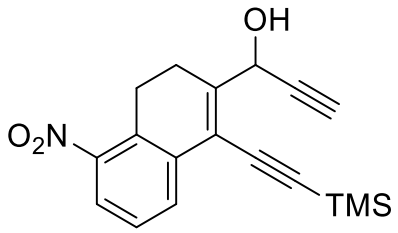
Yellow oil, 1.36 g, Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 5.84 (s, 1H), 2.88 – 2.79 (m, 2H), 2.67 – 2.58 (m, 2H), 2.52 (t, *J* = 2.1 Hz, 1H), 2.27 (s, 1H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 134.9, 132.3, 128.1, 127.2, 126.7, 126.0, 119.1, 102.4, 99.5, 82.1, 73.7, 63.6, 27.5, 22.6, 0.0. EI-MS: m/z = 280.13 $[M]^+$; Found: m/z = 280.13 $[M]^+$.

1-(7-nitro-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(4c)



Yellow solid, 1.56 g, Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.4 Hz, 1H), 8.06 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 5.83 (s, 1H), 2.95 (td, *J* = 9.2, 8.6, 4.7 Hz, 2H), 2.75 – 2.62 (m, 2H), 2.56 (d, *J* = 2.2 Hz, 1H), 2.36 (s, 1H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 146.8, 142.4, 133.9, 128.1, 123.0, 121.0, 117.9, 104.5, 98.3, 81.7, 74.3, 63.5, 27.6, 22.1, 0.0. EI-MS: m/z = 325.11 $[M]^+$; Found: m/z = 325.11 $[M]^+$.

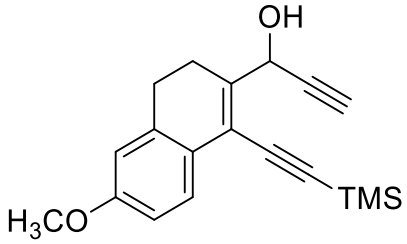
1-(5-nitro-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(4d)



Yellow solid, 1.59 g, Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.76 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 5.81 (d, *J* = 2.2 Hz, 1H), 3.17 – 3.00 (m, 2H), 2.69 – 2.58 (m, 2H), 2.56 (d, *J* = 2.2 Hz, 1H), 2.43 (s, 1H), 0.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.0, 134.8, 130.4, 130.1, 127.1, 123.8, 117.9, 103.7, 98.7, 81.7, 74.3, 63.4, 23.3, 21.7, 0.0. EI-MS: m/z = 325.11 $[M]^+$; Found:

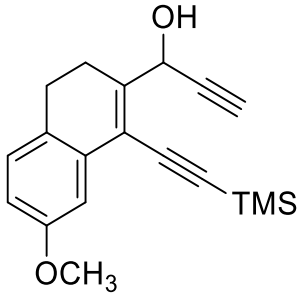
m/z = 325.11 $[M]^+$.

1-(6-Methoxy-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(4e)



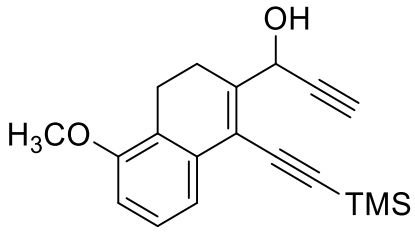
Yellow oil, 1.52 g, Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.67 (s, 1H), 5.81 (s, 1H), 3.81 (s, 3H), 2.80 (td, *J* = 8.0, 4.2 Hz, 2H), 2.58 (q, *J* = 7.8 Hz, 2H), 2.52 (s, 1H), 2.28 (s, 1H), 0.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 142.4, 136.7, 127.3, 125.3, 118.7, 113.2, 111.3, 102.0, 99.7, 82.2, 73.6, 63.6, 55.3, 27.9, 22.5, 0.0. EI-MS: m/z = 310.14 $[M]^+$; Found: m/z = 310.14 $[M]^+$.

1-(7-Methoxy-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(4f)



Yellow oil, 1.53 g, Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.82 (s, 1H), 3.82 (s, 3H), 2.77 (q, *J* = 7.0 Hz, 2H), 2.59 (q, *J* = 8.5, 7.2 Hz, 2H), 2.52 (s, 1H), 2.32 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 145.5, 133.3, 128.0, 127.1, 119.1, 113.5, 111.6, 102.5, 99.5, 82.1, 73.7, 63.7, 55.3, 26.6, 23.0, 0.0. EI-MS: m/z = 310.14 $[M]^+$; Found: m/z = 310.14 $[M]^+$.

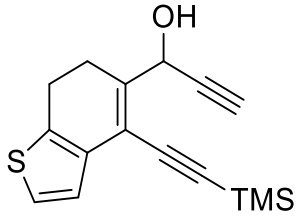
1-(5-Methoxy-1-((trimethylsilyl)ethynyl)-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(4g)



Yellow oil, 1.49 g, Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.3 Hz, 1H),

7.20 (t, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.82 (s, 1H), 3.83 (s, 3H), 2.83 (dq, *J* = 48.9, 8.1 Hz, 2H), 2.59 (dq, *J* = 17.7, 8.8, 8.1 Hz, 2H), 2.52 (s, 1H), 2.30 (s, 1H), 0.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 145.2, 133.2, 126.8, 123.0, 118.9, 118.7, 110.6, 102.1, 99.8, 82.1, 73.7, 63.7, 55.6, 22.1, 19.5, 0.0. EI-MS: m/z = 310.14 $[M]^+$; Found: m/z = 310.14 $[M]^+$.

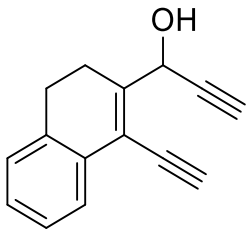
1-(4-((trimethylsilyl)ethynyl)-6,7-dihydrobenzo[b]thiophen-5-yl)prop-2-yn-1-ol(4h)



Orange oil, 1.36 g, Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 5.1 Hz, 1H), 5.75 (d, *J* = 2.2 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.78 – 2.69 (m, 2H), 2.52 (d, *J* = 2.3 Hz, 1H), 2.20 (s, 1H). 0.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 135.2, 133.7, 125.5, 121.8, 115.8, 101.2, 99.9, 82.3, 73.7, 63.2, 23.8, 22.7, 0.0. EI-MS: m/z = 286.08 $[M]^+$; Found: m/z = 286.08 $[M]^+$.

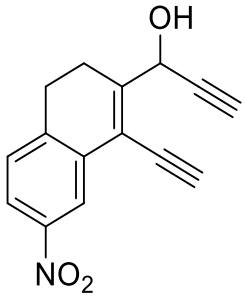
5b−h are prepared according to the basic steps of 5a.

1-(1-Ethynyl-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(5b)



Yellow oil, 0.94 g, Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.21 (q, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 7.1 Hz, 1H), 5.85 (s, 1H), 3.42 (s, 1H), 2.85 (s, 2H), 2.62 (q, *J* = 8.5, 7.8 Hz, 2H), 2.52 (s, 1H), 2.40 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 134.9, 132.1, 128.2, 127.3, 126.7, 125.9, 118.1, 84.7, 82.1, 78.4, 73.8, 63.4, 27.4, 22.5. EI-MS: m/z = 208.09 $[M]^+$; Found: m/z = 208.09 $[M]^+$.

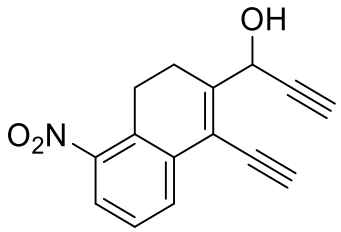
1-(1-ethynyl-7-nitro-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(5c)



Yellow oil, 1.14 g, Yield: 90%. EI-MS: m/z = 253.07 $[M]^+$; Found: m/z = 253.07 $[M]^+$. *R* chiral structure: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.4 Hz, 1H), 8.07 (dd, *J* = 5.9, 2.3 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 5.86 (dd, *J* = 4.4, 2.3 Hz, 1H), 3.56 (s, 1H), 3.04 – 2.94 (m, 2H), 2.74 – 2.67 (m, 2H), 2.56 (d, *J* = 2.3 Hz, 1H), 2.29 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.2, 142.3, 133.7, 128.1, 123.1, 120.7, 116.8, 86.1, 81.6, 77.2, 74.3, 63.2, 27.5, 21.9.

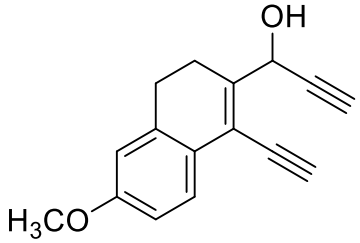
S chiral structure: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 2.3 Hz, 1H), 8.31 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.04 – 7.95 (m, 1H), 6.21 (d, *J* = 2.6 Hz, 1H), 3.97 (s, 1H), 2.91 (d, *J* = 6.8 Hz, 2H), 2.77 (d, *J* = 7.4 Hz, 2H), 2.71 (s, 1H), 2.64 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.2, 129.9, 129.5, 127.7, 123.3, 120.5, 116.8, 90.3, 81.6, 77.2, 75.5, 62.7, 27.5, 21.9.

1-(1-ethynyl-5-nitro-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(5d)



Yellow oil, 1.15 g, Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 5.83 (d, *J* = 2.3 Hz, 1H), 3.50 (s, 1H), 3.15 – 2.99 (m, 2H), 2.63 (dd, *J* = 15.7, 7.1 Hz, 2H), 2.56 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 147.8, 134.6, 130.3, 130.0, 127.0, 123.8, 116.7, 85.6, 81.6, 77.7, 74.3, 63.1, 23.2, 21.6. EI-MS: m/z = 253.07 $[M]^+$; Found: m/z = 253.07 $[M]^+$.

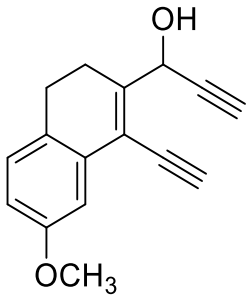
1-(1-Ethynyl-6-methoxy-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(5e)



Yellow oil, 1.11 g, Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 1H),

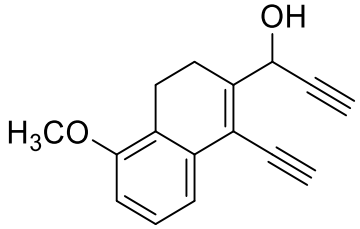
6.76 (d, *J* = 8.4 Hz, 1H), 6.69 (s, 1H), 5.83 (s, 1H), 3.81 (s, 3H), 3.40 (s, 1H), 2.87 – 2.78 (m, 2H), 2.60 (q, *J* = 7.9, 7.3 Hz, 2H), 2.52 (s, 1H), 2.25 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 143.1, 136.7, 127.3, 125.2, 117.7, 113.3, 111.4, 84.3, 82.2, 78.6, 73.7, 63.5, 55.3, 27.9, 22.4. EI-MS: m/z = 238.10 $[M]^+$; Found: m/z = 238.10 $[M]^+$.

1-(1-Ethynyl-7-methoxy-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(5f)



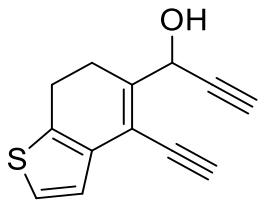
Yellow oil, 1.09 g, Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.85 (s, 1H), 3.82 (s, 3H), 3.43 (s, 1H), 2.79 (q, *J* = 6.9, 6.4 Hz, 2H), 2.61 (q, *J* = 8.5, 7.7 Hz, 2H), 2.53 (s, 1H), 2.21 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 146.3, 133.1, 128.0, 127.1, 118.1, 113.3, 111.9, 84.7, 82.0, 78.3, 73.9, 63.5, 55.4, 26.6, 22.9. EI-MS: m/z = 238.10 $[M]^+$; Found: m/z = 238.10 $[M]^+$.

1-(1-Ethynyl-5-methoxy-3,4-dihydronaphthalen-2-yl)prop-2-yn-1-ol(5g)



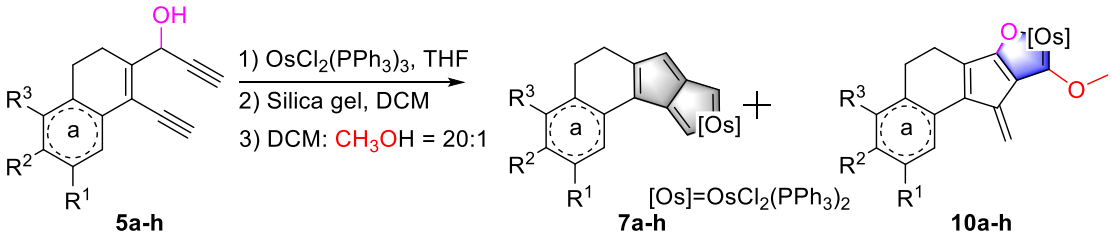
Yellow oil, 1.09 g, Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 5.84 (s, 1H), 3.84 (s, 3H), 3.41 (s, 1H), 2.85 (dq, *J* = 47.1, 8.2 Hz, 2H), 2.67 – 2.55 (m, 2H), 2.52 (s, 1H), 2.30 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.0, 133.1, 126.8, 123.0, 118.7, 117.9, 110.7, 84.4, 82.1, 78.7, 73.8, 63.5, 55.6, 21.9, 19.5. EI-MS: m/z = 238.10 $[M]^+$; Found: m/z = 238.10 $[M]^+$.

1-(4-ethynyl-6,7-dihydrobenzo[b]thiophen-5-yl)prop-2-yn-1-ol(5h)



Orange oil, 1.00 g, Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 5.1 Hz, 1H), 5.76 (dd, *J* = 4.3, 2.2 Hz, 1H), 3.34 (s, 1H), 2.99 – 2.87 (m, 2H), 2.79 – 2.70 (m, 2H), 2.52 (d, *J* = 2.2 Hz, 1H), 2.47 – 2.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 135.3, 133.6, 125.3, 122.0, 114.7, 83.3, 82.2, 78.8, 73.8, 63.0, 23.7, 22.6. EI-MS: m/z = 214.05 $[M]^+$; Found: m/z = 214.05 $[M]^+$.

4.2 Preparation and characterization of 7 and 10



5a-h **7a-h** **10a-h**

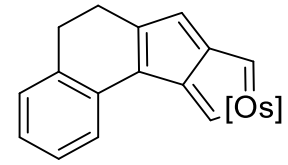
7a: 45%
7b: a = Ph, $R^1 = R^2 = R^3$ = H, 40%
7c: a = Ph, $R^1 = NO_2$, $R^2 = R^3$ = H, 46%
7d: a = Ph, $R^1 = R^2$ = H, $R^3 = NO_2$, 42%
7e: a = Ph, $R^1 = R^3$ = H, $R^2 = OCH_3$, 45%
7f: a = Ph, $R^1 = OCH_3$, $R^2 = R^3$ = H, 40%
7g: a = Ph, $R^1 = R^2$ = H, $R^3 = OCH_3$, 41%
7h: a = Thiophene, 42%

10a: 32%
10b: a = Ph, $R^1 = R^2 = R^3$ = H, 31%
10c: a = Ph, $R^1 = NO_2$, $R^2 = R^3$ = H, 33%
10d: a = Ph, $R^1 = R^2$ = H, $R^3 = NO_2$, 36%
10e: a = Ph, $R^1 = R^3$ = H, $R^2 = OCH_3$, 37%
10f: a = Ph, $R^1 = OCH_3$, $R^2 = R^3$ = H, 31%
10g: a = Ph, $R^1 = R^2$ = H, $R^3 = OCH_3$, 34%
10h: a = Thiophene, 35%

Example for the synthesis of **7a** and **10a**: Under Ar conditions, 1-(2-ethynylcyclohexyl-1-en-1-yl)propyl-2-yn-1-ol (**5a**, 1.2 equiv, 1.2 mmol, 190 mg) and $OsCl_2(PPh_3)_3$ (1.0 equiv, 1.0 mmol, 1.05 g) were dissolved in 20 mL of dry THF. Stir for 4 h at room temperature. The reaction mixture was filtered, and the solids were sequentially washed with THF (3×5 mL) and ether (3×5 mL) and dried in a vacuum to obtain a solid mixture. The solid mixture was purified by flash chromatography (silica gel 300 mesh, DCM→ DCM:MeOH = 20:1) to give **7a** as a reddish-brown solid (45% yield) and **10a** as a yellow-green solid (32% yield).

Note: all metal complexes are paramagnetic.

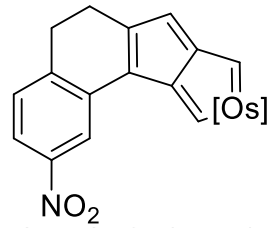
Osmapentalene(7b)



[Os]=$OsCl_2(PPh_3)_2$

Purple-pink solid, 391 mg, Yield: 40%. Anal. Calcd (%) for $C_{51}H_{41}Cl_2OsP_2$: C 62.70, H 4.23, found: C 62.59, H 4.36. HRMS (ESI): *m/z* calcd for $[C_{51}H_{41}Cl_2OsP_2\text{-}Cl^-]^+$: 942.1981, found: 942.1981.

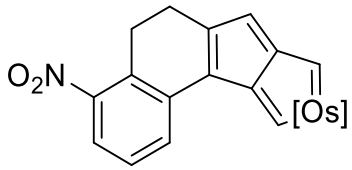
Osmapentalene(7c)



[Os]=$OsCl_2(PPh_3)_2$

Purple-pink solid, 470 mg, Yield: 46%. Anal. Calcd (%) for $C_{51}H_{40}Cl_2NO_2OsP_2$: C 59.94, H 3.95, found: C 59.97, H 3.92. HRMS (ESI): *m/z* calcd for $[C_{51}H_{40}Cl_2NO_2OsP_2\text{-}Cl^-]^+$: 987.1832, found: 987.1827.

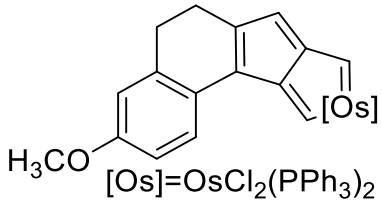
Osmapentalene(7d)



[Os]=$OsCl_2(PPh_3)_2$

Purple-pink solid, 429 mg, Yield: 42%. Anal. Calcd (%) for $C_{51}H_{40}Cl_2NO_2OsP_2$: C 59.94, H 3.95, found: C 59.89, H 4.08. HRMS (ESI): *m/z* calcd for $[C_{51}H_{40}Cl_2NO_2OsP_2\text{-}Cl^-]^+$: 987.1832, found: 987.1826.

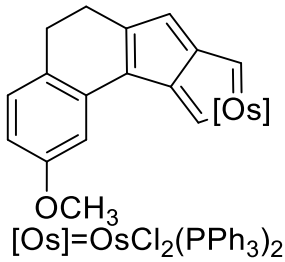
Osmapentalene(7e)



[Os]=$OsCl_2(PPh_3)_2$

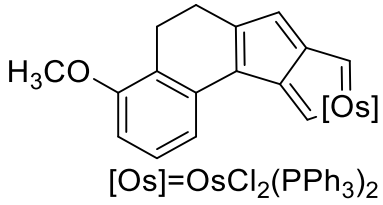
Purple-pink solid, 453 mg, Yield: 45%. Anal. Calcd (%) for $C_{52}H_{43}Cl_2OOsP_2$: C 62.02, H 4.30, found: C 62.00, H 4.34. HRMS (ESI): *m/z* calcd for $[C_{52}H_{43}Cl_2OOsP_2\text{-}Cl^-]^+$: 972.2087, found: 972.2087.

Osmapentalene(7f)



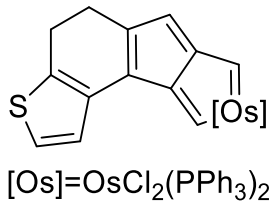
Purple-pink solid, 402 mg, Yield: 40%. Anal. Calcd (%) for $C_{52}H_{43}Cl_2OOsP_2$: C 62.02, H 4.30, found: C 61.98, H 4.38. HRMS (ESI): *m/z* calcd for $[C_{52}H_{43}Cl_2OOsP_2\text{-}Cl^-]^+$: 972.2087, found: 972.2043.

Osmapentalene(7g)



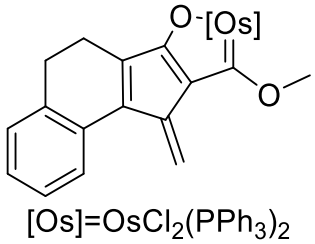
Purple-pink solid, 413 mg, Yield: 41%. Anal. Calcd (%) for $C_{52}H_{43}Cl_2OOsP_2$: C 62.02, H 4.30, found: C 62.01, H 4.31. HRMS (ESI): *m/z* calcd for $[C_{52}H_{43}Cl_2OOsP_2\text{-}Cl^-]^+$: 972.2087, found: 972.2065.

Osmapentalene(7h)



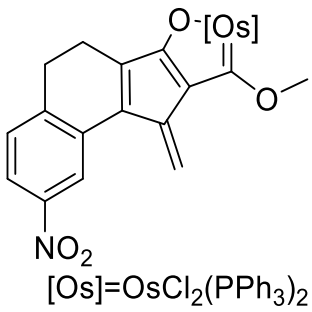
Purple-pink solid, 413 mg, Yield: 42%. Anal. Calcd (%) for $C_{49}H_{39}Cl_2OsP_2S$: C 59.87, H 4.00, found: C 59.82, H 4.07. HRMS (ESI) did not find a suitable ion peak.

Osmafuran(10b)



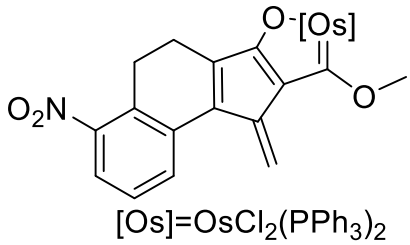
Brownish-yellow solid, 317 mg, Yield: 31%. Anal. Calcd (%) for $C_{52}H_{43}Cl_2O_2OsP_2$: C 61.05, H 4.24, found: C 61.00, H 4.30. HRMS (ESI): *m/z* calcd for $[C_{52}H_{43}Cl_2O_2OsP_2\text{-}Cl^-]^+$: 988.2036, found: 988.2031.

Osmafuran(10c)



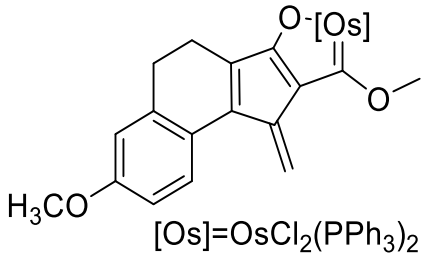
Brownish-yellow solid, 352 mg, Yield: 33%. Anal. Calcd (%) for $C_{52}H_{42}Cl_2NO_4OsP_2$: C 58.48, H 3.96, found: C 58.45, H 3.99. HRMS (ESI): *m/z* calcd for $[C_{52}H_{42}Cl_2NO_4OsP_2\text{-}Cl^-]^+$: 1033.1887, found: 1033.1899.

Osmafuran(10d)



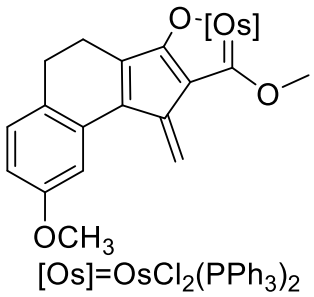
Brownish-yellow solid, 384 mg, Yield: 36%. Anal. Calcd (%) for $C_{52}H_{42}Cl_2NO_4OsP_2$: C 58.48, H 3.96, found: C 58.44, H 4.00. HRMS (ESI): *m/z* calcd for $[C_{52}H_{42}Cl_2NO_4OsP_2\text{-}Cl^-]^+$: 1033.1887, found: 1033.1864.

Osmafuran(10e)



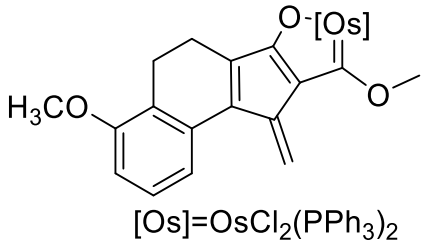
Brownish-yellow solid, 384 mg, Yield: 37%. Anal. Calcd (%) for $C_{53}H_{45}Cl_2O_3OsP_2$: C 60.11, H 4.17, found: C 60.01, H 4.22. HRMS (ESI): *m/z* calcd for $[C_{53}H_{45}Cl_2O_3OsP_2\text{-}Cl^-]^+$: 1018.2142, found: 1018.2154.

Osmafuran(10f)



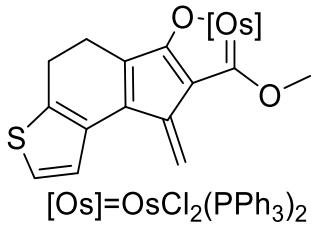
Brownish-yellow solid, 322 mg, Yield: 31%. Anal. Calcd (%) for $C_{53}H_{45}Cl_2O_3OsP_2$: C 60.11, H 4.17, found: C 60.03, H 4.19. HRMS (ESI): *m/z* calcd for $[C_{53}H_{45}Cl_2O_3OsP_2\text{-}Cl^-]^+$: 1018.2142, found: 1018.2145.

Osmafuran(10g)



Brownish-yellow solid, 353 mg, Yield: 34%. Anal. Calcd (%) for $C_{53}H_{45}Cl_2O_3OsP_2$: C 60.11, H 4.17, found: C 60.07, H 4.20. HRMS (ESI): *m/z* calcd for $[C_{53}H_{45}Cl_2O_3OsP_2\text{-}Cl^-]^+$: 1018.2142, found: 1018.2131.

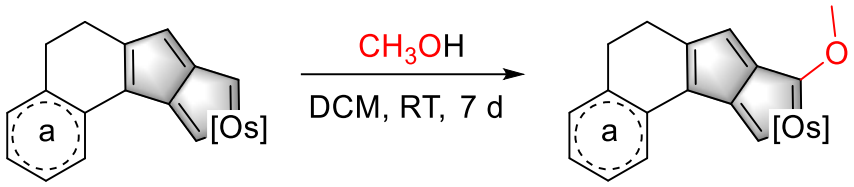
Osmafuran(10h)



Brownish-yellow solid, 360 mg, Yield: 35%. Anal. Calcd (%) for $C_{50}H_{41}Cl_2O_2OsP_2S$: C 58.36, H 4.02, found: C 58.34, H 4.08. HRMS (ESI): *m/z* calcd for $[C_{50}H_{41}Cl_2O_2OsP_2S\text{-}Cl^-]^+$: 994.1600, found: 994.1592.

5. Reactivity of 7a−b

5.1 Nucleophilic reaction of 7a−b



[Os]=$OsCl_2(PPh_3)_2$

7a

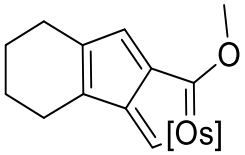
7b: a = Ph

11a: 89%

11b: a = Ph, 95%

Example for the synthesis of **11a**: Under Ar conditions, 5 mL of MeOH was added to the DCM solution of osmapentalene (**7a**, 1.0 equiv, 0.1 mmol, 93 mg). Stir at room temperature for 7 days. The reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel 300 mesh, PE: DCM = 2:3) to obtain **11a** as a yellow-green solid (89% yield).

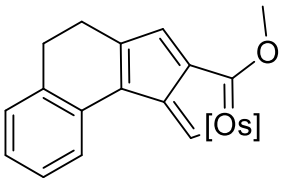
Osmapentalene(11a)



[Os]=$OsCl_2(PPh_3)_2$

Yellow-green solid, 85 mg, Yield: 89%. Anal. Calcd (%) for $C_{48}H_{43}Cl_2OOsP_2$: C 60.12, H 4.52, found: C 60.10, H 4.54. HRMS (ESI): *m/z* calcd for $[C_{48}H_{43}Cl_2OOsP_2\text{-}Cl^-]^+$: 924.2087, found: 924.2087.

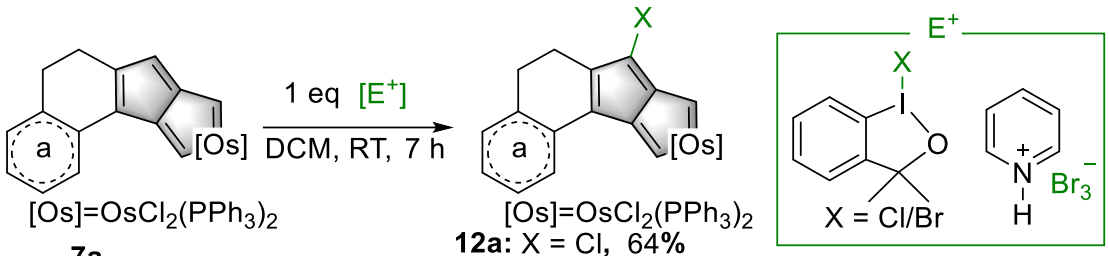
Osmapentalene(11b)



[Os]=$OsCl_2(PPh_3)_2$

Brownish-yellow solid, 96 mg, Yield: 95%. Anal. Calcd (%) for $C_{52}H_{43}Cl_2OOsP_2$: C 62.02, H 4.30, found: C 62.01, H 4.32. HRMS (ESI): *m/z* calcd for $[C_{52}H_{43}Cl_2OOsP_2\text{-}Cl^-]^+$: 972.2087, found: 972.2064.

5.2 Electrophilic reaction of 7a−b



[Os]=$OsCl_2(PPh_3)_2$

7a

7b: a = Ph

[Os]=$OsCl_2(PPh_3)_2$

12a: X = Cl, 64%

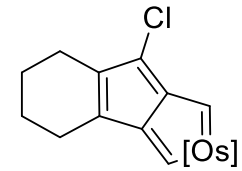
12b: a = Ph, X = Cl, 59%

12c: X = Br, 62%

12d: a = Ph, X = Br, 54%

Example for the synthesis of **12a**: Under Ar conditions, osmapentalene (**7a**, 1.0 equiv, 0.1 mmol, 93 mg) and 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (1.0 equiv, 0.1 mmol, 30 mg) were dissolved in 10 mL dry DCM. Stir for 7 h at room temperature. The reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel 300 mesh, PE: DCM = 2:3) to give **12a** as a brownish-yellow solid (64% yield).

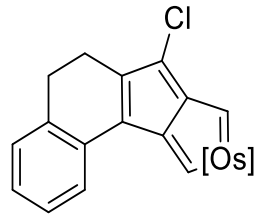
Osmapentalene(12a)



[Os]=$OsCl_2(PPh_3)_2$

Brownish-yellow solid, 62 mg, Yield: 64%. Anal. Calcd (%) for $C_{47}H_{40}Cl_3OsP_2$: C 58.60, H 4.19, found: C 58.58, H 4.23. HRMS (ESI): *m/z* calcd for $[C_{47}H_{40}Cl_3OsP_2\text{-}Cl^-]^+$: 928.1592, found: 928.1570.

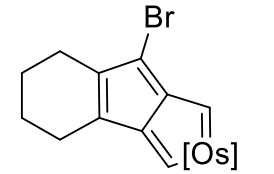
Osmapentalene(12b)



[Os]=$OsCl_2(PPh_3)_2$

Purple-pink solid, 60 mg, Yield: 59%. Anal. Calcd (%) for $C_{51}H_{40}Cl_3OsP_2$: C 60.57, H 3.99, found: C 60.56, H 4.01. HRMS (ESI): *m/z* calcd for $[C_{51}H_{40}Cl_3OsP_2\text{-}Cl^-]^+$: 976.1592, found: 976.1576.

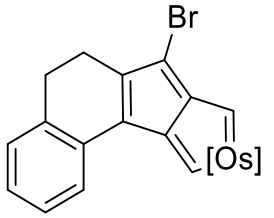
Osmapentalene(12c)



$[Os]=OsCl_2(PPh_3)_2$

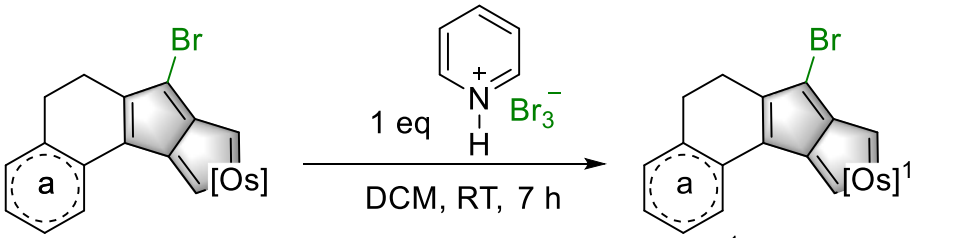
Brownish-yellow solid, 62 mg, Yield: 62%. Anal. Calcd (%) for $C_{47}H_{40}BrCl_2OsP_2$: C 56.01, H 4.00, found: C 55.90, H 4.06. HRMS (ESI) did not find a suitable ion peak.

Osmapentalene(12d)



$[Os]=OsCl_2(PPh_3)_2$

Purple-pink solid, 57 mg, Yield: 54%. Anal. Calcd (%) for $C_{51}H_{40}BrCl_2OsP_2$: C 58.02, H 3.82, found: C 58.04, H 3.79. HRMS (ESI): *m/z* calcd for $[C_{51}H_{40}BrCl_2OsP_2\text{-}Cl^-]^+$: 1020.1086, found: 1020.1065.



$[Os]=OsCl_2(PPh_3)_2$

12c

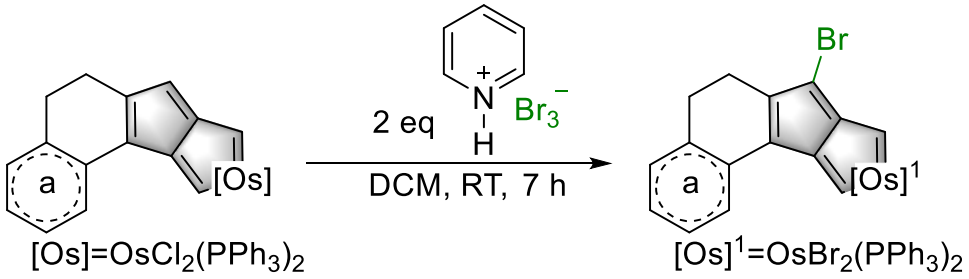
12d: a = Ph

$[Os]^1=OsBr_2(PPh_3)_2$

12e: 69%

12f: a = Ph, 75%

Method 1 of the synthesis of 12e−f: Under Ar conditions, osmapentalene (**12c−d**, 1.0 equiv, 0.1 mmol) and monopyridin-1-ium tribromide (1.0 equiv, 0.1 mmol, 32 mg) were dissolved in 10 mL dry DCM. Stir for 7 h at room temperature. The reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel 300 mesh, PE: DCM = 2:3) to give **12e−f** as yellow-green solids (69-75% yield).

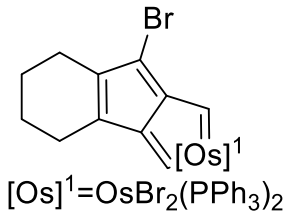


7a
7b: a = Ph

12e: 32%
12f: a = Ph, 34%

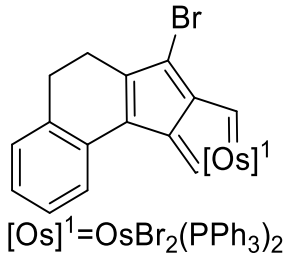
Method 2 of the synthesis of 12e−f: Under Ar conditions, osmapentalene (**7a−b**, 1.0 equiv, 0.1 mmol) and electrophiles (2.0 equiv, 0.2 mmol, 64 mg) were dissolved in 10 mL dry DCM. Stir for 7 h at room temperature. The reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel 300 mesh, PE: DCM = 2:3) to give **12e−f** as yellow-green solids (32-34% yield).

Osmapentalene(12e)



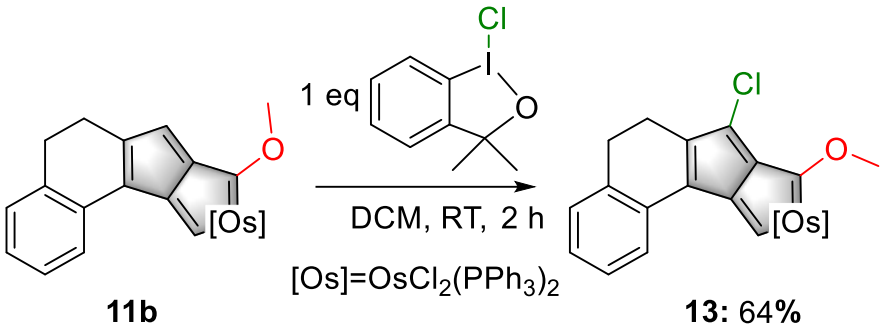
Purple-pink solid, 35 mg, Yield: 32%. Anal. Calcd (%) for $C_{47}H_{40}Br_3OsP_2$: C 51.47, H 3.68, found: C 51.45, H 3.70. HRMS (ESI): *m/z* calcd for $[C_{47}H_{40}Br_3OsP_2\text{-}Br^-]^+$: 1018.0561, found: 1018.0562.

Osmapentalene(12f)



Purple-pink solid, 39 mg, Yield: 34%. Anal. Calcd (%) for $C_{51}H_{40}Br_3OsP_2$: C 53.51, H 3.52, found: C 53.50, H 3.55. HRMS (ESI): *m/z* calcd for $[C_{51}H_{40}Br_3OsP_2\text{-}Br^-]^+$: 1066.0561, found: 1066.0538.

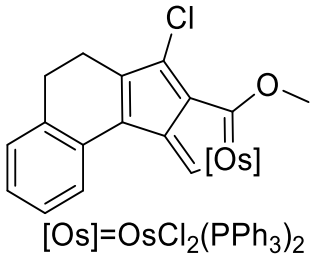
5.3 Electrophilic reaction of 11b



11b **13:** 64%

Synthesis of 13: Under Ar conditions, osmapentalene (**11b**, 1.0 equiv, 0.1 mmol, 101 mg) and electrophiles (1.0 equiv, 0.1 mmol, 32 mg) were dissolved in 10 mL dry DCM. Stir for 2 h at room temperature. The reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel 300 mesh, PE: DCM = 1:1) to give **13** as a brown solid (64% yield).

Osmapentalene(13)



Brown solid, 67 mg, Yield: 64%. Anal. Calcd (%) for $C_{52}H_{42}Cl_3OOsP_2$: C 59.97, H 4.07, found: C 59.91, H 4.14. HRMS (ESI): *m/z* calcd for $[C_{52}H_{42}Cl_3OOsP_2\text{-}Cl^-]^+$: 1006.1697, found: 1006.1697.

6. Magnetic experiments of 7a−b, 8, 9 and 10−12a−b

6.1 Magnetic experiments of 7a−b, 8, 9 and 10−12a−b

All metal complexes (7−13) are paramagnetic, and here the complexes (7a−b, 8, 9 and 10−12a−b) are taken as an example.

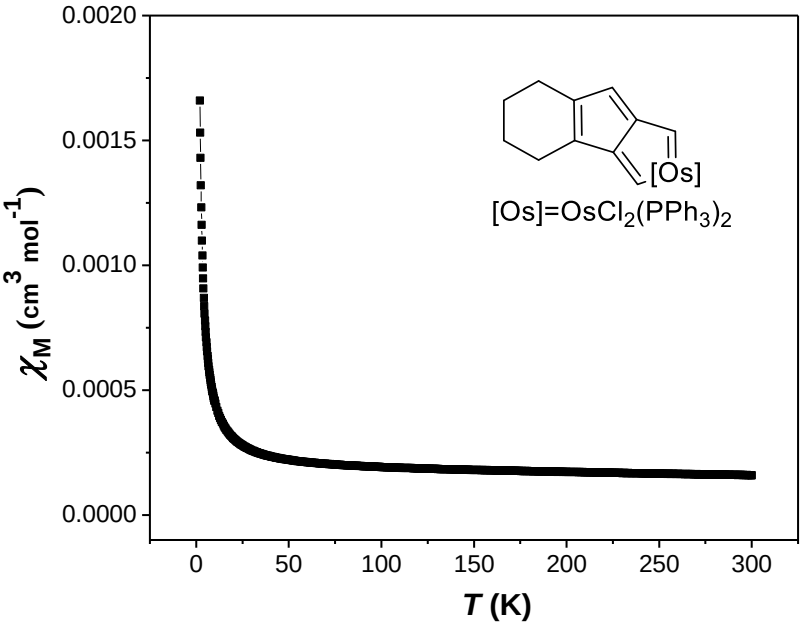


Figure S3. The temperature-dependent susceptibilities of **7a** measured under applied field of 1000Oe.

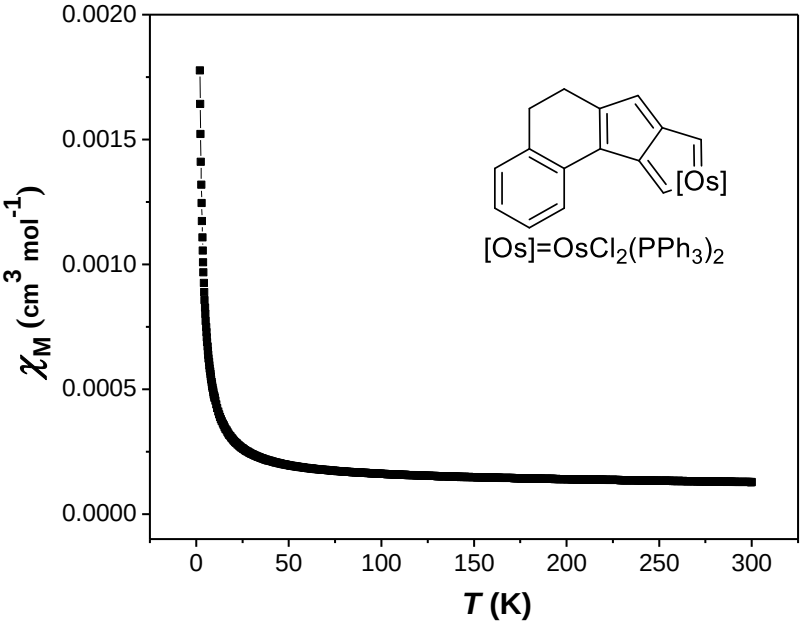


Figure S4. The temperature-dependent susceptibilities of **7b** measured under applied field of 1000Oe.

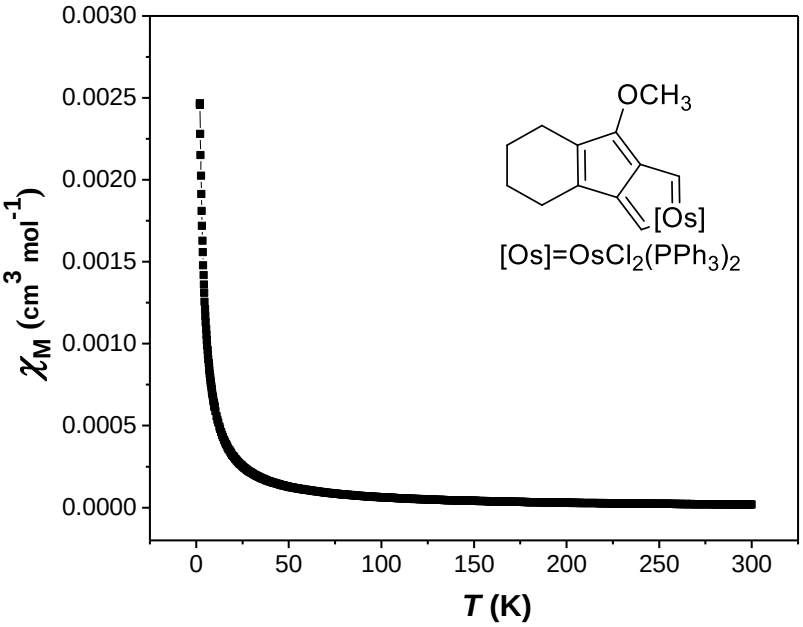


Figure S5. The temperature-dependent susceptibilities of **8** measured under applied field of 1000Oe.

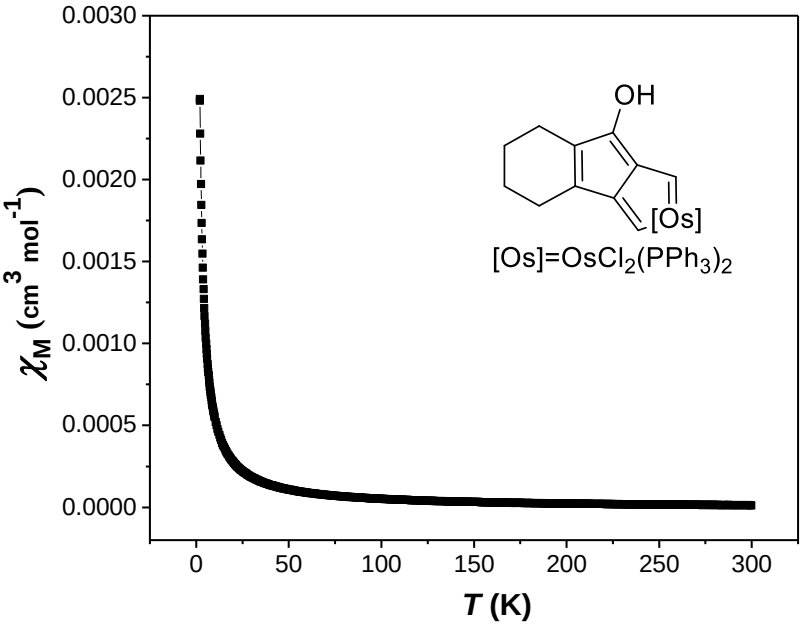


Figure S6. The temperature-dependent susceptibilities of **9** measured under applied field of 1000Oe.

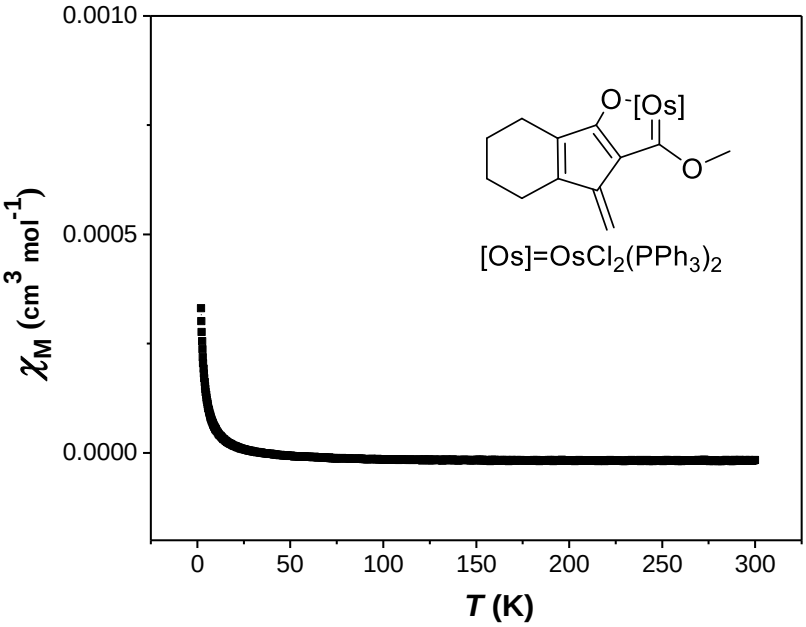


Figure S7. The temperature-dependent susceptibilities of **10a** measured under applied field of 2500Oe.

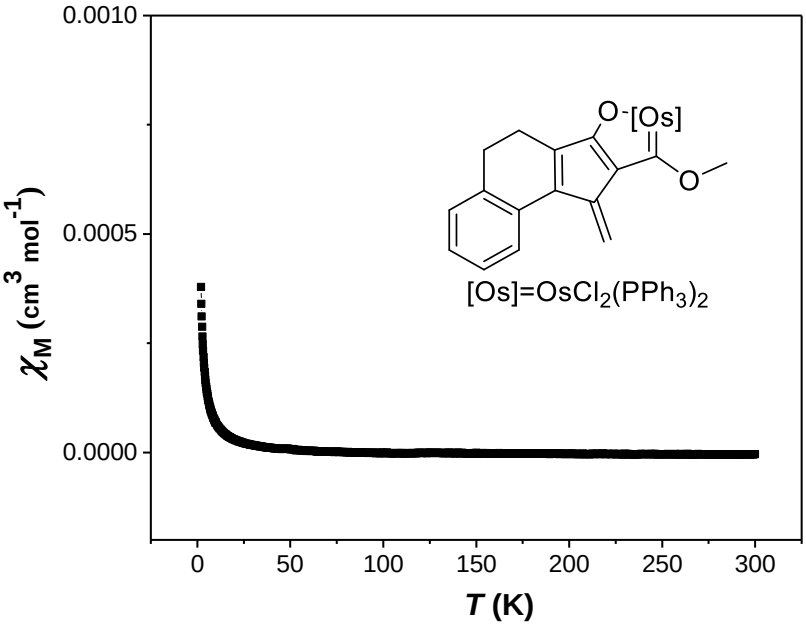


Figure S8 The temperature-dependent susceptibilities of **10b** measured under applied field of 2500Oe.

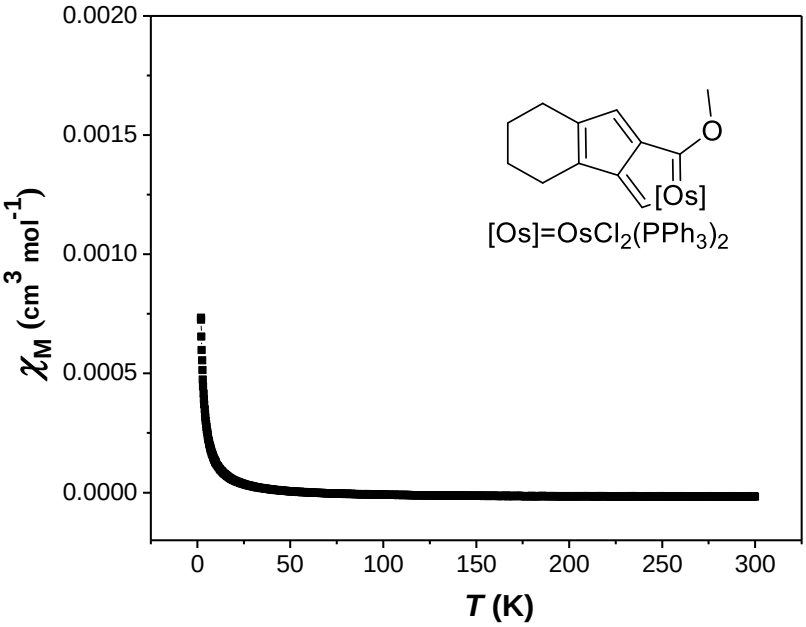


Figure S9. The temperature-dependent susceptibilities of **11a** measured under applied field of 1000Oe.

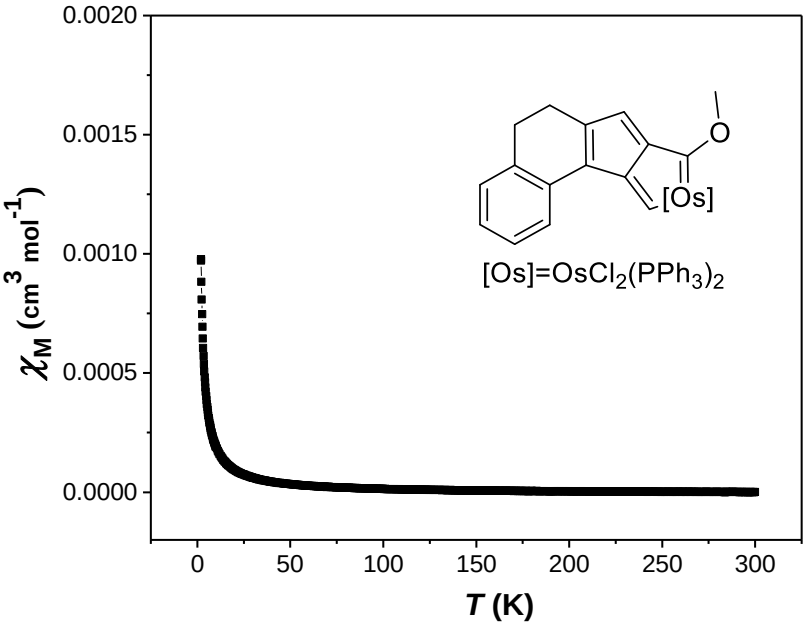


Figure S10. The temperature-dependent susceptibilities of **11b** measured under applied field of 1000Oe.

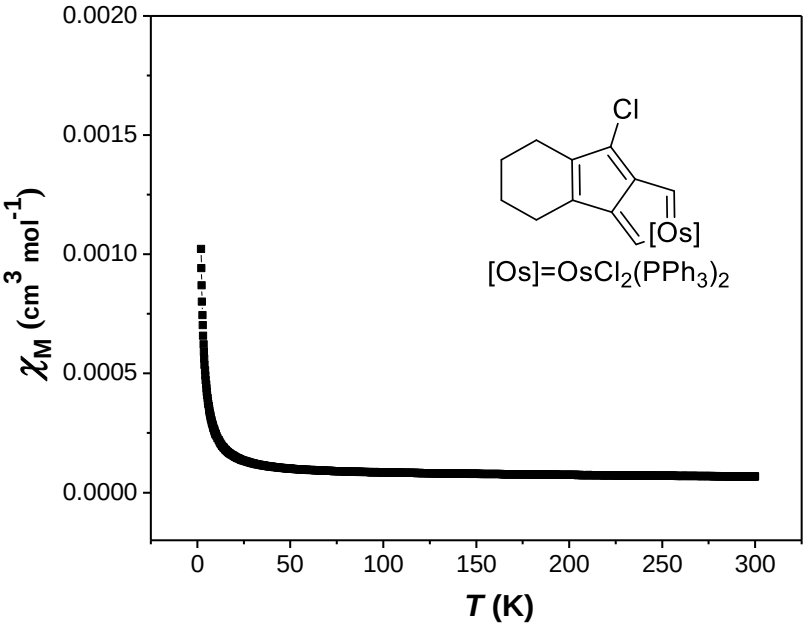


Figure S11. The temperature-dependent susceptibilities of **12a** measured under applied field of 1000Oe.

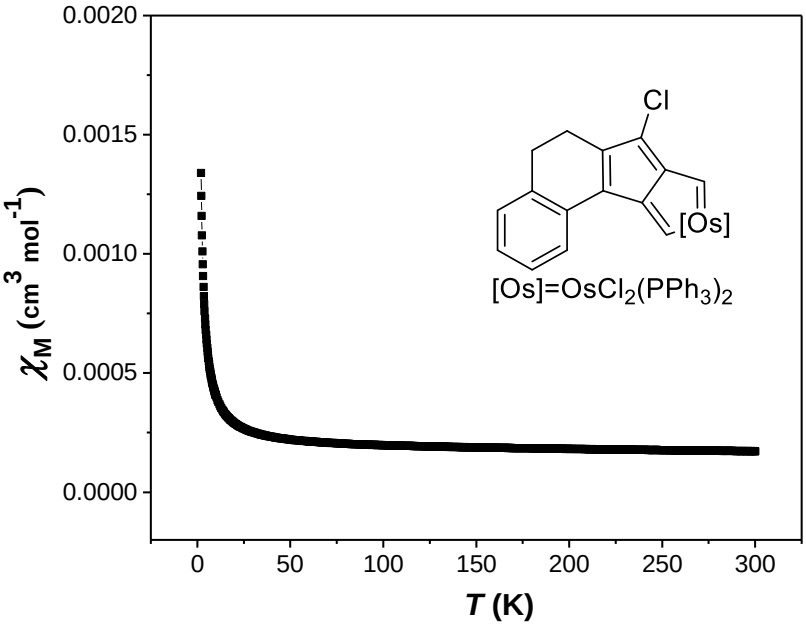


Figure S12. The temperature-dependent susceptibilities of **12b** measured under applied field of 1000Oe.

6.2 The spin densities of 7a′ and 8′

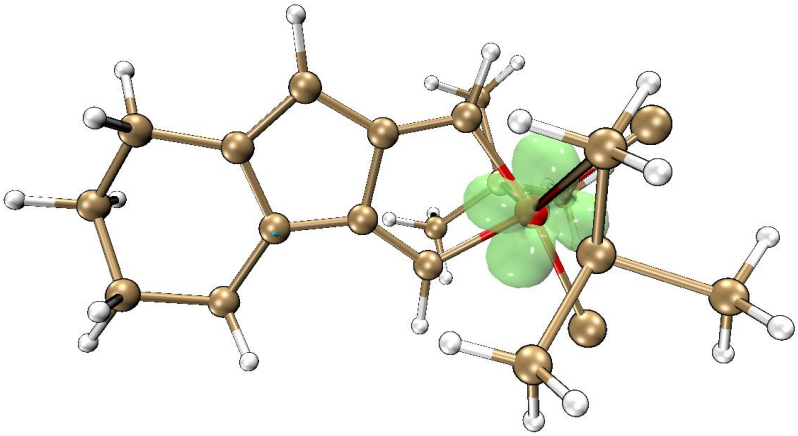


Figure S13. The spin densities of **7a′**.

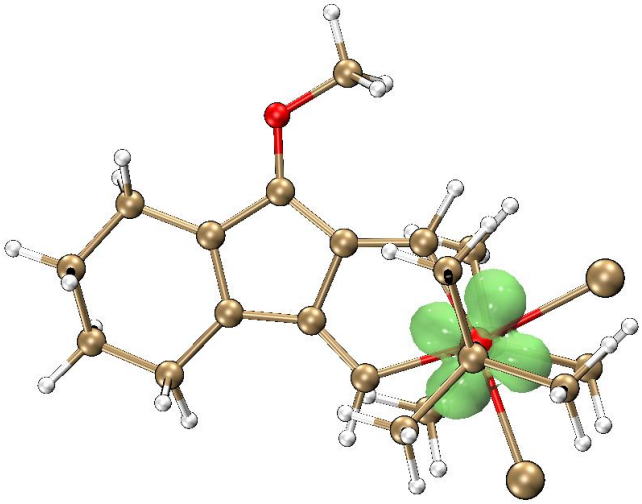


Figure S14. The spin densities of **8′**.

For the closed-shell neutral system in the lowest singlet state, there is no spin density due to the fact that the α electron density distribution is the same as the β electron density distribution. For the open-shell system, the α electron density distribution is different from the β electron density distribution, and the spin density is the difference between them. We have provided the spin densities of **7a′** and **8′** in Figure S14, the unpaired α+ single electrons are mainly distributed around the osmium center for **7a′** and **8′**, which further suggests that **7a′** and **8′** are open-shell systems.

7. Aromaticity evaluations

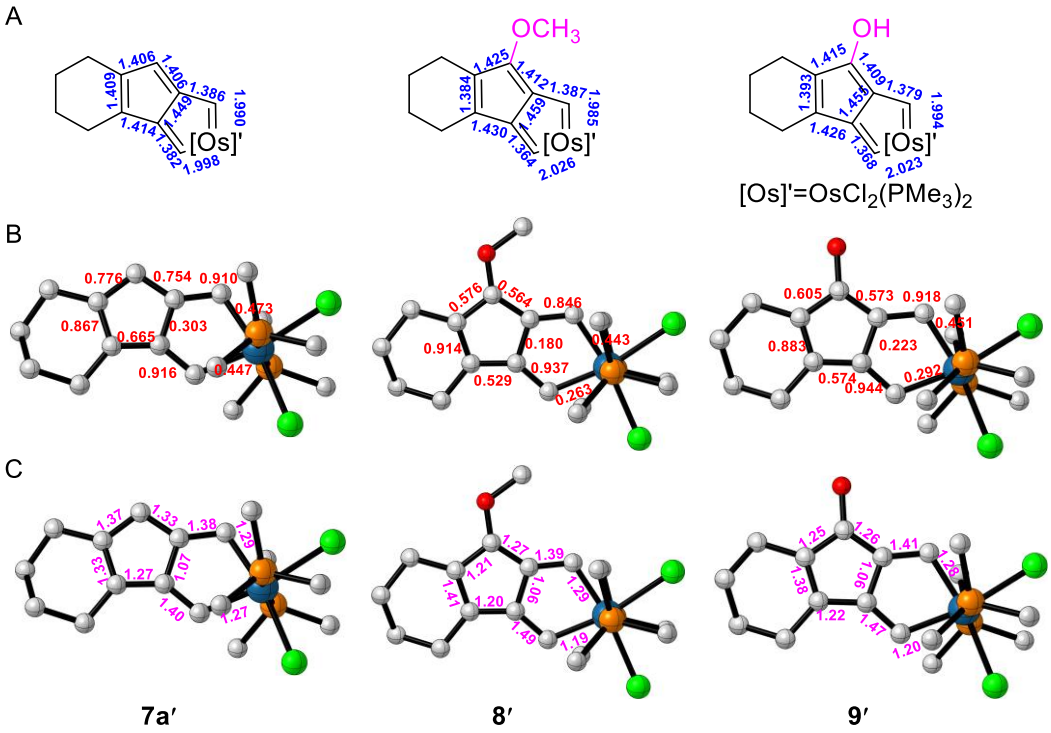


Figure S15. A) Bond lengths (Å, blue) of **7a′**, **8′** and **9′**. B) ELF$_\pi$ bifurcation values (red) of **7a′**, **8′** and **9′**. Hydrogen atoms were omitted for clarity. C) Bond orders (pink) of **7a′**, **8′** and **9′**. Hydrogen atoms were omitted for clarity.

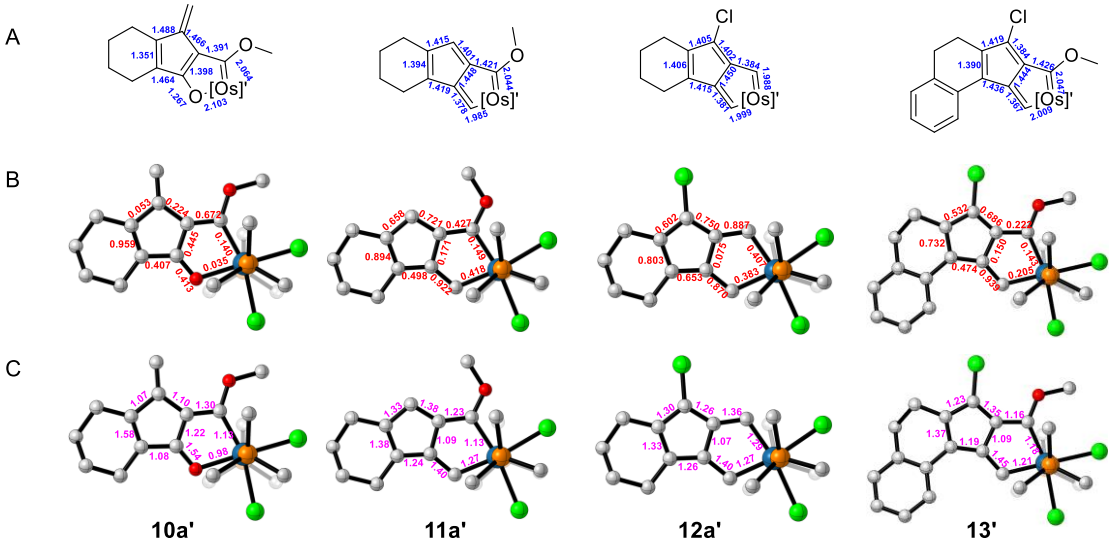


Figure S16. A) Bond lengths (Å, blue) of **10a′**, **11a′**, **12a′** and **13′**. B) ELF$_\pi$ bifurcation values (red) of **10a′**, **11a′**, **12a′** and **13′**. Hydrogen atoms were omitted for clarity. C) Bond orders (pink) of **10a′**, **11a′**, **12a′** and **13′**. Hydrogen atoms were omitted for clarity.

8.UV/Vis absorption spectra of 7 and 10

8.1 UV/Vis absorption spectra of 7a−h

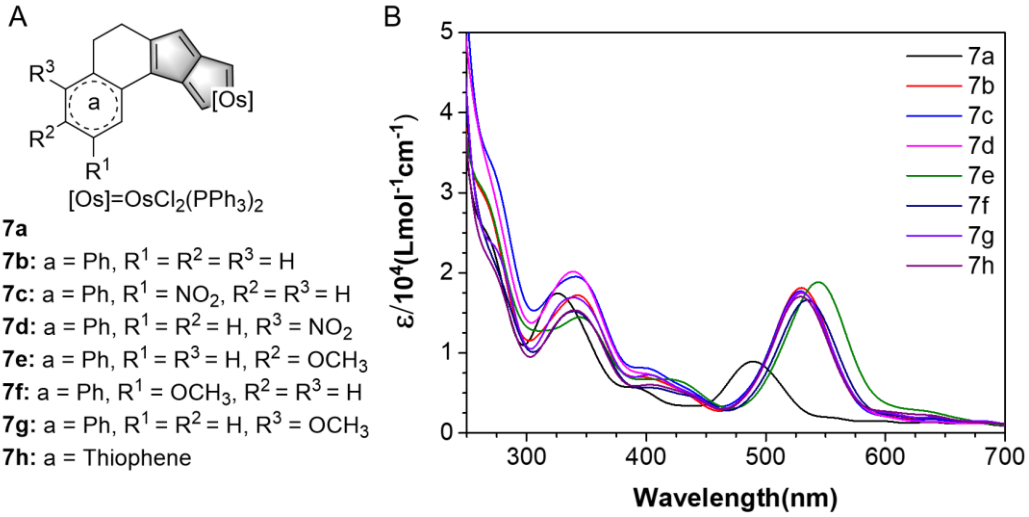


Figure S17. Structures (A) and UV/Vis-NIR absorption spectra (B) of **7a−h** measured in CH_2Cl_2 at room temperature.

8.2 UV/Vis absorption spectra of 10a−h

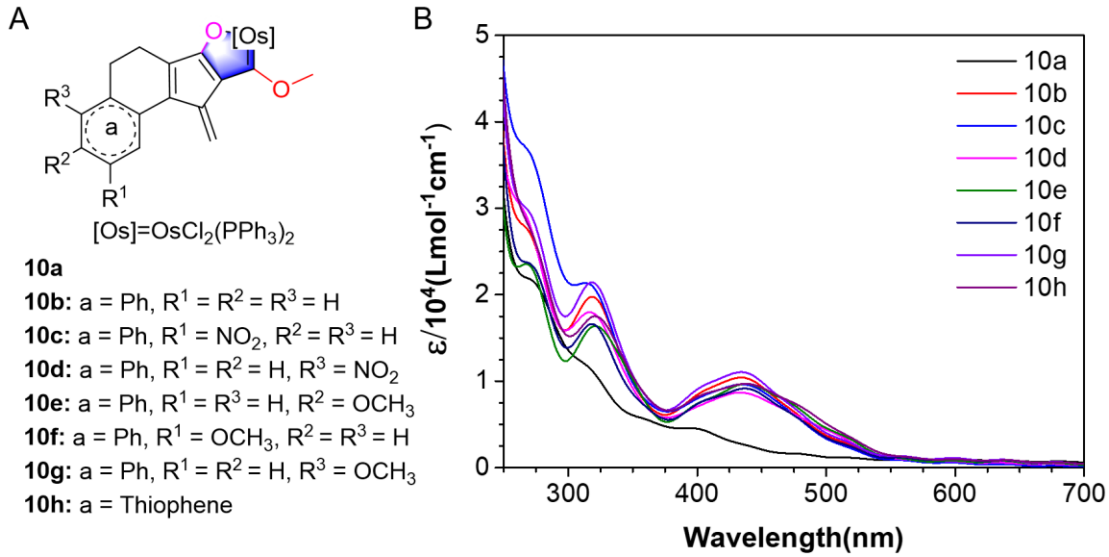


Figure S18. Structures (A) and UV/Vis-NIR absorption spectra (B) of **10a−h** measured in CH_2Cl_2 at room temperature.

8.3 TD-DFT of 7a−b and 11−12a−b

Table S1. Main electronic transitions in **7a−b** and **11−12a−b** in the ground state calculated by TD-DFT.

Complex	Excitation (percentage)	*f*	λ_{max}(calc)/ nm	λ_{max}(exp)/ nm	Main assignement

7a	α–HOSO-1→α–LUSO (22%) β–HOSO-3→β–LUSO+1 (14%) β–HOSO-1→β–LUSO+1 (34%)	0.0662	479	488	π(osmapentalene) PPh_3→Os
7b	α–HOSO-1→α–LUSO (23%) α–HOSO→α–LUSO (12%) β–HOSO-3→β–LUSO+1 (13%) β–HOSO-1→β–LUSO+1 (21%) β–HOSO→β–LUSO+1 (14%)	0.1561	516	531	π(osmapentalene)→π* (Ph-osmapentalene) π(Ph-osmapentalene) PPh_3→Os
11a	β–HOSO-4→β–LUSO (70%)	0.0113	461	458	π(OCH_3-osmapentalene) PPh_3→Os
	α–HOSO-4→α–LUSO (14%) β–HOSO-4→β–LUSO (14%) β–HOSO-3→β–LUSO+1 (17%) β–HOSO-2→β–LUSO+1 (16%) β–HOSO-1→β–LUSO+1 (19%)	0.0221	459		
11b	α–HOSO-3→α–LUSO (10%) α–HOSO-1→α–LUSO (19%) α–HOSO→α–LUSO (14%) β–HOSO-4→β–LUSO (12%) β–HOSO-2→β–LUSO+1 (12%) β–HOSO-1→β–LUSO+1 (10%)	0.1217	468	492	π(OCH_3-osmapentalene) →π* (Ph-OCH_3-osmapentalene) π(Ph-OCH_3-osmapentalene) PPh_3→Os

12a	α–HOSO-1→α–LUSO (20%) α–HOSO→α–LUSO (10%) β–HOSO-3→β–LUSO+1 (12%) β–HOSO-1→β–LUSO+1 (26%) β–HOSO→β–LUSO+1 (10%)	0.0883	488	500	π(Cl-osmapentalene) PPh_3/Cl/π(pentalene)→Os
12b	α–HOSO-1→α–LUSO (11%) α–HOSO→α–LUSO (28%) β–HOSO-3→β–LUSO+1 (9%) β–HOSO→β–LUSO+1 (30%)	0.1821	526	540	π(Cl-osmapentalene) →π* (Ph-Cl-osmapentalene) π(Ph-Cl-osmapentalene)

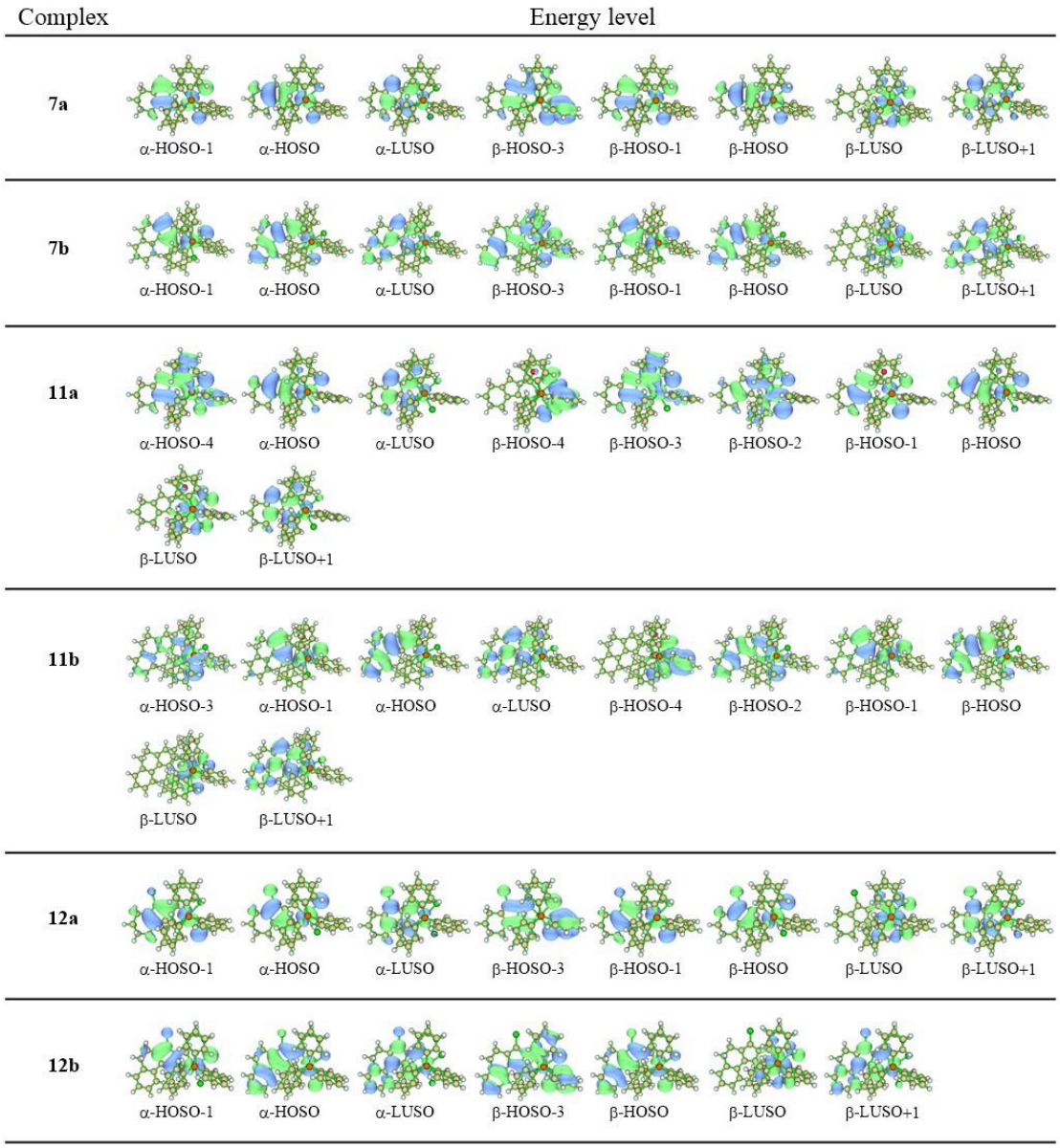


Figure S19. Different energy levels of **7a−b** and **11−12a−b**. Contour values: ±0.02 (e/bohr3)$^{1/2}$. B3LYP/6-31G*(Os: Lanl2DZ) /CPCM /CH_2Cl_2.

9. Cyclic voltammetry (CV) experiments of 7b

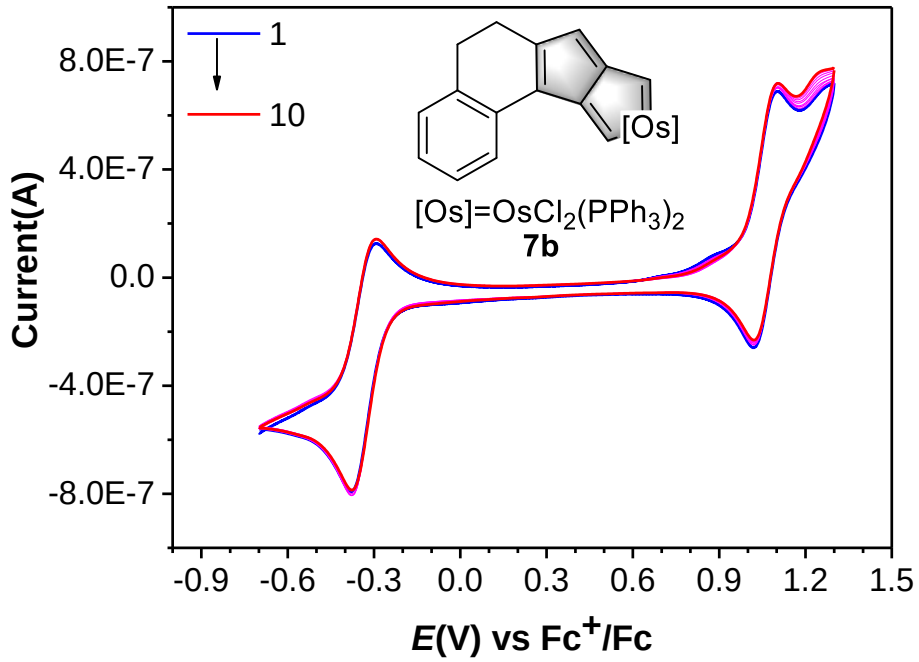


Figure S20. Cyclic voltammograms of **7b** in CH_2Cl_2 obtained by scanning 10 times continuously by the cyclic voltammetry (CV) with a glassy carbon as the working electrode, a platinum rod as the auxiliary electrode, Ag/AgCl as the reference electrode, nBu_4NPF_6 as the supporting electrolyte and a ferrocenium/ferrocene couple as the external standard.

10. X-ray crystallographic analysis

Single-crystal X-ray diffraction data were collected on a Diffractometer Bruker *APEX*-II CCD or Diffractometer Bruker D8 with PHOTON III 28detector with Ga *K*α or Synchrotron radiation (λ = 1.34139 Å). Single crystals for X-ray diffraction were obtained by recrystallization from a solution of DCM layered with *n*-hexane or MeOH. The crystal was kept at a steady T $\leqq$ 200 K during the data collection. The programs used to parse the crystals: olex2.solve 1.5 (Bourhis *et al.*, 2015), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2 1.5 (Dolomanov *et al.*, 2009). Non-H atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. CCDC 2322404 (**7a**), 2351699 (**8**), 2322410 (**9**), 2322417 (**10a**), 2322457 (**11a**), 2322406 (**7b**), 2322422 (**7c**), 2322423 (**7d**), 2395310 (**7f**), 2322424 (**7g**), 2322425 (**10b**), 2322471 (**10c**), 2322458 (**10e**), 2322459 (**10f**), 2322464 (**10g**), 2322465 (**10h**), 2322421 (**11b**), 2322466 (**12a**), 2322467 (**12b**), 2322468 (**12d**), 2322469 (**12f**), 2354505 (**13**) contain

the supplementary crystallographic data for this paper. Further details on the crystal data are provided in Supplementary Tables S2-S23. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/?access=referee.

Crystal data for 7a:

Chemical formula $C_{47}H_{41}Cl_2OsP_2$, M_r 928.92, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 200, *a*, *b*, *c* (Å) 17.914 (2), 12.2791 (16), 20.867 (3), β (°) 107.106 (4), *V* (Å^3) 4387.0 (10), *Z* 4, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 5.07, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 79954, 9002, 8614, R_{int} 0.054, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.056, 0.161, 1.05, Final *R* indexes (R_1 and WR_2) 0.056, 0.161, No. of reflections 9002, No. of parameters 523, No. of restraints 312, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 2.36, -1.55. CCDC 2322404

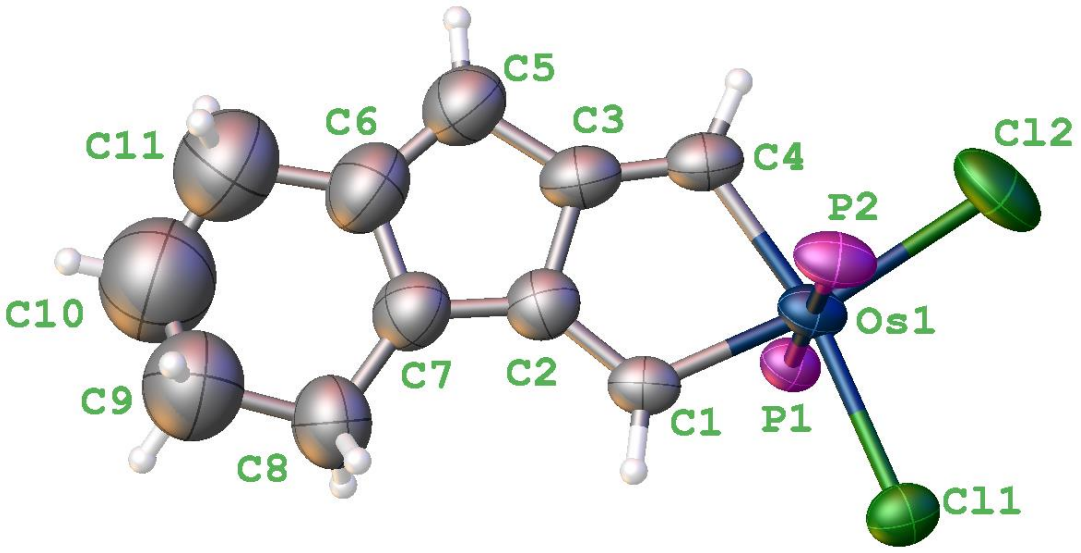


Figure S21. X-ray crystal structure of **7a** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S2. Bond lengths [Å] and angles [°] for **7a**.

Bond lengths [Å]			
Os1—Cl1	2.4131 (15)	C3—C2	1.445 (10)
Os1—Cl2	2.4203 (18)	C3—C5	1.473 (11)
Os1—P1	2.4191 (13)	C2—C7	1.409 (11)
Os1—P2	2.4122 (15)	C10—C11	1.44 (2)

Os1—C1	1.996 (6)	C10—C9	1.46 (2)
Os1—C4	1.989 (7)	C5—C6	1.382 (14)
C4—C3	1.341 (11)	C6—C11	1.533 (17)
C1—C2	1.397 (9)	C8—C9	1.533 (16)
C7—C6	1.433 (13)	C7—C8	1.486 (13)

Bond angles [°]			
Cl1—Os1—Cl2	100.86 (7)	C2—C7—C6	105.3 (8)
Cl1—Os1—P1	89.55 (4)	C2—C7—C8	129.1 (8)
P1—Os1—Cl2	90.14 (6)	C6—C7—C8	125.5 (8)
P2—Os1—Cl1	90.01 (5)	C6—C5—C3	106.2 (8)
P2—Os1—Cl2	89.93 (7)	C7—C6—C11	118.3 (11)
P2—Os1—P1	179.56 (5)	C5—C6—C7	112.3 (8)
C1—Os1—Cl1	88.69 (17)	C5—C6—C11	129.3 (11)
C1—Os1—Cl2	170.41 (17)	C7—C8—C9	111.5 (10)
C1—Os1—P1	89.03 (16)	C10—C11—C6	112.0 (14)
C1—Os1—P2	90.98 (16)	C10—C9—C8	114.8 (14)
C4—Os1—Cl1	168.0 (2)	C2—C1—Os1	115.9 (5)
C4—Os1—Cl2	91.1 (2)	C4—C3—C2	114.6 (6)
C4—Os1—P1	90.58 (18)	C4—C3—C5	139.3 (7)
C4—Os1—P2	89.85 (18)	C2—C3—C5	106.0 (7)
C4—Os1—C1	79.3 (3)	C1—C2—C3	112.7 (6)
C3—C4—Os1	117.4 (5)	C1—C2—C7	137.2 (7)
C7—C2—C3	110.1 (7)		

Crystal data for 8:

Chemical formula $C_{48}H_{43}Cl_2OOsP_2$, M_r 958.86, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 200, *a*, *b*, *c* (Å) 17.3755 (5), 12.4229 (4), 21.1442 (6), β (°) 102.291 (1), *V* (Å^3) 4459.4 (2), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.00, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 42162, 9145, 8539, R_{int} 0.048, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.035, 0.097, 1.05, Final *R* indexes (R_1 and WR_2) 0.035, 0.097, No. of reflections 9145, No. of parameters 488, No. of restraints 324, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.29, -0.82. CCDC 2351699

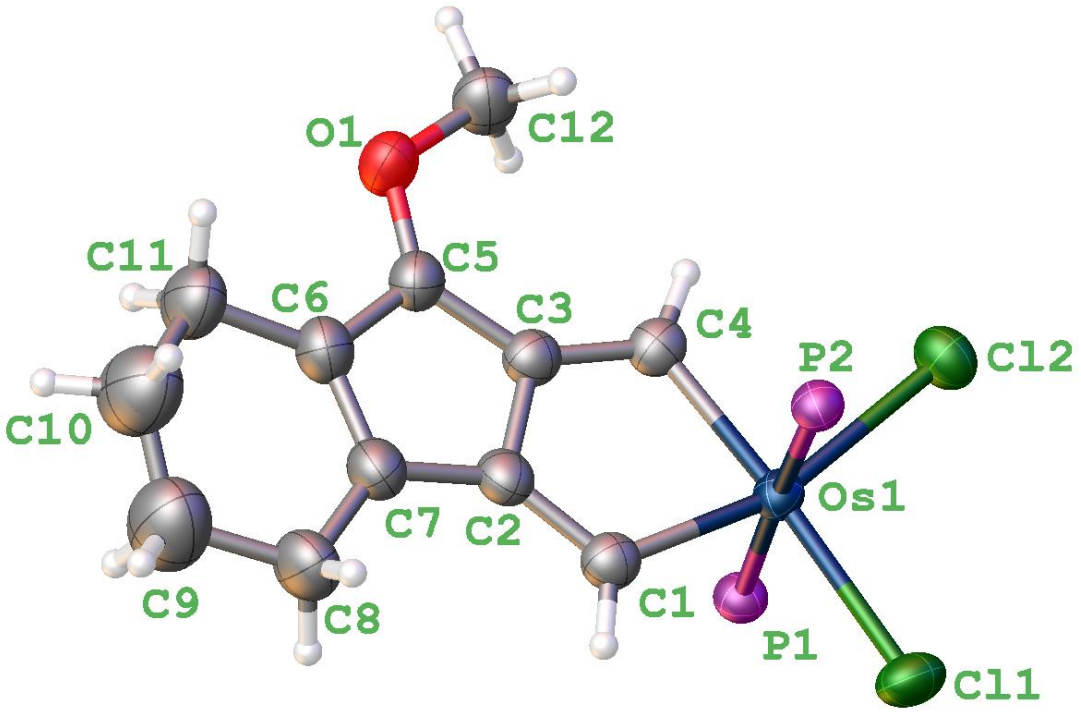


Figure S22. X-ray crystal structure of **8** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S3. Bond lengths [Å] and angles [°] for **8**.

Bond lengths [Å]			
Os1—P2	2.3997 (8)	C7—C8	1.495 (7)
Os1—P1	2.3877 (9)	C8—C9	1.496 (9)
Os1—Cl2	2.4396 (9)	C5—C3	1.428 (5)
Os1—Cl1	2.4346 (9)	C5—C6	1.425 (6)
Os1—C4	2.017 (4)	C3—C2	1.440 (6)
Os1—C1	2.009 (4)	C2—C7	1.436 (6)
C1—C2	1.389 (6)	C10—C9	1.407 (11)
C4—C3	1.367 (5)	C6—C7	1.380 (7)
O1—C5	1.330 (5)	C6—C11	1.508 (7)
O1—C12	1.448 (5)	C11—C10	1.487 (9)
Bond angles [°]			
P2—Os1—Cl2	92.05 (3)	O1—C5—C6	120.2 (4)
P2—Os1—Cl1	87.31 (3)	C6—C5—C3	108.8 (4)
P1—Os1—P2	176.22 (3)	C4—C3—C5	139.7 (4)
P1—Os1—Cl2	90.40 (3)	C4—C3—C2	113.9 (4)

P1—Os1—Cl1	89.44 (3)	C5—C3—C2	106.0 (3)
Cl1—Os1—Cl2	99.89 (4)	C1—C2—C3	113.8 (4)
C4—Os1—P2	90.76 (10)	C1—C2—C7	137.7 (4)
C4—Os1—P1	92.32 (10)	C7—C2—C3	108.2 (4)
C4—Os1—Cl2	84.93 (11)	C7—C8—C9	111.2 (5)
C4—Os1—Cl1	174.86 (11)	C10—C11—C6	109.9 (5)
C1—Os1—P2	85.98 (11)	C5—C6—C11	126.9 (4)
C1—Os1—P1	92.48 (11)	C7—C6—C5	108.7 (4)
C1—Os1—Cl2	163.53 (12)	C7—C6—C11	124.3 (4)
C1—Os1—Cl1	96.35 (12)	C9—C10—C11	119.9 (7)
C1—Os1—C4	78.75 (16)	C10—C9—C8	118.9 (7)
C5—O1—C12	117.3 (3)	C2—C7—C8	128.7 (4)
C3—C4—Os1	117.0 (3)	C6—C7—C2	108.3 (4)
C2—C1—Os1	116.4 (3)	C6—C7—C8	122.9 (4)
O1—C5—C3	131.0 (4)		

Crystal data for 9:

Chemical formula $C_{47}H_{41}Cl_2OOsP_2 \cdot O$, M_r 958.84, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 151, a, b, c (Å) 17.3755 (12), 12.1966 (9), 21.0967 (16), β (°) 100.328 (3), V (Å^3) 4398.4 (6), Z 4, Radiation type Ga Ka, λ = 1.34139 Å, μ (mm^{-1}) 5.06, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 104569, 9034, 6887, R_{int} 0.110, $(\sin \theta/\lambda)_{max}$ (Å^{-1}) 0.627, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.054, 0.149, 1.04, Final R indexes (R_1 and WR_2) 0.054, 0.149, No. of reflections 9034, No. of parameters 497, No. of restraints 86, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.10, -1.54. CCDC 2322410

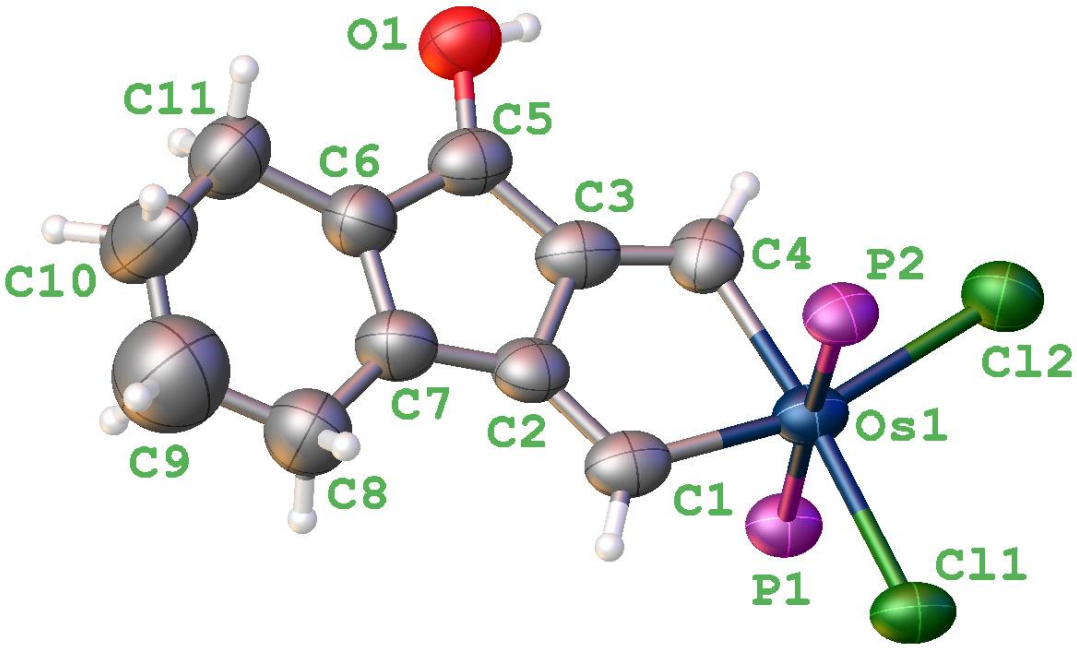


Figure S23. X-ray crystal structure of **9** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S4. Bond lengths [Å] and angles [°] for **9**.

Bond lengths [Å]			
Os1—Cl1	2.4337 (15)	C8—C9	1.513 (15)
Os1—P1	2.3886 (14)	C5—C6	1.431 (11)
Os1—P2	2.3989 (14)	C10—C9	1.405 (13)
Os1—Cl2	2.4555 (19)	C11—C10	1.471 (14)
Os1—C4	2.028 (7)	C7—C8	1.469 (13)
Os1—C1	2.008 (8)	C6—C7	1.388 (10)
C3—C2	1.444 (10)	C6—C11	1.502 (11)
C3—C4	1.331 (10)	O1—C5	1.308 (8)
C3—C5	1.441 (9)	C2—C7	1.433 (11)
C2—C1	1.391 (9)		
Bond angles [°]			
Cl1—Os1—Cl2	101.60 (6)	C5—C6—C11	126.4 (7)
P1—Os1—Cl1	89.58 (5)	C7—C6—C5	109.0 (7)
P1—Os1—P2	177.09 (5)	C7—C6—C11	124.5 (8)
P1—Os1—Cl2	89.68 (6)	C4—C3—C2	115.8 (6)
P2—Os1—Cl1	87.54 (5)	C4—C3—C5	137.5 (7)
P2—Os1—Cl2	91.29 (6)	C5—C3—C2	106.3 (7)

C4—Os1—Cl1	173.1 (2)	C1—C2—C3	113.2 (7)
C4—Os1—P1	92.28 (18)	C1—C2—C7	138.2 (7)
C4—Os1—P2	90.54 (18)	C7—C2—C3	108.1 (6)
C4—Os1—Cl2	85.0 (2)	C3—C4—Os1	116.0 (6)
C1—Os1—Cl1	94.2 (2)	O1—C5—C3	131.3 (7)
C1—Os1—P1	92.67 (17)	O1—C5—C6	120.7 (7)
C1—Os1—P2	87.14 (17)	C6—C5—C3	108.0 (6)
C1—Os1—Cl2	164.1 (2)	C9—C10—C11	122.2 (10)
C1—Os1—C4	79.1 (3)	C10—C9—C8	120.7 (12)
C2—C1—Os1	115.7 (6)	C2—C7—C8	128.1 (7)
C7—C8—C9	111.7 (9)	C6—C7—C2	108.5 (7)
C10—C11—C6	110.9 (8)	C6—C7—C8	123.4 (8)

Crystal data for 10a:

Chemical formula $C_{48}H_{43}Cl_2O_2OsP_2$, M_r 974.86, Crystal system, space group Monoclinic, $P2_1/n$, Temperature (K) 200, *a*, *b*, *c* (Å) 11.5624 (3), 18.8290 (6), 19.9939 (5), β (°) 105.744 (1), *V* (Å^3) 4189.5 (2), *Z* 4, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 5.34, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 95457, 8591, 7141, R_{int} 0.063, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.032, 0.080, 1.03, Final *R* indexes (R_1 and WR_2) 0.032, 0.080, No. of reflections 8591, No. of parameters 497, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 0.69, -1.05. CCDC 2322417

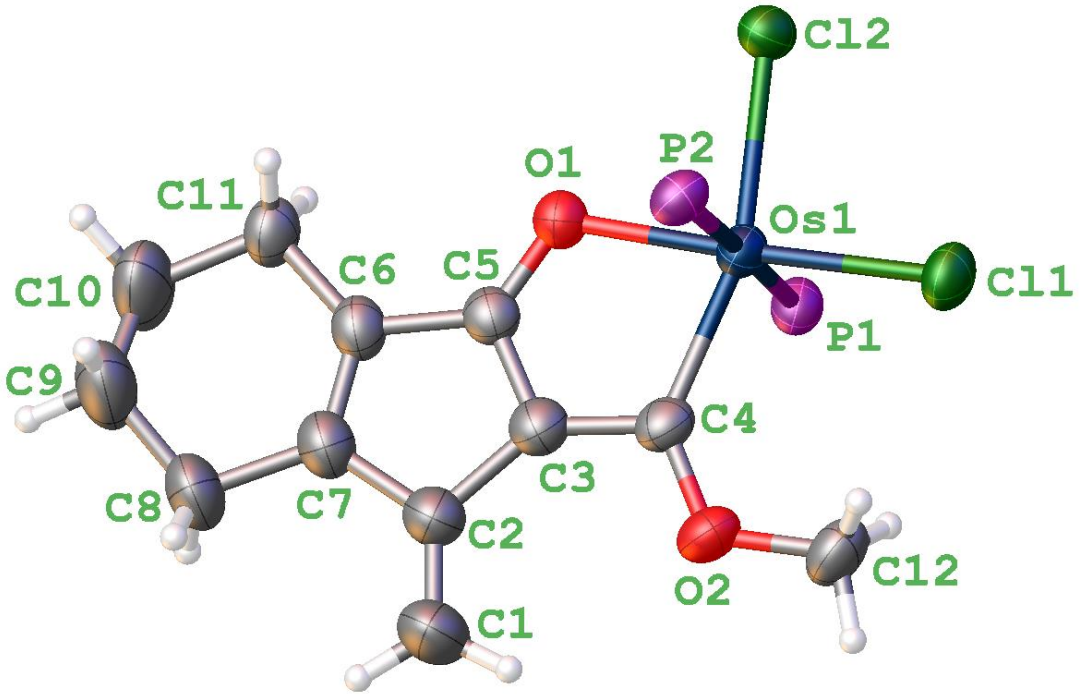


Figure S24. X-ray crystal structure of **10a** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S5. Bond lengths [Å] and angles [°] for **10a**.

Bond lengths [Å]			
Os1—Cl2	2.4227 (9)	C10—C9	1.407 (8)
Os1—P1	2.3942 (10)	C2—C7	1.484 (6)
Os1—Cl1	2.3605 (9)	C2—C1	1.328 (7)
Os1—P2	2.4026 (10)	C7—C8	1.501 (6)
Os1—O1	2.081 (2)	C8—C9	1.505 (8)
Os1—C4	2.060 (4)	C6—C7	1.349 (6)
C3—C2	1.486 (6)	C11—C6	1.492 (5)
O1—C5	1.280 (4)	C11—C10	1.512 (6)
O2—C4	1.354 (4)	C5—C6	1.460 (5)
O2—C12	1.428 (5)	C4—C3	1.382 (5)
C5—C3	1.393 (5)		
Bond angles [°]			
P1—Os1—Cl2	90.03 (3)	C7—C8—C9	110.3 (4)
P1—Os1—P2	178.13 (3)	C5—C3—C2	107.2 (3)
Cl1—Os1—Cl2	94.44 (3)	C4—C3—C5	114.9 (4)
Cl1—Os1—P1	91.96 (3)	C4—C3—C2	137.9 (4)

Cl1—Os1—P2	89.74 (3)	C9—C10—C11	118.0 (5)
P2—Os1—Cl2	90.61 (3)	C10—C9—C8	118.3 (5)
O1—Os1—Cl2	83.07 (7)	C6—C7—C2	111.9 (4)
O1—Os1—P1	88.88 (7)	C6—C7—C8	122.8 (4)
O1—Os1—Cl1	177.37 (7)	C2—C7—C8	125.3 (4)
O1—Os1—P2	89.45 (7)	C3—C4—Os1	112.3 (3)
C4—Os1—Cl2	162.26 (10)	C6—C11—C10	110.8 (4)
C4—Os1—P1	90.65 (11)	C5—C6—C11	128.1 (4)
C4—Os1—Cl1	103.25 (11)	C7—C6—C5	106.6 (4)
C4—Os1—P2	88.20 (11)	C7—C6—C11	125.3 (4)
C4—Os1—O1	79.22 (12)	C7—C2—C3	103.7 (4)
O1—C5—C6	128.2 (3)	C1—C2—C3	129.0 (4)
C3—C5—C6	110.7 (3)	C1—C2—C7	127.2 (4)
O2—C4—Os1	134.3 (3)	C4—O2—C12	121.7 (3)
O2—C4—C3	113.3 (3)	O1—C5—C3	121.1 (3)
C5—O1—Os1	112.3 (2)		

Crystal data for 7b:

Chemical formula $C_{51}H_{41}Cl_2OsP_2 \cdot 2(CH_2Cl_2)$, M_r 1146.73, Crystal system, space group Monoclinic, $P2_1/n$, Temperature (K) 100, *a*, *b*, *c* (Å) 13.814 (2), 25.118 (4), 14.979 (2), β (°) 113.326 (5), *V* (Å^3) 4772.6 (12), *Z* 4, Radiation type Synchrotron, λ = 1.34139 Å, μ (mm^{-1}) 6.07, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker D8 with PHOTON III 28detector, Absorption correction Multi-scan, T_{min}, T_{max} 0.512, 0.751, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 3278, 9780, 8990, R_{int} 0.102, $(\sin \theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.048, 0.129, 1.03, Final *R* indexes (R_1 and WR_2) 0.048, 0.129, No. of reflections 9780, No. of parameters 559, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 2.09, -1.81. CCDC 2322406

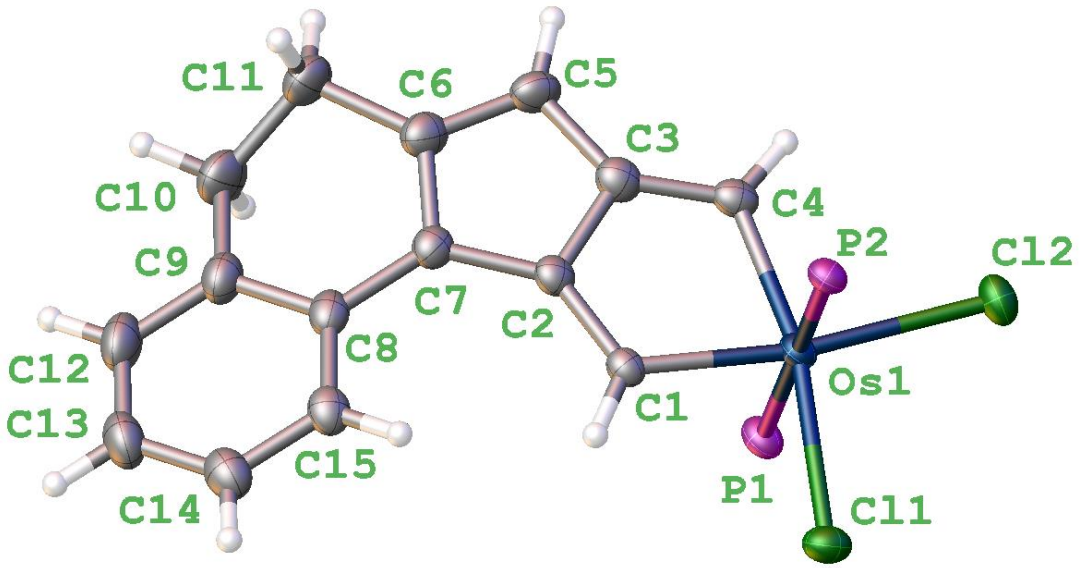


Figure S25. X-ray crystal structure of **7b** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S6. Bond lengths [Å] and angles [°] for **7b**.

Bond lengths [Å]			
Os1—Cl2	2.4358 (10)	C14—C13	1.393 (7)
Os1—Cl1	2.4206 (10)	C14—C15	1.386 (6)
Os1—P2	2.4064 (10)	C11—C10	1.532 (7)
Os1—P1	2.4001 (11)	C11—C6	1.503 (6)
Os1—C1	2.025 (4)	C13—C12	1.390 (8)
Os1—C4	2.016 (4)	C10—C9	1.509 (7)
C3—C2	1.449 (6)	C15—C8	1.405 (7)
C3—C5	1.441 (6)	C8—C9	1.421 (6)
C3—C4	1.368 (6)	C9—C12	1.393 (7)
C1—C2	1.381 (6)	C7—C6	1.421 (6)
C2—C7	1.435 (6)	C5—C6	1.403 (7)
C7—C8	1.447 (6)		
Bond angles [°]			
Cl1—Os1—Cl2	100.30 (4)	C9—C10—C11	112.6 (4)
P2—Os1—Cl2	90.12 (4)	C14—C15—C8	121.3 (4)
P2—Os1—Cl1	87.71 (4)	C15—C14—C13	119.7 (5)
P1—Os1—Cl2	92.77 (4)	C6—C11—C10	108.1 (4)
P1—Os1—Cl1	88.83 (4)	C12—C13—C14	120.1 (4)

P1—Os1—P2	175.84 (3)	C15—C8—C7	123.6 (4)
C1—Os1—Cl2	171.12 (12)	C15—C8—C9	118.6 (4)
C1—Os1—Cl1	88.55 (12)	C9—C8—C7	117.7 (4)
C1—Os1—P2	89.38 (11)	C2—C7—C8	132.2 (4)
C1—Os1—P1	88.22 (11)	C6—C7—C2	107.0 (4)
C4—Os1—Cl2	92.57 (12)	C6—C7—C8	120.6 (4)
C4—Os1—Cl1	167.03 (12)	C6—C5—C3	107.0 (4)
C4—Os1—P2	93.91 (11)	C3—C4—Os1	116.6 (3)
C4—Os1—P1	88.96 (11)	C8—C9—C10	119.5 (4)
C4—Os1—C1	78.61 (16)	C12—C9—C10	121.1 (4)
C5—C3—C2	107.8 (4)	C12—C9—C8	119.3 (5)
C4—C3—C2	114.9 (4)	C13—C12—C9	121.0 (5)
C4—C3—C5	137.1 (4)	C7—C6—C11	120.6 (4)
C2—C1—Os1	117.0 (3)	C5—C6—C7	110.6 (4)
C1—C2—C3	112.8 (4)	C5—C6—C11	128.7 (4)
C1—C2—C7	139.5 (4)	C7—C2—C3	107.6 (4)

Crystal data for 7c:

Chemical formula $C_{51}H_{40}Cl_2NO_2OsP_2$, M_r 1021.88, Crystal system, space group Orthorhombic, *Aea*2, Temperature (K) 100, *a*, *b*, *c* (Å) 18.4781 (12), 27.9229 (18), 16.8045 (11), *V* (Å^3) 8670.5 (10), *Z* 8, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 5.18, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 48164, 7686, 7181, R_{int} 0.072, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.024, 0.055, 1.06, Final *R* indexes (R_1 and WR_2) 0.024, 0.055, No. of reflections 7686, No. of parameters 532, No. of restraints 37, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 0.55, -0.80. CCDC 2322422

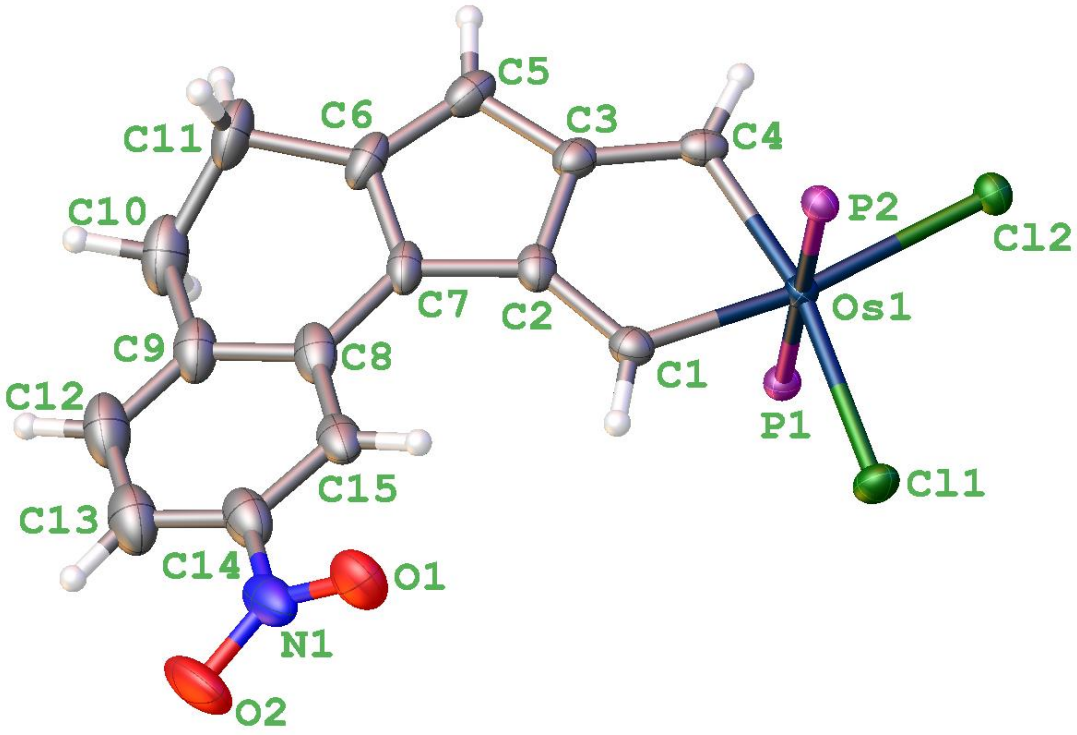


Figure S26. X-ray crystal structure of **7c** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S7. Bond lengths [Å] and angles [°] for **7c**.

Bond lengths [Å]			
Os1—P2	2.4029 (11)	O2—N1	1.225 (7)
Os1—Cl1	2.4087 (9)	O1—N1	1.225 (7)
Os1—Cl2	2.4322 (11)	C3—C5	1.417 (7)
Os1—P1	2.4082 (11)	C3—C2	1.440 (7)
Os1—C4	2.006 (4)	C14—C15	1.388 (9)
Os1—C1	2.004 (5)	C14—C13	1.378 (10)
C4—C3	1.404 (9)	C14—N1	1.465 (9)
C7—C8	1.442 (8)	C1—C2	1.381 (7)
C7—C6	1.425 (8)	C6—C5	1.401 (9)
C7—C2	1.433 (7)	C6—C11	1.508 (8)
C12—C9	1.366 (9)	C13—C12	1.409 (10)
C9—C10	1.537 (9)	C8—C15	1.411 (8)
C11—C10	1.523 (10)	C8—C9	1.419 (8)
Bond angles [°]			
P2—Os1—Cl1	89.48 (4)	C15—C14—N1	119.4 (6)

P2—Os1—Cl2	90.05 (4)	C13—C14—C15	122.4 (6)
P2—Os1—P1	178.79 (4)	C13—C14—N1	118.1 (6)
Cl1—Os1—Cl2	100.57 (4)	C14—C15—C8	119.7 (6)
P1—Os1—Cl1	89.44 (4)	C3—C4—Os1	115.9 (4)
P1—Os1—Cl2	90.67 (4)	C6—C7—C8	120.4 (5)
C4—Os1—P2	92.11 (14)	C6—C7—C2	106.8 (5)
C4—Os1—Cl1	167.4 (2)	C2—C7—C8	132.7 (5)
C4—Os1—Cl2	91.9 (2)	C2—C1—Os1	117.1 (4)
C4—Os1—P1	88.83 (14)	C7—C6—C11	120.1 (6)
C1—Os1—P2	88.99 (13)	C5—C6—C7	110.0 (5)
C1—Os1—Cl1	88.14 (13)	C5—C6—C11	129.9 (6)
C1—Os1—Cl2	171.22 (13)	C14—C13—C12	117.9 (7)
C1—Os1—P1	90.44 (13)	C6—C5—C3	107.4 (5)
C1—Os1—C4	79.4 (3)	C7—C2—C3	107.1 (4)
O1—N1—O2	124.0 (6)	C1—C2—C7	138.8 (5)
O1—N1—C14	118.2 (5)	C1—C2—C3	113.6 (4)
O2—N1—C14	117.9 (6)	C5—C3—C2	108.6 (5)
C15—C8—C7	123.8 (5)	C9—C12—C13	120.9 (6)
C15—C8—C9	117.6 (5)	C8—C9—C10	118.6 (6)
C9—C8—C7	118.6 (5)	C12—C9—C8	121.3 (6)
C6—C11—C10	108.9 (5)	C12—C9—C10	120.0 (6)
C4—C3—C5	137.4 (5)	C11—C10—C9	112.4 (5)
C4—C3—C2	113.9 (4)		

Crystal data for 7d:

Chemical formula $2(C_{51}H_{40}Cl_2NO_2OsP_2)$, M_r 2043.76, Crystal system, space group Triclinic, $P\bar{1}$, Temperature (K) 200, *a*, *b*, *c* (Å) 15.1799 (5), 18.8711 (8), 19.6962 (8), α, β, γ (°) 67.675 (2), 88.251 (2), 71.816 (2), *V* (Å^3) 4933.7 (3), *Z* 2, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 4.55, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 96611, 17081, 12473, R_{int} 0.083, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.591, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.049, 0.141, 1.06, Final *R* indexes (R_1 and WR_2) 0.049, 0.141, No. of reflections 17081, No. of parameters 1063, No. of restraints 84, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.38, -2.25. CCDC 2322423

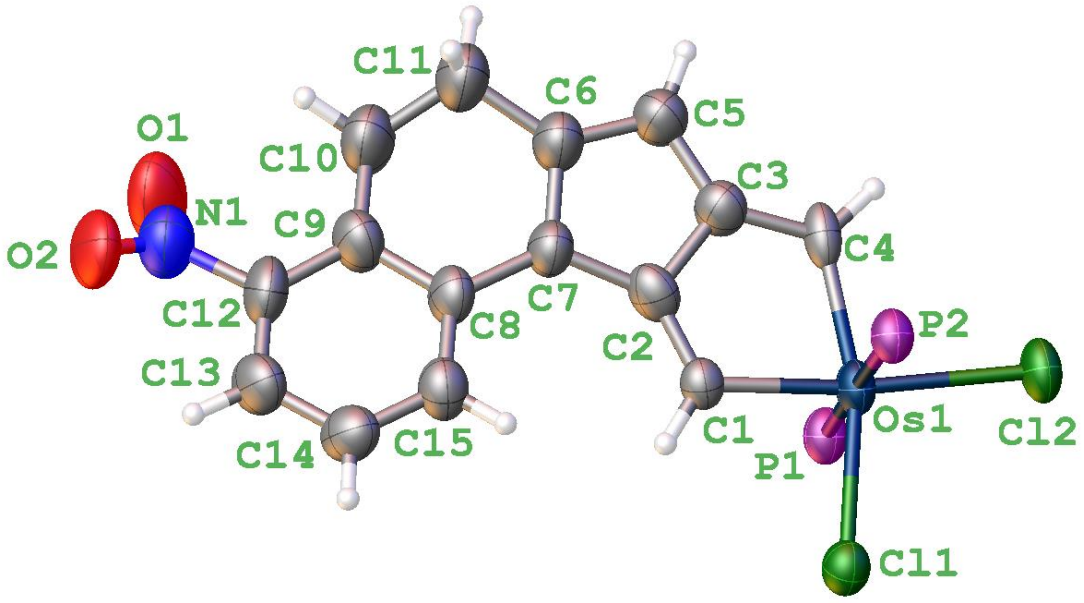


Figure S27. X-ray crystal structure of **7d** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S8. Bond lengths [Å] and angles [°] for **7d**.

Bond lengths [Å]			
Os1—Cl1	2.4210 (15)	C7—C2	1.451 (8)
Os1—Cl2	2.4264 (12)	C7—C8	1.458 (8)
Os1—P2	2.4005 (15)	C7—C6	1.422 (9)
Os1—P1	2.4196 (15)	C6—C11	1.487 (9)
Os1—C4	2.057 (7)	C14—C15	1.369 (8)
Os1—C1	2.008 (5)	C14—C13	1.384 (9)
O1—N1	1.244 (8)	C8—C15	1.381 (9)
N1—C12	1.467 (9)	C8—C9	1.431 (9)
O2—N1	1.225 (8)	C5—C6	1.392 (9)
C1—C2	1.343 (8)	C4—C3	1.371 (8)
C3—C2	1.452 (8)	C10—C11	1.522 (10)
C3—C5	1.414 (9)	C10—C11	1.522 (10)
C9—C12	1.389 (9)	C13—C12	1.371 (10)
C9—C10	1.519 (10)		
Bond angles [°]			
P2—Os1—P1	177.63 (5)	Cl1—Os1—Cl2	100.40 (5)
P1—Os1—Cl1	90.73 (5)	P2—Os1—Cl1	90.68 (5)
P1—Os1—Cl2	92.08 (5)	P2—Os1—Cl2	85.79 (5)

C4—Os1—Cl1	164.82 (15)	C7—C6—C11	118.5 (6)
C4—Os1—Cl2	94.77 (15)	C5—C6—C7	110.0 (6)
C4—Os1—P2	89.99 (16)	C5—C6—C11	131.5 (7)
C4—Os1—P1	89.14 (16)	O2—N1—O1	123.8 (7)
C1—Os1—Cl1	85.84 (17)	C7—C2—C3	105.7 (5)
C1—Os1—Cl2	173.30 (17)	C1—C2—C7	139.4 (6)
C1—Os1—P2	91.73 (16)	C1—C2—C3	115.0 (5)
C1—Os1—P1	90.27 (16)	C4—C3—C5	136.5 (6)
C1—Os1—C4	79.0 (2)	C5—C3—C2	109.0 (5)
C3—C4—Os1	114.5 (4)	C15—C8—C7	122.7 (6)
C14—C15—C8	122.6 (6)	C15—C8—C9	119.1 (6)
C9—C10—C11	111.8 (6)	C9—C8—C7	118.2 (6)
C6—C11—C10	111.3 (7)	C12—C13—C14	118.1 (6)
O2—N1—C12	118.2 (7)	C6—C5—C3	107.9 (6)
O1—N1—C12	118.0 (7)	C13—C12—N1	115.0 (6)
C2—C1—Os1	117.0 (4)	C13—C12—C9	124.8 (6)
C2—C7—C8	131.3 (6)	C9—C12—N1	120.2 (7)
C6—C7—C2	107.4 (5)	C8—C9—C10	118.4 (6)
C6—C7—C8	121.3 (6)	C12—C9—C8	115.7 (6)
C4—C3—C2	114.4 (6)	C12—C9—C10	125.7 (6)

Crystal data for 7f:

Chemical formula $C_{52}H_{43}Cl_2OOsP_2$, M_r 1006.90, Crystal system, space group Triclinic, $P\bar{1}$, Temperature (K) 200, *a*, *b*, *c* (Å) 10.2959 (2), 12.7539 (3), 17.4231 (4), α, β, γ (°) 78.776 (1), 75.314 (1), 73.868 (1), *Z* 2, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.31, Crystal size (mm) 0.06 × 0.02 × 0.02, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 33934, 8604, 8120, R_{int} 0.033, $(\sin\theta/\lambda)_{max}$ ($Å^{-1}$) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.023, 0.058, 1.03, Final *R* indexes (R_1 and WR_2) 0.023, 0.058, No. of reflections 8604, No. of parameters 525, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$) 0.86, -0.64. CCDC 2395310

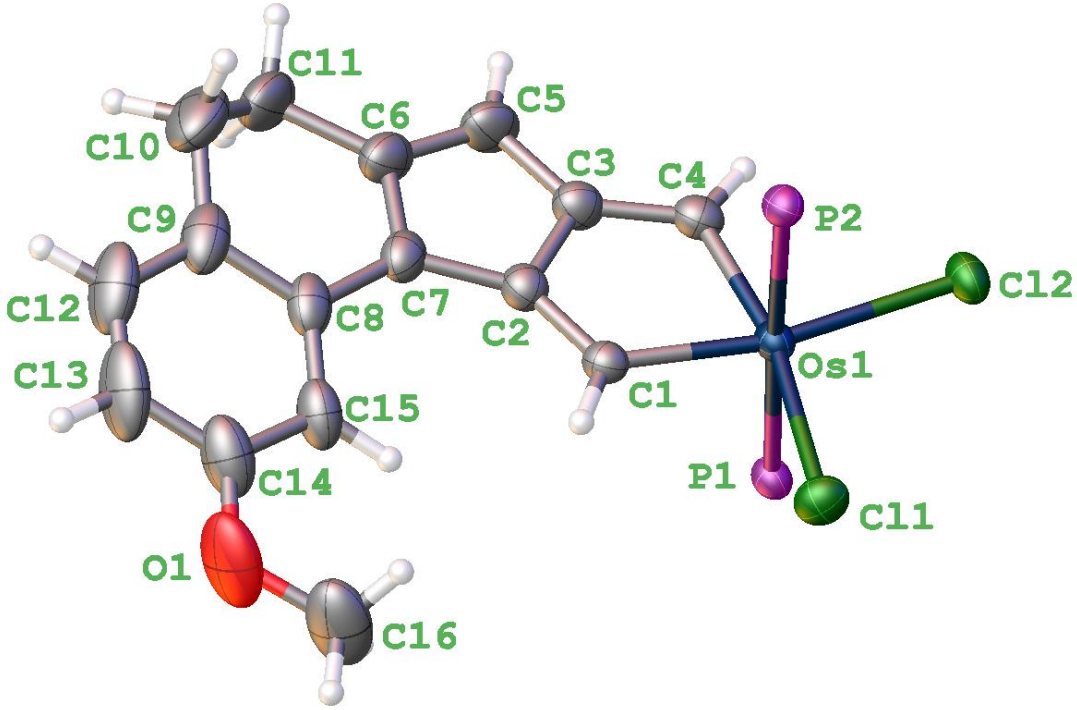


Figure S28. X-ray crystal structure of **7f** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S9. Bond lengths [Å] and angles [°] for **7f**.

Bond lengths [Å]			
Os1—C1	2.001 (3)	C15—C14	1.388 (5)
Os1—C4	2.012 (3)	C15—C8	1.402 (5)
Os1—P2	2.4126 (6)	C12—C13	1.336 (7)
Os1—P1	2.4167 (6)	C1—C2	1.389 (4)
Os1—Cl1	2.4269 (6)	C11—C10	1.497 (6)
Os1—Cl2	2.4280 (6)	C14—C13	1.395 (6)
C8—C9	1.415 (4)	C9—C12	1.401 (6)
C7—C8	1.448 (4)	C9—C10	1.493 (6)
C4—C3	1.386 (4)	C2—C3	1.443 (4)
O1—C14	1.372 (5)	C6—C7	1.411 (4)
O1—C16	1.412 (5)	C6—C11	1.511 (4)
C3—C5	1.418 (4)	C2—C7	1.428 (4)
C6—C5	1.386 (5)		
Bond lengths [Å]			
C1—Os1—C4	78.59 (11)	C6—C7—C8	121.7 (3)

C1—Os1—P2	95.00 (7)	C2—C7—C8	131.3 (3)
C4—Os1—P2	90.75 (7)	C14—C15—C8	120.0 (3)
C1—Os1—P1	86.35 (7)	C2—C1—Os1	117.9 (2)
C4—Os1—P1	90.45 (7)	C15—C8—C9	120.1 (3)
P2—Os1—P1	178.35 (2)	C15—C8—C7	122.2 (3)
C1—Os1—Cl1	88.60 (8)	C6—C5—C3	107.6 (3)
C4—Os1—Cl1	167.18 (8)	C9—C8—C7	117.7 (3)
P2—Os1—Cl1	89.80 (2)	C10—C11—C6	111.5 (3)
P1—Os1—Cl1	89.28 (2)	C12—C13—C14	120.8 (4
C1—Os1—Cl2	168.92 (7)	C6—C7—C2	106.9 (3)
C4—Os1—Cl2	90.92 (8)	C13—C12—C9	122.6 (4)
P2—Os1—Cl2	88.65 (2)	C9—C10—C11	115.1 (3)
P1—Os1—Cl2	90.19 (2)	C5—C3—C2	107.9 (3)
C3—C4—Os1	116.9 (2)	O1—C14—C15	123.7 (3)
C14—O1—C16	117.8 (3)	O1—C14—C13	117.0 (3)
C5—C6—C7	110.5 (3)	C15—C14—C13	119.2 (4)
C5—C6—C11	129.2 (3)	C12—C9—C8	117.1 (4)
C7—C6—C11	120.2 (3)	C12—C9—C10	122.5 (3)
C1—C2—C7	139.9 (3)	C8—C9—C10	120.4 (3)
C1—C2—C3	112.7 (2)	C4—C3—C5	137.8 (3)
C7—C2—C3	107.1 (2)	C4—C3—C2	113.9 (2)

Crystal data for 7g:

Chemical formula $C_{52}H_{43}Cl_2OOsP_2$, M_r 1006.90, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 100, *a*, *b*, *c* (Å) 14.7048 (8), 15.4032 (9), 19.1719 (10), β (°) 96.067 (2), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.18, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, T_{min}, T_{max} 0.650, 0.751, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 84652, 7479, 6280, R_{int} 0.075, $(\sin\theta/\lambda)_{max}$ ($Å^{-1}$) 0.591, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.047, 0.127, 1.04, Final *R* indexes (R_1 and WR_2) 0.047, 0.127, No. of reflections 7479, No. of parameters 656, No. of restraints 300, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$) 2.52, -1.03. CCDC 2322424

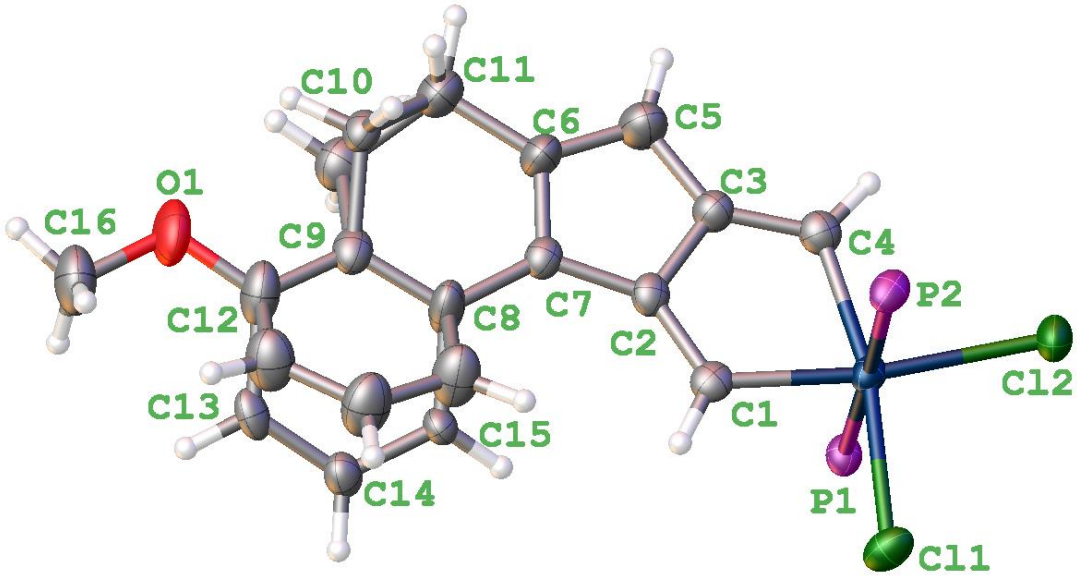


Figure S29. X-ray crystal structure of **7g** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S10. Bond lengths [Å] and angles [°] for **7g**.

Bond lengths [Å]			
Os1—P1	2.4042 (15)	C11—C10	1.532 (17)
Os1—Cl1	2.4106 (15)	C12—C13	1.399 (17)
Os1—Cl2	2.4315 (15)	C12—O1	1.351 (9)
Os1—P2	2.4102 (15)	C2—C3	1.447 (9)
Os1—C1	1.999 (6)	C2—C7	1.425 (8)
Os1—C4	2.020 (6)	C2—C1	1.386 (9)
C9—C10	1.648 (16)	C3—C4	1.373 (9)
C6—C11	1.496 (9)	C3—C5	1.422 (10)
C6—C5	1.396 (10)	C7—C8	1.458 (9)
C15—C14	1.39 (2)	C7—C6	1.400 (9)
C13—C14	1.36 (2)	C9—C8	1.383 (9)
O1—C16	1.437 (9)	C9—C12	1.371 (10)
Bond angles [°]			
P1—Os1—Cl1	88.94 (5)	C4—C3—C2	114.3 (6)
P1—Os1—Cl2	90.84 (5)	C4—C3—C5	138.6 (6)
P1—Os1—P2	178.70 (5)	C5—C3—C2	107.1 (6)
Cl1—Os1—Cl2	98.78 (6)	C2—C7—C8	131.7 (6)
P2—Os1—Cl1	91.79 (5)	C6—C7—C2	107.5 (5)

P2—Os1—Cl2	90.11 (5)	C6—C7—C8	120.8 (6)
C1—Os1—P1	89.34 (16)	C2—C1—Os1	118.2 (5)
C1—Os1—Cl1	90.01 (18)	C12—C9—C10	116.8 (8)
C1—Os1—Cl2	171.21 (18)	C8—C9—C10	113.9 (8)
C1—Os1—P2	89.59 (16)	C12—C9—C8	122.1 (7)
C1—Os1—C4	78.3 (3)	C3—C4—Os1	116.9 (5)
C4—Os1—P1	90.32 (17)	C9—C8—C7	120.1 (6)
C4—Os1—Cl1	168.29 (19)	C7—C2—C3	107.4 (5)
C4—Os1—Cl2	92.92 (19)	C1—C2—C3	112.3 (5)
C4—Os1—P2	88.74 (17)	C1—C2—C7	140.3 (6)
C11—C10—C9	106.5 (10)	C6—C5—C3	108.0 (6)
C14—C13—C12	117.9 (13)	C9—C8—C15	111.4 (8)
C13—C14—C15	121.5 (15)	C15—C8—C7	117.9 (8)
C12—O1—C16	117.4 (7)	C7—C6—C11	121.5 (6)
C14—C15—C8	120.6 (13)	C5—C6—C7	110.0 (6)
C6—C11—C10	112.9 (8)	C5—C6—C11	128.5 (7)
O1—C12—C13	114.3 (9)	C9—C12—C13	116.4 (9)
O1—C12—C9	118.6 (7)		

Crystal data for 10b:

Chemical formula $C_{52}H_{43}Cl_2O_2OsP_2 \cdot CH_2Cl_2$, M_r 1107.83, Crystal system, space group Monoclinic, $P2_1/n$, Temperature (K) 100, *a*, *b*, *c* (Å) 11.419 (2), 18.242 (4), 23.692 (4), β (°) 102.992 (6), *V* (Å^3) 4808.6 (16), *Z* 4, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 2.98, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 55032, 9829, 8996, R_{int} 0.062, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.025, 0.066, 1.05, Final *R* indexes (R_1 and WR_2) 0.025, 0.066, No. of reflections 9829, No. of parameters 560, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.41, -1.01. CCDC 2322425

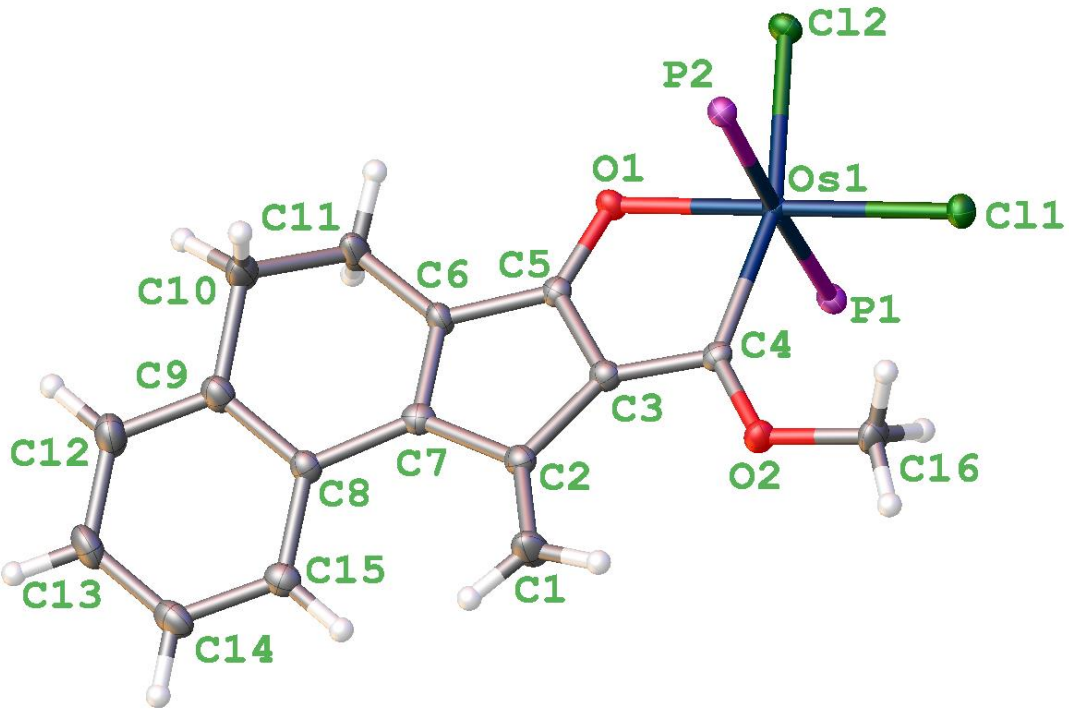


Figure S30. X-ray crystal structure of **10b** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S11. Bond lengths [Å] and angles [°] for **10b**.

Bond lengths [Å]			
Os1—Cl2	2.4304 (6)	C6—C7	1.365 (3)
Os1—Cl1	2.3529 (6)	C6—C11	1.482 (3)
Os1—P1	2.3921 (6)	C11—C10	1.533 (4)
Os1—P2	2.3939 (6)	C9—C10	1.510 (4)
Os1—O1	2.0741 (16)	C7—C8	1.472 (3)
Os1—C4	2.069 (2)	C15—C8	1.396 (3)
C5—C6	1.456 (3)	C15—C14	1.397 (4)
C2—C7	1.494 (3)	C13—C12	1.389 (4)
C2—C1	1.336 (4)	C13—C14	1.380 (4)
O2—C16	1.436 (3)	C9—C12	1.385 (4)
C4—C3	1.398 (3)	C9—C8	1.412 (4)
C3—C5	1.397 (3)	O1—C5	1.286 (3)
C3—C2	1.470 (3)	O2—C4	1.334 (3)
Bond angles [°]			
Cl1—Os1—Cl2	95.99 (2)	C6—C11—C10	108.3 (2)

Cl1—Os1—P1	88.46 (2)	C5—C6—C11	128.1 (2)
Cl1—Os1—P2	90.26 (2)	C7—C6—C5	107.9 (2)
P1—Os1—Cl2	89.98 (2)	C7—C6—C11	124.0 (2)
P1—Os1—P2	177.997 (19)	C9—C12—C13	121.0 (3)
P2—Os1—Cl2	88.62 (2)	C9—C8—C7	117.2 (2)
O1—Os1—Cl2	83.48 (5)	C15—C8—C9	118.9 (2)
O1—Os1—Cl1	178.68 (4)	C15—C8—C7	123.9 (2)
O1—Os1—P1	90.34 (5)	C13—C14—C15	120.1 (3)
O1—Os1—P2	90.93 (5)	C9—C10—C11	112.6 (2)
C4—Os1—Cl2	163.12 (7)	C14—C13—C12	119.8 (3)
C4—Os1—Cl1	100.87 (7)	C12—C9—C8	119.6 (2)
C4—Os1—P1	91.38 (6)	C12—C9—C10	120.7 (2)
C4—Os1—P2	90.37 (6)	C8—C9—C10	119.7 (2)
C4—Os1—O1	79.69 (8)	C6—C7—C2	110.1 (2)
C5—C3—C4	114.0 (2)	C6—C7—C8	119.7 (2)
C5—C3—C2	108.5 (2)	C8—C7—C2	130.2 (2)
C1—C2—C7	128.4 (2)	C8—C15—C14	120.5 (3)
C5—O1—Os1	112.08 (15)	O1—C5—C3	122.0 (2)
C4—O2—C16	122.47 (19)	O1—C5—C6	128.7 (2)
O2—C4—Os1	135.46 (17)	C3—C5—C6	109.3 (2)
O2—C4—C3	112.4 (2)	C3—C2—C7	104.2 (2)
C3—C4—Os1	112.17 (16)	C1—C2—C3	127.2 (2)
C4—C3—C2	137.4 (2)		

Crystal data for 10c:

Chemical formula $C_{52}H_{42}Cl_2NO_4OsP_2 \cdot CH_2Cl_2$, M_r 1152.83, Crystal system, space group Triclinic, $P\bar{1}$, Temperature (K) 150, *a*, *b*, *c* (Å) 10.5376 (9), 13.7307 (13), 17.1190 (17), α, β, γ (°) 74.925 (4), 85.757 (4), 77.998 (4), *V* (Å^3) 2338.9 (4), *Z* 2, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 5.56, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 45664, 9553, 8401, R_{int} 0.064, $(\sin \theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.048, 0.126, 1.03, Final *R* indexes (R_1 and WR_2) 0.048, 0.126, No. of reflections 9553, No. of parameters 587, No. of restraints 6, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.73, -2.10. CCDC 2322471

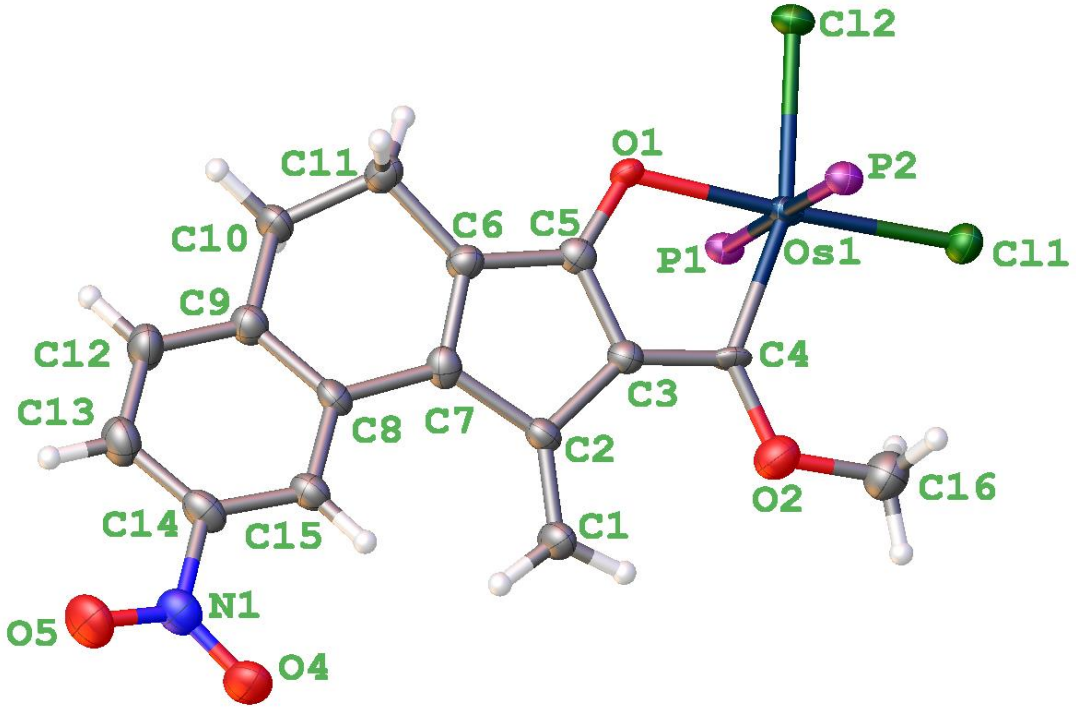


Figure S31. X-ray crystal structure of **10c** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S12. Bond lengths [Å] and angles [°] for **10c**.

Bond lengths [Å]			
Os1—Cl1	2.3483 (14)	C4—O2	1.354 (7)
Os1—Cl2	2.4165 (13)	C6—C7	1.373 (8)
Os1—P1	2.3998 (14)	C16—O2	1.441 (8)
Os1—P2	2.3956 (14)	C7—C2	1.497 (8)
Os1—C4	2.045 (5)	C2—C1	1.332 (8)
Os1—O1	2.090 (4)	C9—C10	1.518 (8)
O4—N1	1.221 (7)	C9—C12	1.382 (8)
O5—N1	1.236 (7)	C14—C15	1.385 (8)
N1—C14	1.469 (8)	C14—C13	1.376 (9)
C3—C4	1.390 (8)	C12—C13	1.388 (9)
C3—C2	1.492 (7)	C8—C9	1.423 (8)
C11—C6	1.493 (8)	C8—C15	1.398 (8)
C11—C10	1.532 (8)	C5—C3	1.390 (8)
C8—C7	1.471 (8)	C5—C6	1.455 (8)
C5—O1	1.280 (7)		

Bond angles [°]			
Cl1—Os1—Cl2	94.34 (5)	C7—C6—C11	124.4 (5)
Cl1—Os1—P1	90.03 (5)	C14—C13—C12	118.1 (6)
Cl1—Os1—P2	90.51 (5)	C8—C7—C2	130.7 (5)
P1—Os1—Cl2	90.88 (5)	C6—C7—C8	119.1 (5)
P2—Os1—Cl2	90.64 (5)	C6—C7—C2	110.2 (5)
P2—Os1—P1	178.35 (5)	C3—C2—C7	103.8 (5)
C4—Os1—Cl1	104.02 (16)	C1—C2—C3	125.9 (5)
C4—Os1—Cl2	161.61 (16)	C1—C2—C7	130.1 (5)
C4—Os1—P1	90.17 (15)	C8—C9—C10	119.0 (5)
C4—Os1—P2	88.18 (15)	C12—C9—C8	120.3 (5)
C4—Os1—O1	79.24 (19)	C12—C9—C10	120.6 (5)
O1—Os1—Cl1	176.57 (10)	C9—C12—C13	121.0 (6)
O1—Os1—Cl2	82.43 (10)	C5—O1—Os1	111.5 (3)
O1—Os1—P1	88.90 (11)	C4—O2—C16	122.1 (5)
O1—Os1—P2	90.65 (11)	C3—C5—C6	110.2 (5)
C5—C3—C4	113.5 (5)	O1—C5—C3	122.4 (5)
C5—C3—C2	108.1 (5)	O1—C5—C6	127.3 (5)
C4—C3—C2	138.3 (5)	C3—C4—Os1	113.4 (4)
C6—C11—C10	107.5 (5)	O2—C4—Os1	132.7 (4)
C9—C8—C7	117.7 (5)	O2—C4—C3	113.9 (5)
C15—C8—C7	123.9 (5)	C5—C6—C11	127.9 (5)
C15—C8—C9	118.4 (5)	C7—C6—C5	107.7 (5)
O4—N1—O5	123.4 (6)	C15—C14—N1	118.2 (6)
O4—N1—C14	118.6 (5)	C13—C14—N1	118.7 (6)
O5—N1—C14	118.0 (6)	C13—C14—C15	123.1 (6)
C14—C15—C8	119.0 (6)	C9—C10—C11	112.9 (5)

Crystal data for 10e:

Chemical formula $C_{53}H_{45}Cl_2O_3OsP_2 \cdot CH_2Cl_2$, M_r 1137.85, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 100, *a*, *b*, *c* (Å) 11.6278 (11), 17.8600 (17), 24.058 (2), β (°) 103.075 (4), *V* (Å^3) 4866.7 (8), *Z* 4, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 5.32, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [*I* >

$2\sigma(I)$] reflections 72572, 9967, 9490, R_{int} 0.046, $(\sin\theta/\lambda)_{max}$ ($Å^{-1}$) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.022, 0.055, 1.04, Final R indexes (R_1 and WR_2) 0.022, 0.055, No. of reflections 9967, No. of parameters 579, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$) 0.89, -0.65. CCDC 2322458

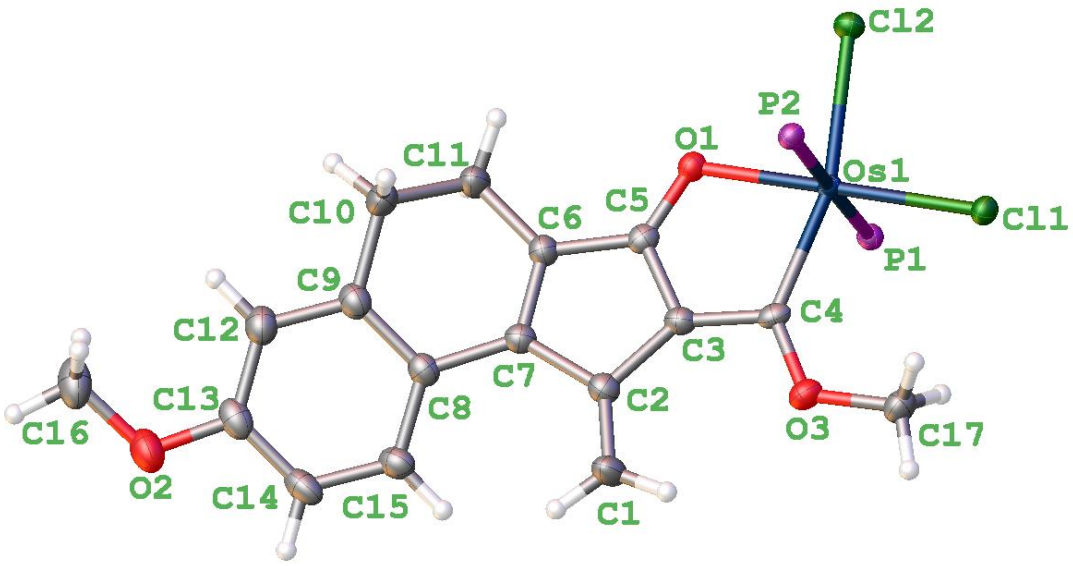


Figure S32. X-ray crystal structure of **10e** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S13. Bond lengths [Å] and angles [°] for **10e**.

Bond lengths [Å]			
Os1—Cl2	2.4368 (5)	C3—C2	1.480 (3)
Os1—Cl1	2.3559 (5)	C6—C11	1.487 (3)
Os1—P2	2.3986 (5)	C6—C7	1.366 (3)
Os1—P1	2.3922 (5)	C11—C10	1.532 (3)
Os1—O1	2.0890 (14)	C15—C14	1.394 (3)
Os1—C4	2.069 (2)	C15—C8	1.400 (3)
C9—C12	1.398 (3)	C8—C7	1.468 (3)
C9—C8	1.407 (3)	C7—C2	1.495 (3)
C9—C10	1.513 (3)	C1—C2	1.325 (3)
C13—C12	1.399 (3)	C5—C6	1.465 (3)
C13—C14	1.385 (4)	C5—C3	1.396 (3)
C4—C3	1.394 (3)	O2—C13	1.362 (3)
O3—C4	1.330 (2)	O2—C16	1.433 (4)
O3—C17	1.432 (3)	O1—C5	1.271 (3)

Bond angles [°]			
Cl1—Os1—Cl2	95.902 (17)	C1—C2—C3	126.7 (2)
Cl1—Os1—P2	90.585 (18)	C1—C2—C7	128.8 (2)
Cl1—Os1—P1	88.649 (18)	C3—C2—C7	104.31 (18)
P2—Os1—Cl2	89.495 (18)	C6—C7—C8	120.2 (2)
P1—Os1—Cl2	90.163 (18)	C6—C7—C2	109.92 (19)
P1—Os1—P2	179.126 (17)	C8—C7—C2	129.82 (19)
O1—Os1—Cl2	84.32 (4)	C12—C9—C8	120.6 (2)
O1—Os1—Cl1	179.57 (4)	C12—C9—C10	119.5 (2)
O1—Os1—P2	89.79 (4)	C8—C9—C10	119.8 (2)
O1—Os1—P1	90.98 (4)	O2—C13—C12	124.9 (2)
C4—Os1—Cl2	163.65 (6)	O2—C13—C14	115.4 (2)
C4—Os1—Cl1	100.43 (6)	C14—C13—C12	119.7 (2)
C4—Os1—P2	89.68 (6)	C5—C6—C11	128.70 (19)
C4—Os1—P1	90.88 (6)	C7—C6—C5	108.17 (19)
C4—Os1—O1	79.35 (7)	C7—C6—C11	123.1 (2)
O3—C4—Os1	135.75 (16)	C6—C11—C10	108.91 (19)
O3—C4—C3	112.04 (18)	C5—C3—C2	108.39 (19)
C3—C4—Os1	112.20 (14)	C4—C3—C5	114.15 (19)
C4—O3—C17	122.49 (17)	C4—C3—C2	137.2 (2)
C13—O2—C16	117.3 (2)	C9—C8—C7	117.4 (2)
C5—O1—Os1	111.90 (13)	C15—C8—C9	118.6 (2)
O1—C5—C6	128.43 (19)	C15—C8—C7	124.0 (2)
O1—C5—C3	122.37 (19)	C14—C15—C8	120.5 (2)
C3—C5—C6	109.16 (18)	C9—C12—C13	119.9 (2)
C13—C14—C15	120.7 (2)	C9—C10—C11	112.5 (2)

Crystal data for 10f:

Chemical formula $C_{53}H_{45}Cl_2O_3OsP_2$, M_r 1052.93, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 200, a, b, c (Å) 10.5154 (7), 27.4387 (18), 17.2779 (12), β (°) 92.345 (3), Z 4, Radiation type Ga $K\alpha$, λ = 1.34139 Å, μ (mm^{-1}) 4.53, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 62700, 10203, 7924, R_{int} 0.077, $(\sin\theta/\lambda)_{max}$ ($Å^{-1}$) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.044, 0.117,

1.05, Final *R* indexes (R_1 and wR_2) 0.044, 0.117, No. of reflections 10203, No. of parameters 540, No. of restraints 168, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.34, -1.49. CCDC 2322459

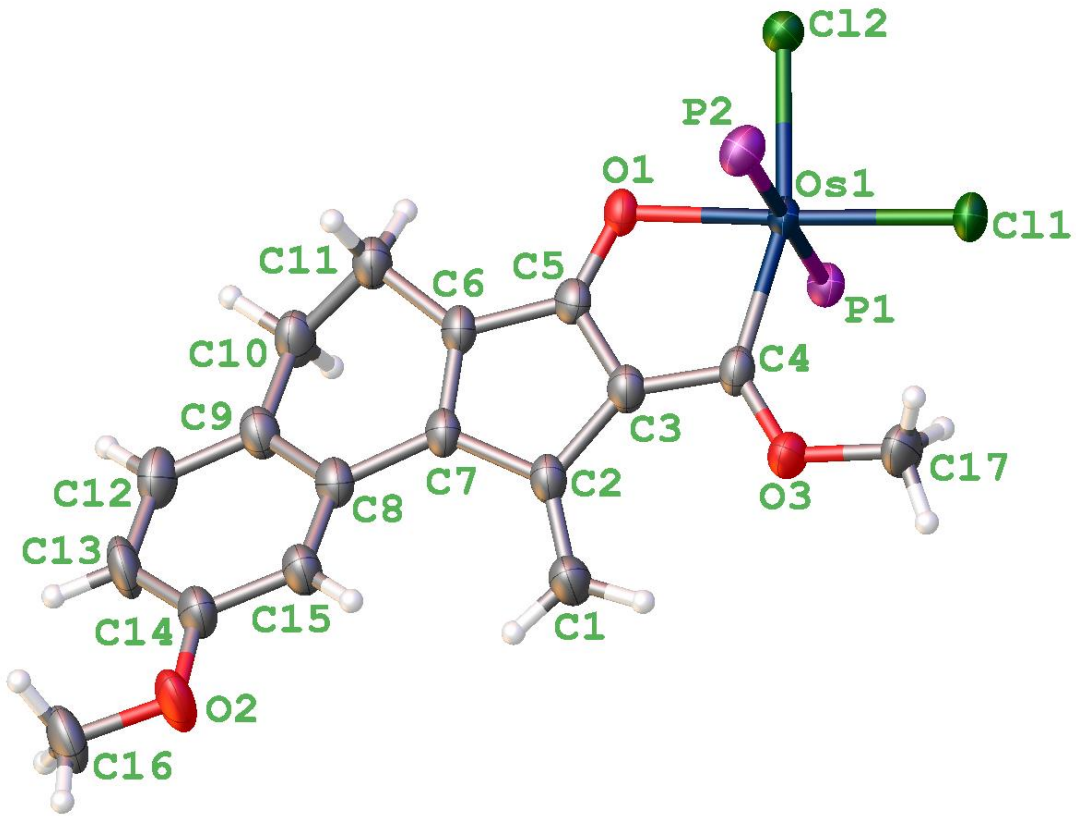


Figure S33. X-ray crystal structure of **10f** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S14. Bond lengths [Å] and angles [°] for **10f**.

Bond lengths [Å]			
Os1—Cl2	2.4298 (11)	C2—C1	1.329 (7)
Os1—Cl1	2.3485 (11)	C15—C14	1.394 (7)
Os1—P1	2.4075 (13)	C12—C13	1.405 (8)
Os1—P2	2.3967 (13)	C5—C6	1.458 (6)
Os1—O1	2.075 (3)	C8—C15	1.389 (7)
Os1—C4	2.056 (5)	C8—C9	1.423 (7)
O1—C5	1.273 (5)	C11—C6	1.497 (6)
O3—C4	1.335 (5)	C11—C10	1.516 (7)
O3—C17	1.440 (5)	C3—C2	1.472 (6)
O2—C14	1.391 (6)	C9—C10	1.500 (7)
O2—C16	1.422 (6)	C9—C12	1.384 (7)
C4—C3	1.398 (6)	C14—C13	1.369 (8)

C7—C6	1.356 (7)	C5—C3	1.399 (6)
C7—C2	1.503 (6)	C7—C8	1.472 (6)
Bond angles [°]			
Cl1—Os1—Cl2	94.41 (4)	C15—C8—C7	123.4 (4)
Cl1—Os1—P1	89.41 (4)	C15—C8—C9	120.2 (4)
Cl1—Os1—P2	90.73 (5)	C9—C8—C7	116.3 (4)
P1—Os1—Cl2	90.17 (4)	C3—C2—C7	104.3 (4)
P2—Os1—Cl2	89.82 (4)	C1—C2—C7	128.4 (5)
P2—Os1—P1	179.86 (4)	C1—C2—C3	126.9 (4)
O1—Os1—Cl2	83.17 (9)	C8—C15—C14	120.3 (5)
O1—Os1—Cl1	177.38 (9)	C8—C9—C10	120.2 (4)
O1—Os1—P1	89.57 (9)	C12—C9—C8	117.5 (5)
O1—Os1—P2	90.29 (9)	C14—C13—C12	118.9 (5)
C4—Os1—Cl2	162.98 (12)	C9—C12—C13	122.4 (5)
C4—Os1—Cl1	102.60 (12)	C9—C10—C11	112.3 (4)
C4—Os1—P1	90.27 (14)	O2—C14—C15	114.5 (5)
C4—Os1—P2	89.69 (14)	C13—C14—O2	124.7 (5)
C4—Os1—O1	79.82 (15)	C13—C14—C15	120.8 (5)
C7—C6—C5	108.3 (4)	C12—C9—C10	122.3 (5)
C7—C6—C11	123.6 (4)	O1—C5—C3	122.0 (4)
C5—C6—C11	128.0 (4)	O1—C5—C6	128.6 (4)
C5—O1—Os1	112.1 (3)	C3—C5—C6	109.4 (4)
C4—O3—C17	121.1 (4)	C6—C11—C10	108.6 (4)
C14—O2—C16	117.2 (4)	C4—C3—C5	114.1 (4)
O3—C4—Os1	134.3 (3)	C4—C3—C2	137.7 (4)
O3—C4—C3	113.6 (4)	C5—C3—C2	108.1 (4)
C3—C4—Os1	112.1 (3)	C6—C7—C8	120.0 (4)
C6—C7—C2	109.8 (4)	C8—C7—C2	130.2 (4)

Crystal data for 10g:

Chemical formula $C_{53}H_{45}Cl_2O_3OsP_2 \cdot CH_2Cl_2$, M_r 1137.85, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 205, *a*, *b*, *c* (Å) 11.3265 (10), 18.5288 (15), 24.285 (2), β (°) 101.623 (4), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.19, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction

Multi-scan, T_{min}, T_{max} 0.600, 0.751, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 96893, 10253, 8791, R_{int} 0.066, $(\sin\theta/\lambda)_{max}$ ($Å^{-1}$) 0.628, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.041, 0.099, 1.07, Final R indexes (R_1 and WR_2) 0.041, 0.099, No. of reflections 10253, No. of parameters 579, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$) 1.09, -1.86. CCDC 2322464

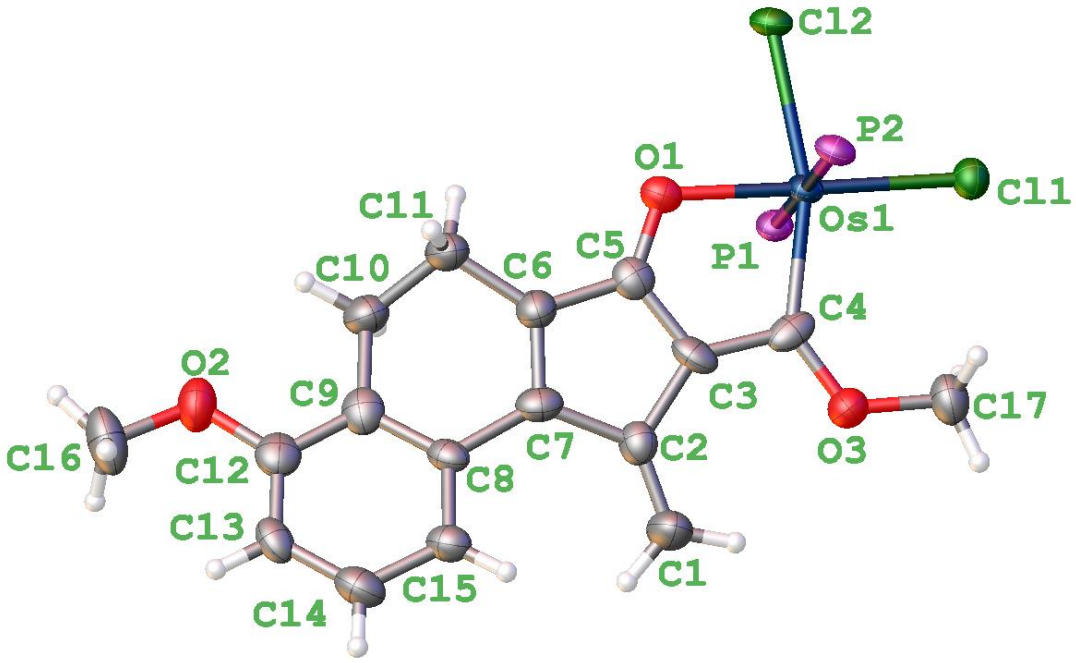


Figure S34. X-ray crystal structure of **10g** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S15. Bond lengths [Å] and angles [°] for **10g**.

Bond lengths [Å]			
Os1—Cl2	2.4291 (10)	C9—C12	1.370 (7)
Os1—Cl1	2.3590 (11)	C9—C10	1.538 (7)
Os1—P1	2.3975 (11)	C7—C6	1.348 (7)
Os1—P2	2.3935 (11)	C15—C14	1.409 (7)
Os1—O1	2.065 (3)	C13—C12	1.350 (7)
Os1—C4	2.070 (5)	C13—C14	1.409 (8)
C8—C9	1.391 (7)	C6—C11	1.487 (7)
C8—C7	1.497 (7)	C11—C10	1.540 (7)
C8—C15	1.408 (6)	C2—C3	1.507 (6)
C3—C5	1.375 (7)	C2—C1	1.299 (7)
C5—C6	1.456 (7)	C2—C7	1.492 (7)
C4—C3	1.417 (7)	O1—C5	1.273 (6)

O2—C12	1.390 (6)	O3—C4	1.337 (5)
O2—C16	1.420 (7)	O3—C17	1.447 (6)
Bond angles [°]			
Cl1—Os1—Cl2	95.84 (4)	C15—C14—C13	119.9 (5)
Cl1—Os1—P1	90.80 (4)	C6—C11—C10	108.2 (4)
Cl1—Os1—P2	89.64 (4)	C4—C3—C2	137.2 (5)
P1—Os1—Cl2	88.53 (4)	C5—C3—C4	114.1 (4)
P2—Os1—Cl2	90.96 (4)	C5—C3—C2	108.6 (4)
P2—Os1—P1	179.36 (4)	O1—C5—C3	122.3 (5)
O1—Os1—Cl2	83.44 (9)	C9—C8—C7	117.7 (4)
O1—Os1—Cl1	178.68 (9)	C9—C8—C15	121.3 (4)
O1—Os1—P1	90.29 (9)	C15—C8—C7	121.0 (4)
O1—Os1—P2	89.26 (9)	O1—C5—C6	127.6 (4)
O1—Os1—C4	79.44 (16)	C3—C5—C6	110.1 (4)
C4—Os1—Cl2	162.79 (14)	C8—C9—C10	119.3 (4)
C4—Os1—Cl1	101.31 (14)	C12—C9—C8	119.5 (5)
C4—Os1—P1	89.75 (12)	C12—C9—C10	121.2 (5)
C4—Os1—P2	90.62 (12)	C2—C7—C8	129.3 (4)
C1—C2—C3	126.6 (5)	C6—C7—C2	112.1 (5)
C1—C2—C7	131.1 (5)	C6—C7—C8	118.6 (4)
C7—C2—C3	101.9 (4)	C5—C6—C11	128.4 (4)
O3—C4—Os1	136.7 (4)	C7—C6—C5	107.3 (4)
O3—C4—C3	112.0 (4)	C7—C6—C11	124.2 (5)
C3—C4—Os1	111.3 (3)	C14—C15—C8	117.4 (5)
C5—O1—Os1	112.8 (3)	C12—C13—C14	120.5 (5)
C4—O3—C17	120.8 (4)	C9—C12—O2	115.1 (5)
C12—O2—C16	118.0 (5)	C13—C12—O2	123.4 (5)
C13—C12—C9	121.4 (5)		

Crystal data for 10h:

Chemical formula $C_{50}H_{41}Cl_2O_2OsP_2S{\cdot}CH_2Cl_2$, M_r 1113.85, Crystal system, space group Triclinic, $P\bar{1}$, Temperature (K) 200, *a*, *b*, *c* (Å) 12.4068 (6), 13.6521 (6), 14.7452 (6), α, β, γ (°) 78.966 (2), 79.775 (2), 72.266 (2), *Z* 2, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.85, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker

APEX-II CCD, Absorption correction Multi-scan, T_{min}, T_{max} 0.600, 0.751, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 41655, 9480, 8627, R_{int} 0.044, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.036, 0.101, 1.06, Final R indexes (R_1 and WR_2) 0.036, 0.101, No. of reflections 9480, No. of parameters 551, No. of restraints 25, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.60, -1.77. CCDC 2322465

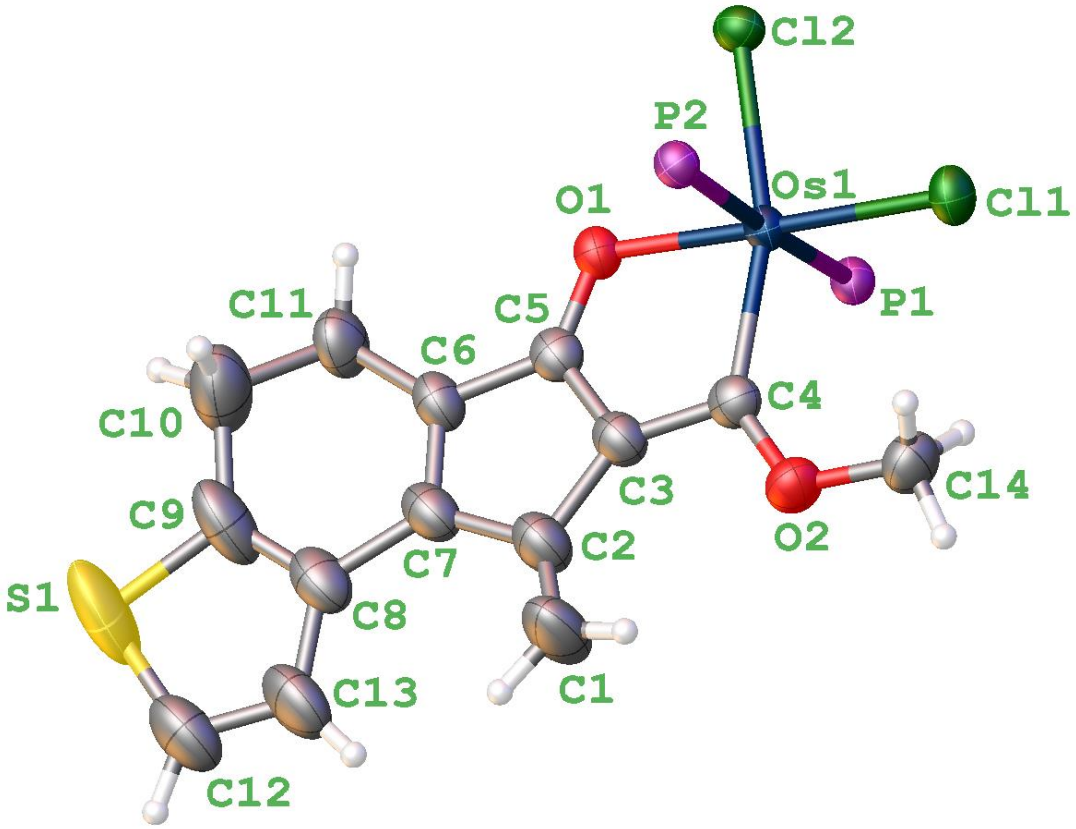


Figure S35. X-ray crystal structure of **10h** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S16. Bond lengths [Å] and angles [°] for **10h**.

Bond lengths [Å]			
Os1—Cl2	2.4269 (10)	C6—C7	1.359 (7)
Os1—P2	2.4030 (9)	C6—C11	1.497 (7)
Os1—Cl1	2.3446 (10)	C2—C7	1.491 (8)
Os1—P1	2.4073 (9)	C2—C1	1.304 (8)
Os1—O1	2.078 (3)	C7—C8	1.469 (7)
Os1—C4	2.056 (4)	C8—C9	1.325 (9)
C3—C5	1.382 (7)	C8—C13	1.427 (9)
C3—C4	1.414 (6)	C9—C10	1.509 (11)
C3—C2	1.479 (7)	C11—C10	1.534 (9)

C5—C6	1.469 (6)	C13—C12	1.344 (9)
O2—C4	1.328 (5)	S1—C12	1.712 (8)
O2—C14	1.440 (6)	O1—C5	1.262 (5)
S1—C9	1.728 (6)		

Bond angles [°]			
P2—Os1—Cl2	89.59 (3)	C9—C8—C7	117.0 (6)
P2—Os1—P1	176.83 (3)	C9—C8—C13	113.2 (6)
Cl1—Os1—Cl2	96.43 (4)	C13—C8—C7	129.7 (6)
Cl1—Os1—P2	88.64 (3)	C8—C9—S1	111.4 (5)
Cl1—Os1—P1	91.48 (3)	C8—C9—C10	125.3 (6)
P1—Os1—Cl2	87.26 (3)	C10—C9—S1	122.8 (5)
O1—Os1—Cl2	82.44 (8)	O2—C4—Os1	135.9 (3)
O1—Os1—P2	90.35 (8)	O2—C4—C3	112.9 (4)
O1—Os1—Cl1	178.49 (8)	C3—C4—Os1	111.1 (3)
O1—Os1—P1	89.47 (8)	C5—C3—C4	114.3 (4)
C4—Os1—Cl2	162.32 (13)	C5—C3—C2	108.5 (4)
C4—Os1—P2	89.23 (12)	C4—C3—C2	137.0 (5)
C4—Os1—Cl1	101.18 (13)	O1—C5—C3	122.7 (4)
C4—Os1—P1	93.85 (12)	O1—C5—C6	127.5 (4)
C4—Os1—O1	79.92 (15)	C3—C5—C6	109.7 (4)
C6—C11—C10	109.7 (5)	C6—C7—C2	110.9 (4)
C12—C13—C8	112.2 (7)	C6—C7—C8	119.1 (5)
C13—C12—S1	111.6 (6)	C8—C7—C2	130.0 (5)
C9—C10—C11	109.9 (6)	C5—C6—C11	128.4 (4)
C12—S1—C9	91.3 (3)	C7—C6—C5	107.1 (4)
C5—O1—Os1	111.8 (3)	C7—C6—C11	124.4 (4)
C4—O2—C14	121.0 (4)	C3—C2—C7	103.7 (4)
C1—C2—C7	126.8 (5)	C1—C2—C3	128.3 (5)

Crystal data for 11a:

Chemical formula $C_{48}H_{43}Cl_2OOsP_2$, M_r 958.86, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 200, *a*, *b*, *c* (Å) 18.7171 (5), 12.2770 (3), 21.0598 (5), β (°) 109.191 (1), *V* (Å^3) 4570.4 (2), *Z* 4, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 4.88, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD,

Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 59092, 9347, 8545, R_{int} 0.053, $(\sin\theta/\lambda)_{max}$ ($Å^{-1}$) 0.625, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.024, 0.070, 1.03, Final R indexes (R_1 and WR_2) 0.024, 0.070, No. of reflections 9347, No. of parameters 488, No. of restraints 24, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$) 0.88, -0.79. CCDC 2322457

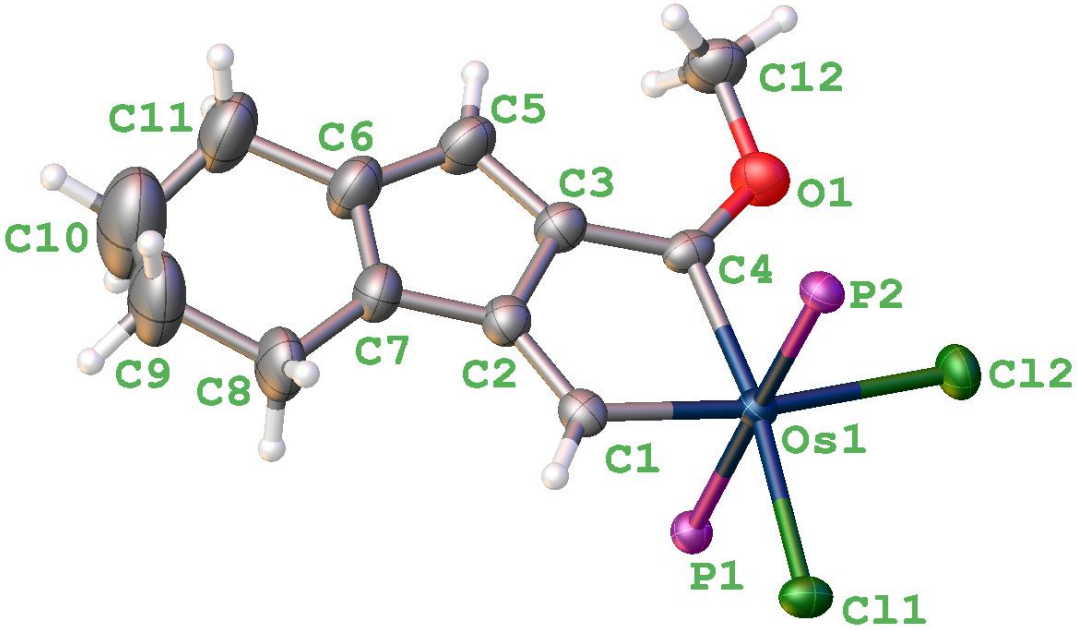


Figure S36. X-ray crystal structure of **11a** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S17. Bond lengths [Å] and angles [°] for **11a**.

Bond lengths [Å]			
Os1—Cl1	2.4166 (6)	C2—C7	1.432 (3)
Os1—P1	2.4153 (5)	C11—C10	1.481 (7)
Os1—P2	2.4045 (6)	C9—C10	1.468 (7)
Os1—Cl2	2.4342 (5)	C6—C11	1.508 (4)
Os1—C4	2.047 (3)	C8—C9	1.518 (5)
Os1—C1	2.005 (2)	C5—C6	1.423 (4)
C3—C2	1.448 (4)	C7—C6	1.390 (4)
C3—C5	1.406 (4)	C7—C8	1.509 (4)
C1—C2	1.361 (4)	O1—C12	1.429 (4)
O1—C4	1.320 (3)	C4—C3	1.431 (4)
Bond angles [°]			
Cl1—Os1—Cl2	98.49 (2)	C2—C1—Os1	116.99 (18)

P1—Os1—Cl1	88.666 (19)	C3—C5—C6	107.6 (3)
P1—Os1—Cl2	91.481 (19)	C4—C3—C2	112.0 (2)
P2—Os1—Cl1	89.297 (19)	C5—C3—C4	140.3 (3)
P2—Os1—P1	177.86 (2)	C5—C3—C2	107.5 (2)
P2—Os1—Cl2	89.480 (19)	C1—C2—C3	116.3 (2)
C4—Os1—Cl1	170.67 (7)	C1—C2—C7	136.0 (3)
C4—Os1—P1	91.56 (6)	C7—C2—C3	107.6 (2)
C4—Os1—P2	90.34 (6)	C4—O1—C12	121.1 (2)
C4—Os1—Cl2	90.82 (7)	O1—C4—Os1	120.53 (19)
C1—Os1—Cl1	91.23 (7)	O1—C4—C3	124.3 (2)
C1—Os1—P1	88.37 (6)	C3—C4—Os1	115.19 (19)
C1—Os1—P2	91.01 (6)	C10—C11—C6	110.7 (4)
C1—Os1—Cl2	170.27 (8)	C10—C9—C8	117.2 (4)
C1—Os1—C4	79.46 (10)	C9—C10—C11	117.5 (5)
C7—C8—C9	110.7 (3)	C2—C7—C8	128.2 (3)
C7—C6—C5	110.0 (3)	C6—C7—C2	107.3 (2)
C7—C6—C11	122.7 (3)	C6—C7—C8	124.6 (3)
C5—C6—C11	127.2 (3)		

Crystal data for 11b:

Chemical formula $3(C_{52}H_{43}Cl_2OOsP_2)\cdot CH_2Cl_2\cdot CH_4O$, M_r 3137.67, Crystal system, space group Monoclinic, *C*2/*c*, Temperature (K) 162, *a*, *b*, *c* (Å) 162, β (°) 103.248 (3), *V* (Å^3) 26587 (3), *Z* 8, Radiation type Ga *K*a, λ = 1.34139 Å, μ (mm^{-1}) 5.31, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 181811, 23002, 16808, R_{int} 0.151, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.591, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.046, 0.118, 1.00, Final *R* indexes (R_1 and WR_2) 0.046, 0.118, No. of reflections 23002, No. of parameters 1617, No. of restraints 120, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.22, -2.18. CCDC 2322421

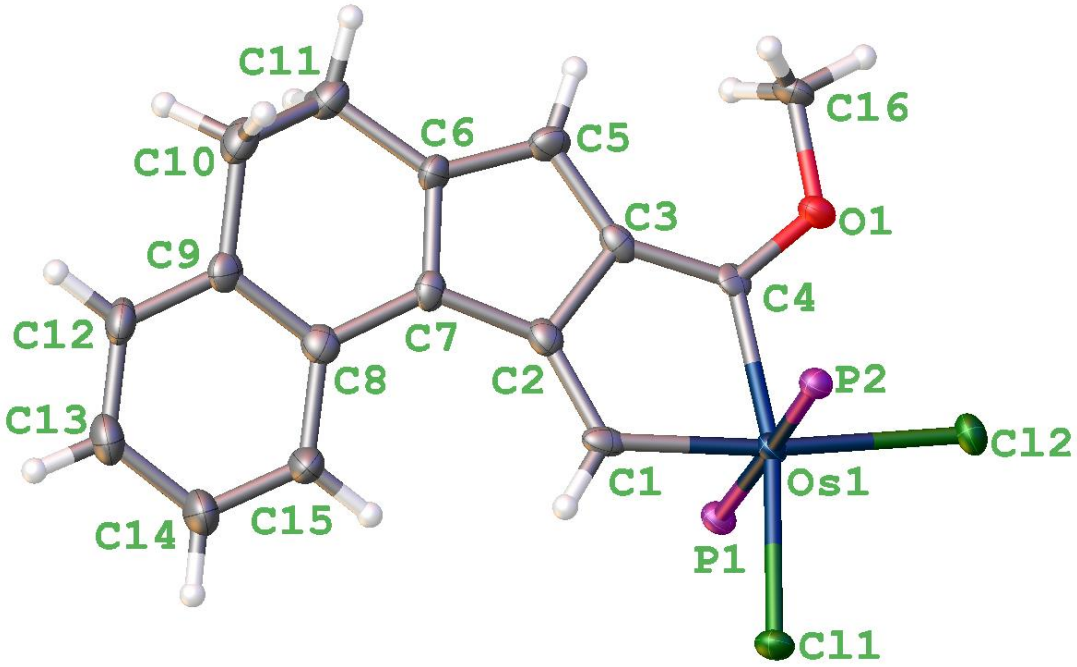


Figure S37. X-ray crystal structure of **11b** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S18. Bond lengths [Å] and angles [°] for **11b**.

Bond lengths [Å]			
Os1—Cl1	2.4274 (14)	C6—C5	1.420 (8)
Os1—Cl2	2.4246 (14)	C6—C11	1.490 (9)
Os1—P2	2.4095 (15)	C9—C12	1.381 (8)
Os1—P1	2.4174 (15)	C9—C8	1.401 (9)
Os1—C4	2.038 (6)	O1—C4	1.321 (7)
Os1—C1	1.989 (6)	O1—C16	1.456 (7)
C7—C6	1.402 (8)	C12—C13	1.373 (10)
C7—C2	1.444 (8)	C8—C15	1.405 (9)
C7—C8	1.465 (8)	C10—C11	1.525 (9)
C3—C2	1.465 (8)	C13—C14	1.390 (10)
C3—C5	1.398 (9)	C15—C14	1.384 (9)
C9—C10	1.518 (9)	C1—C2	1.394 (9)
C4—C3	1.418 (8)		
Bond angles [°]			
Cl2—Os1—Cl1	99.17 (5)	C7—C6—C5	109.6 (5)
P2—Os1—Cl1	87.44 (5)	C7—C6—C11	122.2 (5)

P2—Os1—Cl2	94.04 (5)	C5—C6—C11	128.1 (6)
P2—Os1—P1	176.92 (5)	C1—C2—C7	138.6 (6)
P1—Os1—Cl1	90.84 (5)	C1—C2—C3	114.4 (5)
P1—Os1—Cl2	88.75 (5)	C7—C2—C3	107.0 (5)
C4—Os1—Cl1	166.67 (17)	C12—C9—C8	118.8 (6)
C4—Os1—Cl2	93.82 (16)	C12—C9—C10	121.0 (6)
C4—Os1—P2	88.70 (16)	C8—C9—C10	120.0 (5)
C4—Os1—P1	92.41 (16)	C3—C5—C6	108.7 (5)
C1—Os1—Cl1	88.18 (18)	C13—C12—C9	122.3 (6)
C1—Os1—Cl2	172.15 (18)	C9—C8—C7	118.3 (6)
C1—Os1—P2	89.03 (17)	C9—C8—C15	118.8 (6)
C1—Os1—P1	88.37 (17)	C15—C8—C7	122.9 (6)
C1—Os1—C4	79.0 (2)	C14—C15—C8	121.4 (6)
C2—C1—Os1	118.0 (4)	C9—C10—C11	113.9 (5)
C4—O1—C16	121.3 (5)	C6—C11—C10	110.6 (6)
O1—C4—Os1	119.5 (4)	C15—C14—C13	119.0 (7)
O1—C4—C3	123.5 (5)	C12—C13—C14	119.7 (6)
C3—C4—Os1	117.0 (4)	C6—C7—C2	107.2 (5)
C4—C3—C2	111.6 (5)	C6—C7—C8	120.6 (6)
C5—C3—C4	141.0 (6)	C2—C7—C8	132.1 (6)
C5—C3—C2	107.4 (5)		

Crystal data for 12a:

Chemical formula $C_{47}H_{41}Cl_3OsP_2$, M_r 964.29, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 200, *a*, *b*, *c* (Å) 18.4428 (6), 12.3470 (4), 20.8281 (7), β (°) 97.411 (1), *V* (Å^3) 4703.2 (3), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.07, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 102515, 9639, 9116, R_{int} 0.053, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.055, 0.166, 1.04, Final *R* indexes (R_1 and WR_2) 0.055, 0.166, No. of reflections 9639, No. of parameters 511, No. of restraints 182, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.98, -1.34. CCDC 2322466

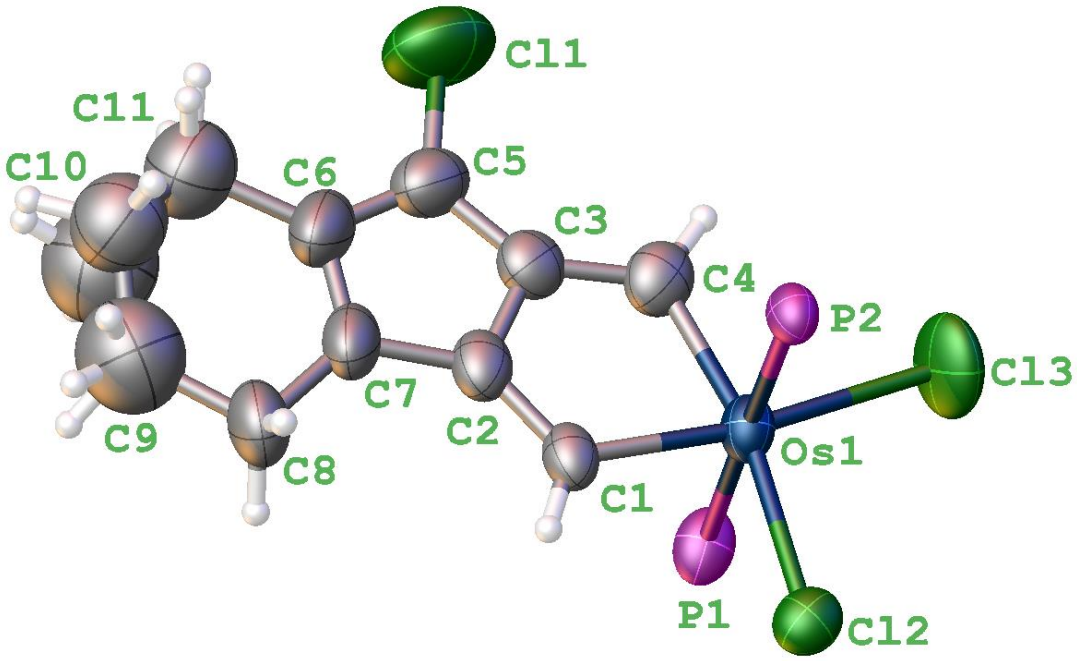


Figure S38. X-ray crystal structure of **12a** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S19. Bond lengths [Å] and angles [°] for **12a**.

Bond lengths [Å]			
Os1—P2	2.4112 (12)	C7—C6	1.415 (12)
Os1—Cl2	2.4109 (15)	C7—C8	1.580 (11)
Os1—P1	2.4090 (14)	C6—C5	1.380 (12)
Os1—Cl3	2.4249 (16)	C6—C11	1.525 (13)
Os1—C1	2.009 (5)	C8—C9	1.571 (14)
Os1—C4	1.989 (7)	C11—C10	1.53 (3)
C3—C2	1.443 (9)	C2—C1	1.390 (8)
C3—C4	1.385 (10)	C2—C7	1.425 (8)
C3—C5	1.412 (9)	Cl1—C5	1.728 (8)
C10—C9	1.40 (3)		
Bond angles [°]			
P2—Os1—Cl3	90.56 (6)	C3—C4—Os1	118.9 (6)
Cl2—Os1—P2	89.37 (4)	C2—C7—C8	126.6 (7)
Cl2—Os1—Cl3	100.13 (7)	C6—C7—C2	106.9 (7)
P1—Os1—P2	179.02 (5)	C6—C7—C8	126.4 (6)
P1—Os1—Cl2	89.66 (5)	C9—C8—C7	102.1 (8)
P1—Os1—Cl3	89.47 (7)	C7—C6—C11	122.6 (9)

C1—Os1—P2	89.47 (15)	C5—C6—C7	109.0 (6)
C1—Os1—Cl2	88.47 (18)	C5—C6—C11	128.3 (9)
C1—Os1—P1	90.65 (15)	C3—C5—Cl1	124.2 (7)
C1—Os1—Cl3	171.40 (18)	C6—C5—Cl1	125.9 (6)
C4—Os1—P2	90.50 (17)	C6—C5—C3	109.9 (7)
C4—Os1—Cl2	166.8 (2)	C4—C3—C2	111.9 (6)
C4—Os1—P1	90.48 (17)	C4—C3—C5	142.0 (7)
C4—Os1—Cl3	93.1 (2)	C5—C3—C2	106.1 (6)
C4—Os1—C1	78.3 (3)	C1—C2—C3	114.0 (5)
C6—C11—C10	108.8 (13)	C1—C2—C7	137.9 (7)
C2—C1—Os1	116.9 (4)	C7—C2—C3	108.1 (6)
C10—C9—C8	123.0 (15)	C9—C10—C11	112.7 (19)

Crystal data for 12b:

Chemical formula $C_{51}H_{40}Cl_3OsP_2$, M_r 1011.32, Crystal system, space group Orthorhombic, *Pnnm*, Temperature (K) 200, *a*, *b*, *c* (Å) 23.3599 (10), 12.6602 (5), 14.6191 (6), *V* (Å^3) 4323.5 (3), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.53, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 111697, 4620, 4605, R_{int} 0.140, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.055, 0.119, 1.36, Final *R* indexes (R_1 and WR_2) 0.055, 0.119, No. of reflections 4620, No. of parameters 287, No. of restraints 139, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.41, -1.27. CCDC 2322467

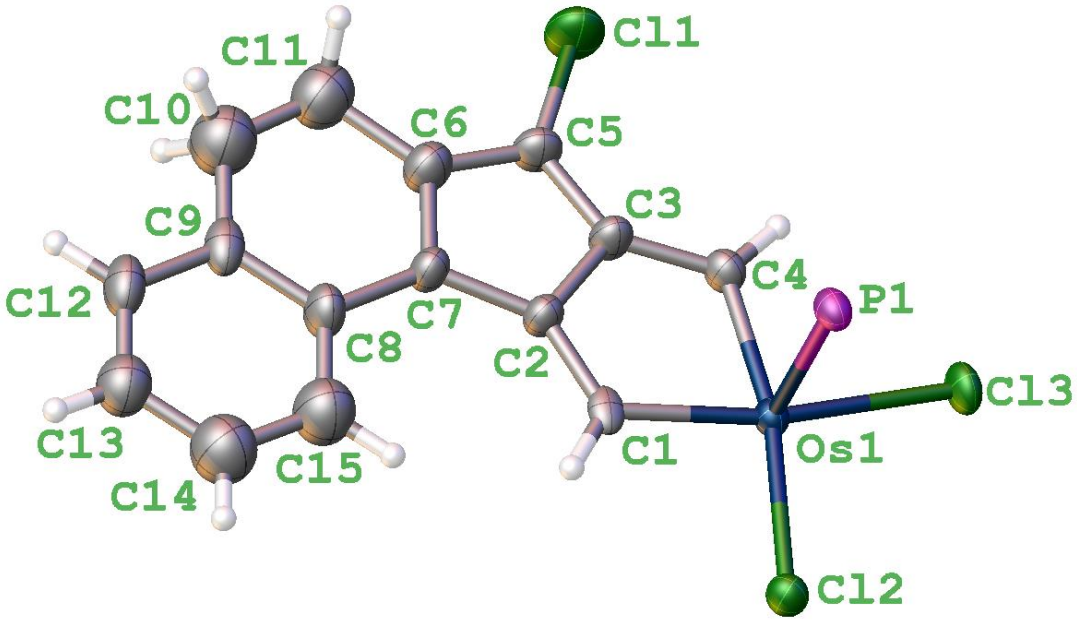


Figure S39. X-ray crystal structure of **12b** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S20. Bond lengths [Å] and angles [°] for **12b**.

Bond lengths [Å]			
Os1—P1^{i}	2.4030 (16)	C12—C13	1.371 (17)
Os1—P1	2.4031 (16)	C6—C5	1.391 (14)
Os1—Cl2	2.435 (2)	C6—C11	1.489 (16)
Os1—Cl3	2.428 (2)	C14—C13	1.387 (19)
Os1—C1	1.999 (8)	C14—C15	1.40 (2)
Os1—C4	2.013 (9)	C3—C5	1.397 (13)
C9—C12	1.405 (14)	C3—C4	1.392 (12)
C9—C10	1.461 (18)	C11—C10	1.443 (14)
C7—C6	1.408 (13)	C8—C7	1.479 (13)
Cl1—C5	1.735 (10)	C8—C9	1.393 (14)
C2—C7	1.431 (12)	C8—C15	1.392 (17)
C2—C1	1.411 (12)	C2—C3	1.448 (12)
Bond angles [°]			
P1^{i}—Os1—P1	173.43 (7)	C2—C7—C8	131.3 (9)
P1^{i}—Os1—Cl2	90.49 (4)	C6—C7—C2	108.1 (8)
P1—Os1—Cl2	90.49 (4)	C6—C7—C8	120.5 (9)
P1^{i}—Os1—Cl3	86.73 (4)	C7—C6—C11	122.9 (10)

P1—Os1—Cl3	86.73 (4)	C5—C6—C7	107.9 (9)
Cl3—Os1—Cl2	103.69 (8)	C5—C6—C11	129.2 (10)
C1—Os1—P1	93.26 (4)	C13—C14—C15	119.3 (15)
C1—Os1—P1^{i}	93.26 (4)	C5—C3—C2	106.6 (8)
C1—Os1—Cl2	88.4 (3)	C4—C3—C2	114.0 (8)
C1—Os1—Cl3	167.9 (3)	C4—C3—C5	139.4 (9)
C1—Os1—C4	79.9 (4)	C12—C13—C14	120.0 (12)
C4—Os1—P1	90.18 (4)	C6—C5—Cl1	123.7 (8)
C4—Os1—P1^{i}	90.18 (4)	C6—C5—C3	110.5 (9)
C4—Os1—Cl2	168.3 (3)	C3—C5—Cl1	125.7 (8)
C4—Os1—Cl3	88.0 (3)	C3—C4—Os1	116.3 (6)
C13—C12—C9	121.6 (11)	C8—C15—C14	120.6 (13)
C2—C1—Os1	116.3 (7)	C10—C11—C6	113.9 (12)
C8—C9—C10	120.8 (10)	C11—C10—C9	123.4 (13)
C12—C9—C10	120.7 (11)	C8—C9—C12	118.5 (11)
C7—C2—C3	106.9 (8)	C9—C8—C7	118.4 (9)
C1—C2—C7	139.6 (8)	C15—C8—C7	121.7 (10)
C1—C2—C3	113.5 (8)	C15—C8—C9	120.0 (10)

Symmetry code(s): (i) *x*, *y*, -*z*.

Crystal data for 12d:

Chemical formula $C_{51}H_{40}BrCl_2OsP_2$, M_r 1055.78, Crystal system, space group Orthorhombic, *Pnnm*, Temperature (K) 200, *a*, *b*, *c* (Å) 23.4797 (7), 12.6596 (4), 14.6894 (4), *V* (Å^3) 4366.3 (2), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 5.82, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 82503, 4665, 4614, R_{int} 0.054, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.039, 0.106, 1.20, Final *R* indexes (R_1 and WR_2) 0.039, 0.106, No. of reflections 4665, No. of parameters 293, No. of restraints 24, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.82, -1.63. CCDC 2322468

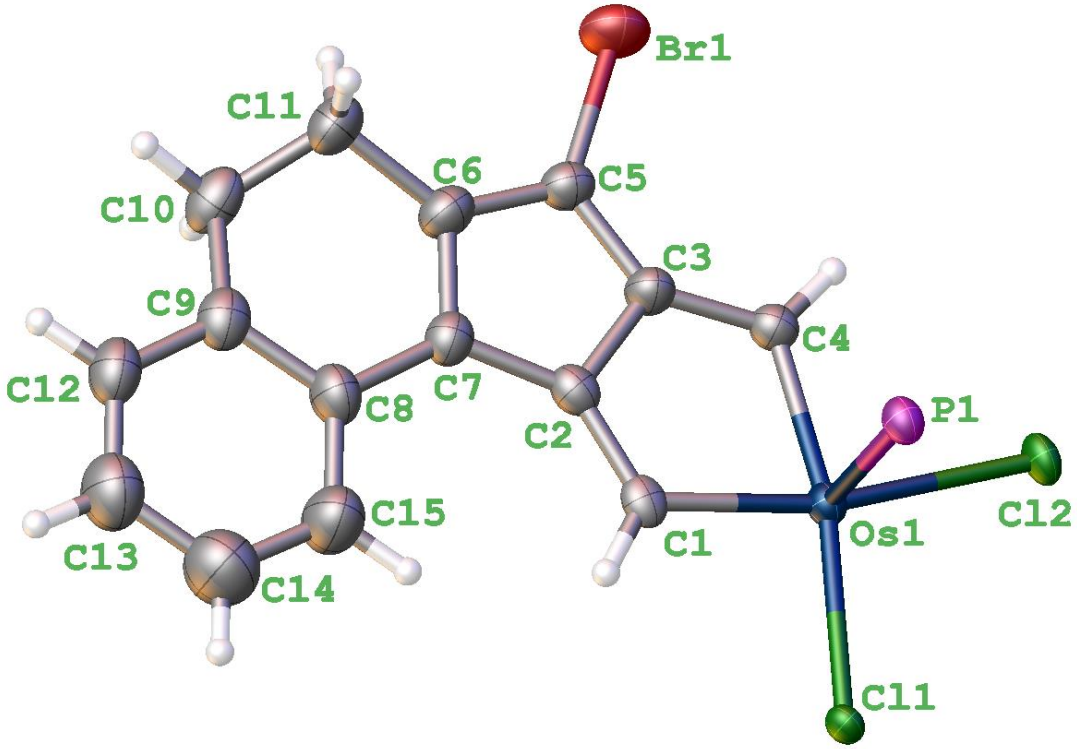


Figure S40. X-ray crystal structure of **12d** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S21. Bond lengths [Å] and angles [°] for **12d**.

Bond lengths [Å]			
Os1—Cl1	2.4745 (13)	C9—C12	1.393 (12)
Os1—Cl2	2.4667 (14)	C9—C10	1.534 (13)
Os1—P1^{i}	2.4066 (12)	C5—C3	1.409 (10)
Os1—P1	2.4066 (12)	C5—C6	1.391 (11)
Os1—C1	2.001 (6)	C6—C11	1.504 (12)
Os1—C4	2.016 (7)	C2—C3	1.458 (9)
Br1—C5	1.877 (7)	C2—C1	1.392 (10)
C7—C8	1.465 (10)	C2—C7	1.436 (10)
C7—C6	1.426 (10)	C3—C4	1.378 (10)
C8—C15	1.417 (13)	C14—C15	1.390 (14)
C13—C12	1.363 (14)	C10—C11	1.488 (18)
C13—C14	1.393 (16)	C9—C8	1.410 (11)
Bond angles [°]			
Cl2—Os1—Cl1	103.58 (5)	C12—C9—C8	117.9 (8)
P1^{i}—Os1—Cl1	90.49 (3)	C12—C9—C10	120.6 (8)

P1—Os1—Cl1	90.49 (3)	C2—C1—Os1	117.3 (5)
P1^{i}—Os1—Cl2	86.73 (3)	C5—C6—C7	107.3 (6)
P1—Os1—Cl2	86.73 (3)	C5—C6—C11	130.5 (8)
P1^{i}—Os1—P1	173.44 (5)	C7—C6—C11	121.2 (8)
C1—Os1—Cl1	89.2 (2)	C11—C10—C9	112.9 (9)
C1—Os1—Cl2	167.3 (2)	C10—C11—C6	109.8 (12)
C1—Os1—P1	93.25 (3)	C14—C15—C8	120.2 (10)
C1—Os1—P1^{i}	93.25 (3)	C15—C14—C13	119.5 (11)
C1—Os1—C4	78.9 (3)	C8—C9—C10	119.4 (7)
C4—Os1—Cl1	168.0 (2)	C2—C7—C8	130.9 (7)
C4—Os1—Cl2	88.4 (2)	C6—C7—C2	108.5 (6)
C4—Os1—P1^{i}	90.20 (3)	C6—C7—C8	120.6 (7)
C4—Os1—P1	90.19 (3)	C3—C4—Os1	117.4 (5)
C1—C2—C3	113.3 (6)	C9—C8—C7	117.5 (7)
C1—C2—C7	140.0 (6)	C9—C8—C15	119.6 (8)
C7—C2—C3	106.7 (6)	C15—C8—C7	122.9 (8)
C5—C3—C2	106.4 (6)	C12—C13—C14	120.2 (10)
C4—C3—C5	140.4 (7)	C13—C12—C9	122.5 (8)
C4—C3—C2	113.2 (6)	C6—C5—Br1	124.5 (6)
C3—C5—Br1	124.5 (6)	C6—C5—C3	111.1 (6)

Symmetry code(s): (i) *x*, *y*, *-z*.

Crystal data for 12f:

Chemical formula $C_{51}H_{40}Br_3OsP_2$, M_r 1144.70, Crystal system, space group Monoclinic, $P2_1/c$, Temperature (K) 200, *a*, *b*, *c* (Å) 12.0847 (3), 19.3058 (5), 19.0941 (5), β (°) 105.287 (1), *V* (Å^3) 4297.12 (19), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 6.60, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 91990, 8815, 7924, R_{int} 0.059, $(\sin\theta/\lambda)_{max}$ (Å^{-1}) 0.626, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.028, 0.066, 1.07, Final *R* indexes (R_1 and WR_2) 0.028, 0.066, No. of reflections 8815, No. of parameters 514, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.55, -1.19. CCDC 2322469

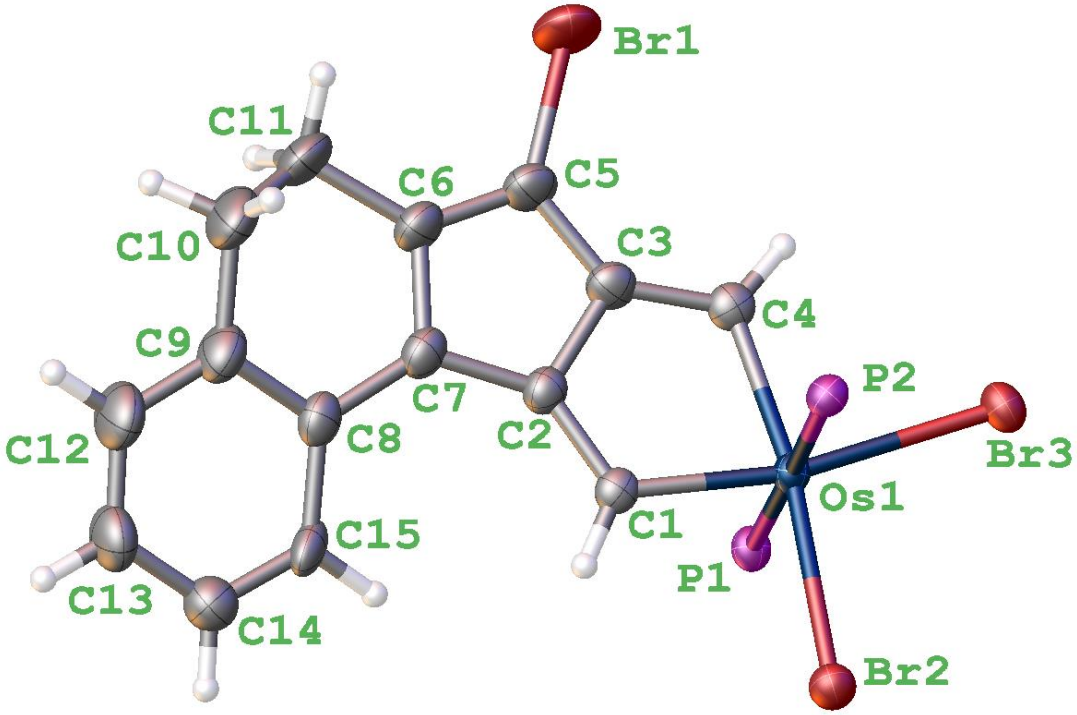


Figure S41. X-ray crystal structure of **12f** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S22. Bond lengths [Å] and angles [°] for **12f**.

Bond lengths [Å]			
Os1—Br2	2.5576 (4)	C7—C8	1.438 (5)
Os1—Br3	2.5599 (4)	C7—C6	1.427 (5)
Os1—P2	2.4345 (8)	C5—C6	1.387 (6)
Os1—P1	2.4070 (8)	C12—C13	1.364 (7)
Os1—C4	2.018 (4)	C1—C2	1.383 (5)
Os1—C1	1.995 (3)	C3—C4	1.380 (5)
Br1—C5	1.863 (4)	C3—C2	1.450 (5)
C9—C12	1.398 (6)	C3—C5	1.420 (5)
C9—C10	1.517 (7)	C2—C7	1.438 (5)
C8—C9	1.412 (5)	C15—C8	1.437 (6)
C6—C11	1.499 (6)	C15—C14	1.313 (6)
C14—C13	1.403 (6)	C11—C10	1.509 (8)
Bond angles [°]			
Br2—Os1—Br3	100.747 (13)	C9—C8—C7	117.3 (4)
P2—Os1—Br2	90.15 (2)	C14—C15—C8	121.9 (4)

P2—Os1—Br3	89.55 (2)	C8—C7—C2	131.5 (3)
P1—Os1—Br2	90.14 (2)	C6—C7—C2	106.8 (3)
P1—Os1—Br3	91.71 (2)	C6—C7—C8	121.6 (3)
P1—Os1—P2	178.63 (3)	C3—C5—Br1	125.3 (3)
C4—Os1—Br2	169.53 (10)	C6—C5—Br1	125.3 (3)
C4—Os1—Br3	89.15 (10)	C6—C5—C3	109.4 (3)
C4—Os1—P2	86.48 (10)	C6—C11—C10	110.2 (4)
C4—Os1—P1	93.01 (10)	C11—C10—C9	113.4 (4)
C1—Os1—Br2	90.93 (10)	C7—C6—C11	120.0 (4)
C1—Os1—Br3	168.32 (10)	C5—C6—C7	109.3 (3)
C1—Os1—P2	90.63 (9)	C2—C1—Os1	117.5 (3)
C1—Os1—P1	88.03 (9)	C15—C8—C7	124.7 (3)
C1—Os1—C4	79.21 (14)	C9—C8—C15	117.9 (4)
C15—C14—C13	120.3 (4)	C1—C2—C3	112.9 (3)
C4—C3—C2	114.3 (3)	C1—C2—C7	139.0 (3)
C4—C3—C5	138.8 (4)	C7—C2—C3	107.7 (3)
C5—C3—C2	106.7 (3)	C12—C9—C8	118.4 (4)
C3—C4—Os1	115.9 (3)	C12—C9—C10	121.9 (4)
C12—C13—C14	120.2 (4)	C5—C6—C11	130.7 (4)
C13—C12—C9	121.3 (4)	C8—C9—C10	119.6 (4)

Crystal data for 13:

Chemical formula $C_{52}H_{42}Cl_3OOsP_2 \cdot 2(CHCl_3)$, M_r 1280.08, Crystal system, space group Triclinic, $P\bar{1}$, Temperature (K) 100, *a*, *b*, *c* (Å) 11.9859 (11), 14.5601 (14), 17.6542 (16), α, β, γ (°) 69.024 (4), 73.548 (4), 66.395 (4), *V* (Å^3) 2600.6 (4), *Z* 4, Radiation type Ga *K*α, λ = 1.34139 Å, μ (mm^{-1}) 6.55, Crystal size (mm) 0.3 × 0.2 × 0.2, Diffractometer Bruker *APEX*-II CCD, Absorption correction Multi-scan, No. of measured, independent and observed [$I > 2\sigma(I)$] reflections 16795, 8917, 7704, R_{int} 0.050, $(\sin \theta/\lambda)_{max}$ (Å^{-1}) 0.595, $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* 0.040, 0.104, 1.05, Final *R* indexes (R_1 and WR_2) 0.040, 0.104, No. of reflections 8917, No. of parameters 605, $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3}) 1.61, -2.03. CCDC 2354505.

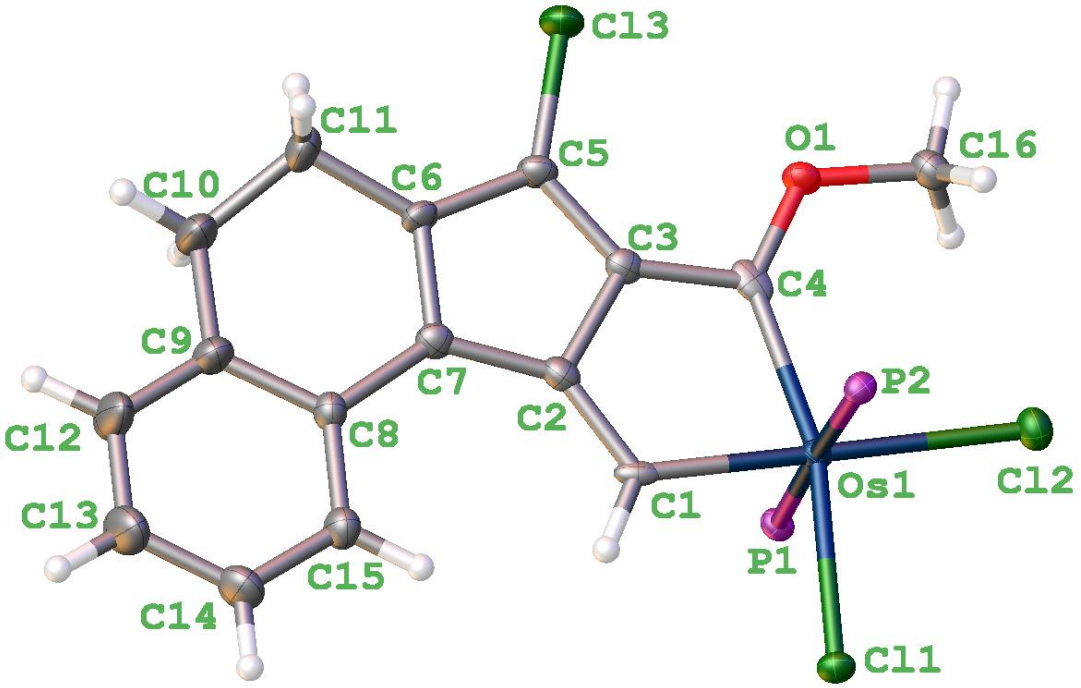


Figure S42. X-ray crystal structure of **13** shown with thermal ellipsoids at the 50% probability level. The phenyl moieties in PPh_3 and the hydrogen atoms are omitted for clarity.

Table S23. Bond lengths [Å] and angles [°] for **13**.

Bond lengths [Å]			
Os1—Cl1	2.4326 (11)	C10—C11	1.486 (8)
Os1—Cl2	2.4386 (12)	C10—C9	1.525 (8)
Os1—P2	2.4047 (11)	C14—C13	1.391 (9)
Os1—P1	2.3993 (11)	C9—C12	1.382 (8)
Os1—C1	2.020 (5)	O1—C4	1.334 (6)
Os1—C4	2.052 (5)	O1—C16	1.460 (6)
C7—C8	1.468 (6)	C3—C2	1.452 (6)
C7—C2	1.437 (7)	C3—C5	1.399 (7)
C7—C6	1.405 (7)	C3—C4	1.423 (7)
C1—C2	1.364 (7)	C15—C14	1.389 (7)
C8—C15	1.398 (7)	C13—C12	1.397 (9)
C8—C9	1.410 (7)	C6—C5	1.433 (7)
Cl3—C5	1.721 (5)	C6—C11	1.478 (7)
Bond angles [°]			
Cl1—Os1—Cl2	94.75 (4)	C7—C2—C3	107.3 (4)
P2—Os1—Cl1	89.87 (4)	C1—C2—C3	113.2 (4)

P2—Os1—Cl2	88.53 (4)	C1—C2—C7	139.5 (4)
P1—Os1—Cl1	88.74 (4)	C14—C15—C8	120.5 (5)
P1—Os1—Cl2	90.64 (4)	C15—C14—C13	120.1 (5)
P1—Os1—P2	178.31 (4)	C7—C6—C5	107.8 (4)
C1—Os1—Cl1	85.27 (13)	C7—C6—C11	123.2 (4)
C1—Os1—Cl2	178.86 (12)	C5—C6—C11	128.9 (4)
C1—Os1—P2	90.33 (12)	C3—C5—Cl3	127.4 (4)
C1—Os1—P1	90.50 (12)	C3—C5—C6	109.4 (4)
C1—Os1—C4	79.43 (18)	C6—C5—Cl3	123.2 (4)
C4—Os1—Cl1	164.70 (14)	C4—O1—C16	122.5 (4)
C4—Os1—Cl2	100.55 (14)	C5—C3—C2	107.2 (4)
C4—Os1—P2	90.52 (12)	C5—C3—C4	137.3 (4)
C4—Os1—P1	91.08 (12)	C4—C3—C2	115.5 (4)
O1—C4—Os1	135.1 (4)	C14—C13—C12	119.1 (5)
O1—C4—C3	111.3 (4)	C9—C12—C13	121.6 (6)
C3—C4—Os1	113.6 (3)	C11—C10—C9	114.6 (6)
C9—C8—C7	117.3 (5)	C2—C7—C8	131.4 (4)
C6—C11—C10	110.8 (5)	C6—C7—C8	120.3 (4)
C8—C9—C10	120.0 (5)	C6—C7—C2	108.3 (4)
C12—C9—C8	118.9 (5)	C2—C1—Os1	118.3 (3)
C12—C9—C10	121.0 (6)	C15—C8—C7	123.0 (5)
C15—C8—C9	119.6 (5)		

11. Computational methods

All calculations were conducted by using the DFT methods with Gaussian16 package. [2] Complexes **7a**, **8**, **9**, **10a**, **11a**, **12a** and **13** are simplified through the way that the PH_3 groups were used to replace the PPh_3 ligands, which are named simplified model complexes **7a′**, **8′**, **9′**, **10a′**, **11a′**, **12a′** and **13′**. In this system, B3LYP[3,4]-GD3BJ[5] was selected for the mechanistic study, [6] 6-311++G(d,p) was used for C, H and O atoms, Lanl2DZ[7] was used for Cl, Os, P atoms. Polarization functions were added for Os(ζ-(f)

= 0.886), Cl(ζ(d) = 0.514) and P(ζ(d) = 0.340). Herein, we selected SMD[8] as the reaction solvent model and THF as solvent. We performed frequency calculations to confirm if the numbers of imaginary frequencies associated with the local minima and transition state are correct. Condensed Fukui Function (CFF) calculations[9] are obtained at the CAM-B3LYP/6-311++G(d,p) ~ Lanl2DZ computational level. We scanned the C-O bond lengths (scanning 7 points at 0.1 Å intervals) in the process of forming **Int3** (Figure S43), and their energies increased and then decreased, indicating the existence of a transition state in this process, but we could not find it.

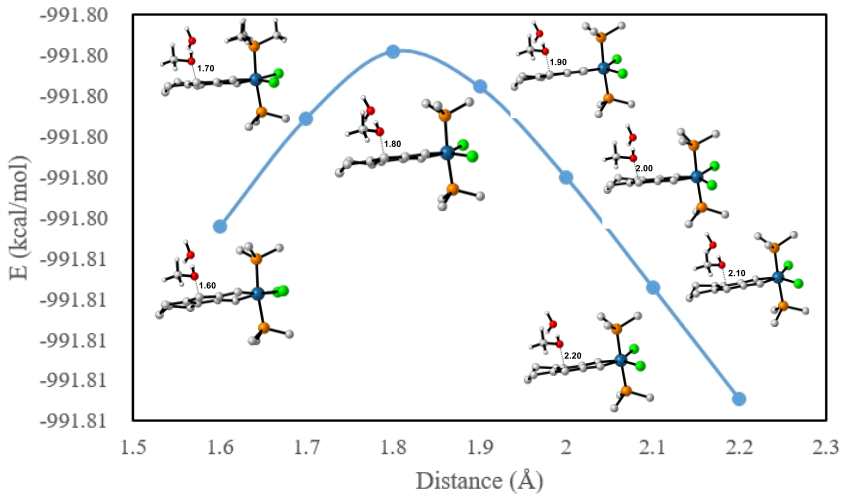


Figure S43. The energy change corresponds to scanning the C-O bond.

Cartesian coordinates

6

O	-1.69348300	-0.47694100	-1.17738900
C	-1.81802900	-0.27812700	1.22530200
C	-0.10685900	1.90456300	-0.18494800
C	-2.40048700	0.16491600	2.18028100
H	-2.91007100	0.57406000	3.02218500
C	-1.10827700	-0.85051800	0.06964400
C	-0.78931900	2.89828400	-0.23715800
C	0.36554300	-0.47178800	0.06077800
C	0.78741000	0.79809600	-0.10192400
C	2.26246300	1.15859600	-0.19690200
H	2.55480200	1.66520700	0.73149200
H	2.38887800	1.89429900	-0.99644400
C	1.31578500	-1.62765200	0.23286400
H	0.95111600	-2.25642300	1.05356400

H	1.26007300	-2.25697500	-0.66703100
C	2.75999300	-1.20002800	0.49473800
H	2.85565900	-0.86297000	1.53342800
H	3.42821300	-2.05670400	0.37213800
C	3.15398100	-0.05846900	-0.44083600
H	3.04525300	-0.38791600	-1.48080600
H	4.20217400	0.21892700	-0.29908500
H	-1.41993000	3.75549600	-0.28505600
H	-1.17123600	-1.94347200	0.16680200
C	-3.01547900	-0.97568900	-1.35057100
H	-3.04209400	-2.06921900	-1.25514800
H	-3.71109700	-0.53656200	-0.62653800
H	-3.32423000	-0.69533400	-2.35799100

$OsCl_2(PMe_3)_2$

Os	0.00113300	-0.31507000	0.10162900
Cl	-0.00109700	-1.18903700	-2.22474400
Cl	0.00292800	0.09306700	2.55136900
P	-0.00381700	1.86877700	-0.36898000
P	2.35522900	-0.56200600	0.08887600
P	-2.35256800	-0.56634600	0.09144500
C	2.74764200	-2.37245700	0.16094000
H	3.82686300	-2.54509600	0.15734400
H	2.31911400	-2.79455300	1.07318200
H	2.29535000	-2.86631200	-0.70092000
C	3.38511300	0.09378400	1.47643500
H	4.41566400	-0.25767800	1.38228200
H	3.37419900	1.18363400	1.47162800
H	2.96207300	-0.25025400	2.42061000
C	3.29435900	-0.02750700	-1.41083900
H	4.32772500	-0.38027800	-1.36598600
H	2.80131500	-0.43866700	-2.29219600
H	3.29362100	1.06109500	-1.48221600
C	1.41958700	2.86449600	0.26827500
H	2.34932400	2.53998500	-0.19754300
H	1.26408500	3.92334400	0.04716500
H	1.49057600	2.72457300	1.34744200
C	-0.02674800	2.31937300	-2.16070400
H	-0.02984900	3.40635000	-2.27687500
H	0.85224400	1.89920600	-2.65019900
H	-0.91559500	1.89659800	-2.62966900
C	-1.41128100	2.86211800	0.30595900

H	-1.25764500	3.92291200	0.09314600
H	-2.35017600	2.54431100	-0.14595400
H	-1.46203500	2.71003800	1.38460500
C	-2.74275700	-2.37786500	0.14347300
H	-3.82176900	-2.55179700	0.14245200
H	-2.29332300	-2.86025700	-0.72633000
H	-2.30966300	-2.81056300	1.04858300
C	-3.29655800	-0.01529000	-1.39921200
H	-2.80356900	-0.41160900	-2.28736300
H	-4.32815200	-0.37361500	-1.35754600
H	-3.30147700	1.07429100	-1.45415700
C	-3.37996700	0.07333000	1.48837500
H	-3.36786700	1.16320500	1.49665700
H	-4.41099200	-0.27593600	1.39118000
H	-2.95627500	-0.28236200	2.42791400

PMe_3

P	0.00005100	-0.00005000	-0.60343300
C	1.40739700	-0.85406600	0.28018800
H	1.30465500	-0.79062100	1.36795300
H	1.43519700	-1.90630800	-0.01504500
H	2.35364600	-0.39390300	-0.01645600
C	-1.44341900	-0.79173500	0.28010900
H	-1.51748900	-1.84163200	-0.01545900
H	-1.33777500	-0.73330900	1.36789100
H	-2.36867000	-0.29042300	-0.01606700
C	0.03595700	1.64586600	0.28011300
H	0.03176900	1.52523900	1.36790800
H	0.93363700	2.19578900	-0.01469800
H	-0.83534900	2.23552100	-0.01699400

Int1

Os	0.83252000	0.08279400	-0.09159700
Cl	1.98051400	0.73779800	-2.22323100
P	-0.51632400	2.08525400	-0.52188600
P	2.57110600	-1.58753700	0.26508600
Cl	2.25185500	1.78291000	1.09134500
O	-2.71483400	0.44762400	2.35611400
C	3.61922700	-2.02642400	-1.18584700
C	0.43225100	3.46141000	-1.30388100
C	-0.61312500	-0.42381200	1.50668100
C	-0.82902600	-1.10147000	-0.95452700
C	-1.97366000	1.98324000	-1.65290600

C	0.53849000	-0.47159900	1.98658700
H	1.23567000	-0.61907100	2.78702600
C	-2.07871500	-0.62409000	1.65326000
C	0.25071400	-1.51150600	-1.43617800
H	0.82723100	-2.16028400	-2.06339100
C	-1.20182200	2.90431400	0.97931700
C	3.85761300	-1.18157100	1.52086300
C	1.93455200	-3.22482000	0.83298800
C	-2.85563100	-0.87294100	0.38652400
C	-2.25288700	-1.11398100	-0.79318100
C	-3.02556700	-1.45457900	-2.05550400
H	-2.85517000	-2.51426800	-2.28440900
H	-2.59412800	-0.89369900	-2.88911500
C	-4.35299600	-0.93487400	0.55686300
H	-4.58320000	-1.41310200	1.51473300
H	-4.74073700	0.08771000	0.64201000
C	-5.05462700	-1.66450600	-0.59034800
H	-4.87458400	-2.74263200	-0.50304200
H	-6.13535400	-1.51267700	-0.51949500
C	-4.52311000	-1.17175600	-1.93499900
H	-4.69769200	-0.09263600	-2.01700000
H	-5.05535000	-1.64541700	-2.76477300
H	0.68183800	3.19796800	-2.32955600
H	-0.18464100	4.36337700	-1.28936200
H	1.35241700	3.62820800	-0.74730900
H	-0.38934800	3.06147600	1.68992700
H	-1.64066200	3.86741200	0.70739500
H	-1.95878300	2.26779000	1.43441900
H	-2.31928700	2.99292500	-1.88731000
H	-1.67754500	1.48317300	-2.57643300
H	-2.78074700	1.42506400	-1.18412400
H	4.15175500	-1.13730200	-1.52133400
H	4.33473700	-2.79661800	-0.88840500
H	3.01308900	-2.39788700	-2.01120900
H	2.75986400	-3.92607700	0.97401200
H	1.39902300	-3.10418800	1.77556400
H	1.24176500	-3.62550400	0.09155800
H	4.37248700	-0.26952100	1.22107700
H	3.41042500	-1.02022000	2.50105600
H	4.57126000	-2.00654700	1.58262700
H	-2.18189400	-1.53295300	2.27039300
C	-2.28141200	0.58654600	3.70412200

H	-1.23077600	0.89041600	3.76089100
H	-2.90345200	1.36075100	4.15432200
H	-2.41470900	-0.35227100	4.25678400

TS1

Os	1.00962600	-0.04016800	-0.06937100
Cl	2.72633300	-0.31660300	-1.85742400
P	0.88332200	2.28801800	-0.65143300
P	1.20302100	-2.35960200	0.53903300
Cl	3.04827700	0.48823800	1.28736100
O	-2.80981500	1.75541800	1.63353800
C	2.47369700	-3.35561100	-0.34446400
C	2.48443800	3.09526100	-1.06454300
C	-1.05321100	0.12053600	1.22667300
C	-1.25734800	-0.41332100	-0.84387900
C	-0.16917600	2.67035900	-2.11885800
C	0.09822900	0.21446000	1.76260100
H	0.53015400	0.39040500	2.73301100
C	-2.50509100	0.35944700	1.46947200
C	-0.24142300	-0.55455000	-1.60787100
H	-0.02773200	-0.83573100	-2.62509500
C	0.17419300	3.39736400	0.64006100
C	1.60870600	-2.65807100	2.31353100
C	-0.33689400	-3.35391600	0.31354900
C	-3.33962100	-0.17260000	0.35315800
C	-2.68103000	-0.51822200	-0.76583600
C	-3.37800500	-1.02781600	-2.00904400
H	-3.19363600	-2.10566300	-2.09463000
H	-2.92381100	-0.56845100	-2.89165300
C	-4.82920800	-0.25514200	0.50524700
H	-5.07176100	-0.66132300	1.49433600
H	-5.24712200	0.75953400	0.49033400
C	-5.47045600	-1.10379800	-0.59908600
H	-5.28536800	-2.16521600	-0.39582400
H	-6.55443400	-0.96073300	-0.59553400
C	-4.88382500	-0.74563300	-1.96651100
H	-5.05872000	0.31792900	-2.16614100
H	-5.38316100	-1.30747400	-2.76087100
H	3.15324200	3.01098400	-0.20786300
H	2.93687500	2.57398000	-1.90783700
H	2.32547000	4.14703700	-1.31373500
H	0.74628400	3.29140100	1.56344800

H	0.21294100	4.43779000	0.30845500
H	-0.86149900	3.11281500	0.82422600
H	-0.16136700	3.74328200	-2.32505700
H	0.21369700	2.13158600	-2.98777900
H	-1.19315100	2.34570300	-1.92828800
H	3.45662200	-2.91473300	-0.17479100
H	2.46323400	-4.38586200	0.01955400
H	2.26950800	-3.33832000	-1.41524900
H	-0.19607700	-4.36434400	0.70416800
H	-1.16131400	-2.87351000	0.84348700
H	-0.58699300	-3.40744000	-0.74683000
H	2.52749500	-2.12588800	2.56190100
H	0.80053400	-2.27469700	2.93902900
H	1.73556200	-3.72616600	2.50468400
H	-2.74890300	-0.15004600	2.41418500
C	-2.42985700	2.26992500	2.90513900
H	-2.94069600	1.73258300	3.71419600
H	-1.34769800	2.20564400	3.06219900
H	-2.72945700	3.31824800	2.92488600

Int2

Os	1.14679000	-0.00489600	-0.10001000
Cl	2.67333000	-0.12668400	-2.12307700
P	1.10166600	2.41536300	-0.32894900
P	1.52599200	-2.38297700	0.21427300
Cl	3.00778800	0.38294700	1.58827100
O	-3.32106000	0.87593700	2.34698100
C	3.28650400	-2.89224500	0.08982400
C	2.74809800	3.17218300	-0.62861400
C	-1.54041900	-0.10579000	0.88514200
C	-1.67809900	-0.19449100	-0.49662300
C	0.05407900	3.07909300	-1.68858600
C	-0.19286700	-0.08953900	1.31791100
H	0.01742300	-0.23702800	2.37982700
C	-2.92281000	-0.19969500	1.50761000
C	-0.42331800	-0.09692500	-1.20486000
H	-0.46316100	0.05709200	-2.28747600
C	0.46636800	3.26835100	1.17224300
C	0.97552100	-3.08456800	1.82370700
C	0.66166100	-3.41862000	-1.03827700
C	-3.82494400	-0.27137200	0.28727300
C	-3.09030700	-0.28542100	-0.85470900

C	-3.68105300	-0.36762500	-2.22958000
H	-3.51467800	-1.37246400	-2.63877300
H	-3.15921300	0.32127400	-2.90191100
C	-5.31530200	-0.33323900	0.33077800
H	-5.64279000	-1.01331800	1.12496800
H	-5.70670200	0.65501700	0.60783800
C	-5.88343400	-0.77015100	-1.03002200
H	-5.74530600	-1.85172200	-1.14488300
H	-6.95995200	-0.58127500	-1.05944700
C	-5.18452900	-0.05030600	-2.19097600
H	-5.31856800	1.03141400	-2.07276400
H	-5.64711700	-0.32686600	-3.14228500
H	3.41575400	2.88980300	0.18531700
H	3.14929300	2.77862400	-1.56283600
H	2.66012000	4.25961700	-0.68508500
H	1.06406000	2.95968100	2.03103000
H	0.52156100	4.35318000	1.05525100
H	-0.57087700	2.97079400	1.33582800
H	0.11627400	4.16943500	-1.72022900
H	0.40007100	2.66806400	-2.63843500
H	-0.98229300	2.77865400	-1.52614400
H	3.85344900	-2.38277700	0.86931800
H	3.37737500	-3.97475600	0.20515100
H	3.67185100	-2.58250000	-0.88155900
H	0.88420300	-4.47784000	-0.88849700
H	-0.41387300	-3.25380700	-0.95257700
H	0.98728700	-3.11150100	-2.03332400
H	1.48481800	-2.56125400	2.63449200
H	-0.10149400	-2.94674100	1.93132400
H	1.21225500	-4.14991100	1.87448200
H	-2.99978800	-1.14800900	2.06966400
C	-2.60322500	0.92966200	3.57467200
H	-2.65434800	-0.03008100	4.10539500
H	-1.55234000	1.19507100	3.41740800
H	-3.07629900	1.70069000	4.18419200

THF

C	-1.13957300	-0.46282500	0.15422500
O	-0.00261000	-1.20748300	-0.29473800
C	1.13489700	-0.46890300	0.16200700
C	0.77997700	1.01081300	-0.05656100
C	-0.77231800	1.01780300	-0.04611000

H	-2.00411700	-0.78879400	-0.42532800
H	-1.32457800	-0.67860400	1.21626700
H	1.30506300	-0.67629500	1.22835400
H	2.00397600	-0.80656300	-0.40391000
H	1.20755700	1.64308700	0.72356100
H	1.16086800	1.35855100	-1.01854200
H	-1.18214900	1.63968800	0.75168100
H	-1.16363300	1.38746500	-0.99553900

TS2

Os	1.64815200	-0.13980000	-0.06705000
Cl	3.57254300	0.04371000	-1.76299000
P	2.39849600	2.02038400	0.73448400
P	1.09069200	-2.34870700	-0.87143200
Cl	3.13828600	-1.30229000	1.68629100
O	-2.94173200	0.66646300	2.26540400
C	2.37038200	-3.21347700	-1.87226800
C	2.52131900	3.30507600	-0.57969800
C	-1.05780000	0.48437400	0.59547100
C	-0.89506200	0.99547300	-0.73140200
C	1.29822800	2.80782300	1.98644900
C	0.09400100	-0.18042000	1.10058000
H	0.02253200	-0.66741800	2.08076800
C	-2.42248600	0.75532600	0.97992900
C	0.41788200	0.76587800	-1.25581600
H	0.64975700	1.16874800	-2.24966300
C	4.05785200	2.05724400	1.52666700
C	0.72299100	-3.56975100	0.45825100
C	-0.40175600	-2.41170600	-1.95294400
C	-3.00671500	1.56459900	-0.06941200
C	-2.09454500	1.64893400	-1.13176600
C	-2.42971300	2.30023400	-2.44302100
H	-2.62738200	1.52642000	-3.19732100
H	-1.57368600	2.87160500	-2.81638800
C	-4.36248800	2.20236800	-0.08961200
H	-5.10064200	1.56805100	0.40976000
H	-4.33167800	3.13475700	0.49160000
C	-4.79221400	2.51761200	-1.53102700
H	-5.06197700	1.58443100	-2.04087200
H	-5.68683600	3.14706900	-1.52202400
C	-3.66410300	3.20747100	-2.31017700
H	-3.38195600	4.12792100	-1.78462200

H	-4.01506500	3.50314700	-3.30310800
H	3.16694100	2.93005200	-1.37420600
H	1.52612400	3.48869800	-0.98891600
H	2.92747900	4.23583500	-0.17641700
H	4.79130600	1.67655100	0.81473500
H	4.31760000	3.07763400	1.81894800
H	4.05281700	1.40401500	2.39869400
H	1.67285700	3.79552600	2.26636200
H	0.29389900	2.90314400	1.57145500
H	1.25704700	2.16943400	2.87069600
H	3.27911700	-3.30975200	-1.27648800
H	2.01387200	-4.20421100	-2.16570000
H	2.60058800	-2.62041000	-2.75688000
H	-0.65775600	-3.44346900	-2.20646400
H	-1.24357700	-1.93572300	-1.45095400
H	-0.18789000	-1.85596900	-2.86827500
H	1.61827700	-3.69503200	1.06704300
H	-0.07253000	-3.18383700	1.09486800
H	0.42418800	-4.53000700	0.03067600
H	-2.85576500	-0.49978000	0.37575900
C	-2.89279100	-2.63100100	0.95126500
O	-3.23130200	-1.55741000	-0.01090600
C	-4.68607600	-1.57538300	-0.29845800
C	-5.17778100	-2.87307300	0.32268600
C	-4.23138500	-3.06812500	1.51641000
H	-2.40019500	-3.41351200	0.37553300
H	-2.19985600	-2.20029900	1.67080100
H	-5.11411700	-0.69398100	0.17722500
H	-4.79267400	-1.51217700	-1.37901700
H	-6.22460700	-2.79699900	0.61801000
H	-5.07485100	-3.69835100	-0.38596500
H	-4.52223300	-2.42401100	2.34943700
H	-4.19849800	-4.10006600	1.86658700
C	-2.45950200	1.69307000	3.14186400
H	-2.98170500	1.57006800	4.09162600
H	-1.38177400	1.59268300	3.30251700
H	-2.67374900	2.68702600	2.73428700

Int3'

Os	-1.51922400	-0.00923200	-0.05567300
Cl	-3.30668000	-0.33934100	-1.92077600
P	-1.88585200	-2.35134700	0.36703000

P	-1.59152700	2.33832900	-0.56666800
Cl	-3.24509200	0.59365400	1.80152600
O	2.99135300	-0.76342700	2.50656900
C	-3.27067600	2.99695300	-0.94061100
C	-0.82228800	-3.11125600	1.66903300
C	1.21030400	-0.33711200	0.76577800
C	1.19407900	-0.69394000	-0.66357100
C	-3.59279100	-2.79148500	0.89526600
C	-0.08847400	0.06357600	1.23871600
H	-0.19761800	0.34470800	2.29130200
C	2.47589800	-0.79165200	1.26013100
C	-0.06573500	-0.52435600	-1.26766200
H	-0.15935000	-0.77240000	-2.33309600
C	-1.60093500	-3.45150800	-1.08467100
C	-1.03364900	3.45090200	0.79646600
C	-0.60960600	2.89707400	-2.02665800
C	3.22723800	-1.33614300	0.18634200
C	2.44109100	-1.28445900	-0.98496100
C	2.94393500	-1.77137800	-2.31087400
H	3.21960900	-0.90761600	-2.93265200
H	2.14790600	-2.28872500	-2.85554200
C	4.61642900	-1.90487100	0.23879000
H	5.27174200	-1.27462300	0.84982000
H	4.60246300	-2.88654100	0.73195200
C	5.19257700	-2.05800500	-1.17872100
H	5.48379700	-1.07154400	-1.56173000
H	6.10205200	-2.66480500	-1.14470400
C	4.17102400	-2.68045300	-2.13912900
H	3.85155300	-3.65179600	-1.74272600
H	4.63097900	-2.86941600	-3.11343900
H	0.22668600	-2.97570700	1.40059900
H	-1.01271700	-2.60671200	2.61817600
H	-1.03640000	-4.17782300	1.77437400
H	-0.54839000	-3.40142600	-1.36852900
H	-1.86558800	-4.48517500	-0.84853400
H	-2.20992600	-3.09299000	-1.91505400
H	-3.68552000	-3.87061000	1.04038200
H	-3.82553800	-2.26293800	1.81933800
H	-4.28592200	-2.45727800	0.12210300
H	-3.92215000	2.77638300	-0.09452600
H	-3.22908200	4.07528300	-1.11365700
H	-3.66119500	2.48628200	-1.82011900

H	-0.70994600	3.97420800	-2.18330300
H	0.43993000	2.64588400	-1.87953400
H	-0.97300900	2.36614300	-2.90874600
H	-1.65874400	3.25110000	1.66803300
H	0.00105100	3.22993700	1.05401500
H	-1.12326600	4.50224900	0.51150200
H	1.78878800	1.20228500	0.25228000
C	2.76444800	2.82722100	1.18689300
O	2.17903900	2.13710300	-0.00625100
C	3.21234200	2.05297700	-1.10172700
C	4.32469200	2.95837600	-0.60956900
C	4.25451600	2.81710200	0.91814100
H	2.33442600	3.82660000	1.18152700
H	2.42962300	2.27171600	2.05865200
H	3.50005100	1.00796400	-1.15968600
H	2.71195200	2.37486400	-2.01047300
H	5.28479600	2.64140900	-1.01726500
H	4.14181200	3.99273100	-0.90886800
H	4.69627200	1.87205600	1.24104800
H	4.75199100	3.63490300	1.43954600
C	2.11987800	-0.37982000	3.57534800
H	1.78538700	0.65469300	3.46233800
H	1.25064100	-1.04036300	3.61945300
H	2.70378100	-0.47518200	4.48968100

$OPPh_3$

P	0.00000000	0.00000000	0.17125700
C	0.00000000	1.67967200	-0.55626700
H	0.00000000	1.62814900	-1.64736300
H	-0.88951700	2.21478100	-0.21663600
H	0.88951700	2.21478100	-0.21663600
C	-1.45463900	-0.83983600	-0.55626700
H	-2.36281500	-0.33704600	-0.21663600
H	-1.41001800	-0.81407400	-1.64736300
H	-1.47329800	-1.87773500	-0.21663600
C	1.45463900	-0.83983600	-0.55626700
H	1.41001800	-0.81407400	-1.64736300
H	2.36281500	-0.33704600	-0.21663600
H	1.47329800	-1.87773500	-0.21663600
O	0.00000000	0.00000000	1.71073200

8′

Os	-1.17781300	0.00121900	-0.05488300
Cl	-2.70350600	-0.02171000	-2.03603400
P	-1.26451300	-2.40278800	-0.08904900
P	-1.26176300	2.40332700	-0.15271300
Cl	-2.92984300	0.02327800	1.73674900
O	3.35398200	0.01987500	2.64061500
C	-2.95648900	3.11518100	-0.07770000
C	-2.95928500	-3.11244000	0.00671000
C	1.55949700	0.01279100	0.89321900
C	1.67600100	-0.00507400	-0.56925800
C	-0.56473500	-3.16511100	-1.61272900
C	0.24587000	0.01896800	1.33807000
H	0.00951800	0.03355800	2.39900700
C	2.89224700	0.01302400	1.39239100
C	0.47060700	-0.01554400	-1.22282300
H	0.43221200	-0.03413700	-2.31246700
C	-0.35715700	-3.25147000	1.27089000
C	-0.35555900	3.28724500	1.18523100
C	-0.55974300	3.12397100	-1.69542100
C	3.80267100	0.00207400	0.28959000
C	3.06933800	-0.01072800	-0.89933900
C	3.71564800	-0.01631700	-2.24772400
H	3.62928700	0.98809200	-2.68392500
H	3.17261600	-0.68413900	-2.92385400
C	5.30078000	-0.00712300	0.35413200
H	5.65460400	0.69291000	1.11767700
H	5.65078700	-0.99925900	0.66942100
C	5.90282400	0.34205300	-1.01689200
H	5.80406300	1.42035800	-1.19037200
H	6.97260000	0.11584100	-1.01749500
C	5.19782500	-0.41155200	-2.15185000
H	5.27389500	-1.49015000	-1.96963700
H	5.69413100	-0.21346300	-3.10575800
H	-3.42270200	-2.79801400	0.94203500
H	-3.54960200	-2.72187900	-0.82324000
H	-2.92117700	-4.20307000	-0.04464800
H	-0.76247200	-2.92030400	2.22890300
H	-0.45935600	-4.33609800	1.18798900
H	0.69882700	-2.98078500	1.22238900
H	-0.68383100	-4.25096000	-1.59240200
H	-1.08333200	-2.75655300	-2.48145600
H	0.49530900	-2.91613000	-1.68458000

H	-3.42047800	2.82643600	0.86560600
H	-2.91887500	4.20397600	-0.15919100
H	-3.54584600	2.70146100	-0.89701000
H	-0.67954700	4.20988600	-1.70544400
H	0.50055800	2.87368400	-1.75846000
H	-1.07648800	2.69102000	-2.55334300
H	-0.76378400	2.98354400	2.15108500
H	0.69991600	3.01301200	1.14650600
H	-0.45519000	4.36939300	1.07213600
C	2.39763100	0.04008900	3.71296400
H	1.77995800	0.93911000	3.65456800
H	1.76880900	-0.85239500	3.67804500
H	2.98076300	0.04842500	4.63155200

H_3O^+

O	0.00000000	0.08325800	0.00000000
H	-0.46919300	-0.22182300	0.81283600
H	-0.46919300	-0.22182300	-0.81283600
H	0.93838600	-0.22242100	0.00000000

H_2O

O	0.00000000	0.00000000	0.11808100
H	0.00000000	0.76298600	-0.47232500
H	0.00000000	-0.76298600	-0.47232500

MeOH

C	0.04734300	0.66869700	0.00000000
H	1.09071300	0.98748300	0.00000000
H	-0.44236800	1.07616400	0.89233200
H	-0.44236800	1.07616400	-0.89233200
O	0.04734300	-0.76140100	0.00000000
H	-0.86878400	-1.06079200	0.00000000

Int3

Os	1.09379200	0.00430300	0.02051500
Cl	1.93294900	-0.00480000	2.22156100
P	1.17706100	-2.42563800	0.01757900
P	1.13952800	2.43525400	0.04920200
Cl	2.72186400	0.02855200	-1.68146700
C	2.79894400	3.10562600	0.45955500
C	2.84895600	-3.07423400	0.41151700
C	-1.60081400	-0.00651000	-1.25698100

C	-1.88254500	-0.01602400	0.16906800
C	0.06583400	-3.22071300	1.24366500
C	-0.26538000	0.00449100	-1.51917200
H	0.10995900	0.01477200	-2.53800000
C	-2.84806300	-0.01252800	-1.93570400
C	-0.74755200	-0.01581200	0.92020200
H	-0.79310600	-0.02770200	2.00501000
C	0.73956100	-3.19861000	-1.58883700
C	0.69860100	3.22033200	-1.55041500
C	0.00841300	3.19656700	1.27840400
C	-3.87089200	-0.02462700	-0.96992200
C	-3.29524100	-0.02349900	0.33195600
C	-4.10347300	-0.00308400	1.58143200
H	-4.05103400	1.01251400	1.99860600
H	-3.65129800	-0.65654700	2.33387800
C	-5.35446100	-0.04888500	-1.19258400
H	-5.62015000	0.60220400	-2.03021700
H	-5.65142400	-1.06390500	-1.48540800
C	-6.11306900	0.35698300	0.08065700
H	-6.01630200	1.43829200	0.23352300
H	-7.17775100	0.14668200	-0.04645400
C	-5.56965200	-0.37626600	1.31265000
H	-5.64525800	-1.45785100	1.15298400
H	-6.17091900	-0.14025500	2.19374100
H	3.56422100	-2.69963700	-0.32192500
H	3.14417700	-2.72980500	1.40349200
H	2.84031100	-4.16625000	0.39026900
H	1.40222200	-2.81498600	-2.36613400
H	0.84438000	-4.28373700	-1.52409600
H	-0.29156200	-2.94686300	-1.84140300
H	0.18805400	-4.30546100	1.21355300
H	0.31144800	-2.85539900	2.24202600
H	-0.96917200	-2.96421800	1.01268500
H	3.52381300	2.74723100	-0.27266300
H	2.77473800	4.19750200	0.44668800
H	3.09376000	2.75772300	1.45038000
H	0.11429400	4.28335500	1.26459200
H	-1.02099700	2.92821800	1.03641800
H	0.25235500	2.82033600	2.27315600
H	1.37264800	2.85738700	-2.32781500
H	-0.32636400	2.95380400	-1.81267700
H	0.78418300	4.30623200	-1.47211900

H	-2.99905000	-0.00787500	-3.00750600

7a′

Os	-1.01118900	0.00393300	0.01966900
Cl	-2.22794100	-0.01189200	2.19760100
Cl	-3.00143700	0.03450900	-1.48337900
P	-1.08745700	2.41794000	0.01656300
P	-1.12839900	-2.40786900	-0.02167500
C	0.18482100	3.25156500	1.05294500
C	-0.85878700	3.16943500	-1.64800200
C	-2.67771300	3.13000600	0.60307900
C	0.09229900	-3.27775200	1.04627800
C	0.73521100	-0.01904500	0.98063000
H	0.81877900	-0.03496800	2.06786800
C	-2.75018800	-3.09600800	0.50376700
C	0.23852100	0.01050800	-1.53874500
H	-0.09646300	0.02585500	-2.57682000
C	1.59384400	-0.00277800	-1.24061900
C	1.87565600	-0.01678800	0.19064900
C	6.10727300	0.35185600	0.10921800
H	6.00966500	1.43245300	0.26996600
H	7.17352300	0.14311800	-0.01511900
C	3.28409800	-0.02360600	0.35226500
C	2.83835300	-0.00503700	-1.91628100
H	2.99148300	0.00262900	-2.98855700
C	3.86296600	-0.01884700	-0.94602500
C	4.09564200	-0.00558500	1.60821400
H	3.64986100	-0.66530200	2.35952100
H	4.05807700	1.00548600	2.03678600
C	5.34959800	-0.04467700	-1.16784000
H	5.65485000	-1.05620300	-1.46716300
H	5.62283100	0.61405100	-1.99823000
C	5.55892000	-0.38808100	1.33565400
H	6.16648800	-0.16758100	2.21762300
H	5.62632100	-1.46886800	1.16289000
C	-0.85860300	-3.14332000	-1.68715800
H	-0.96496000	4.25567800	-1.59984100
H	0.13509700	2.91711700	-2.02166900
H	-1.60743400	2.75767200	-2.32650600
H	0.06838000	2.92565400	2.08830800
H	1.17808800	2.96562700	0.70321800
H	0.07689500	4.33733800	0.99819700

H	-2.84666500	2.82162400	1.63477800
H	-2.65355000	4.22018600	0.53696300
H	-3.48635600	2.73870900	-0.01561700
H	-1.58017900	-2.71340800	-2.38361400
H	0.14971900	-2.90094000	-2.02715400
H	-0.98169100	-4.22838700	-1.65541600
H	-0.05247900	-2.96188500	2.08110100
H	-0.03455800	-4.36052100	0.97478500
H	1.10200400	-3.00741700	0.73308800
H	-2.94815600	-2.79286900	1.53187900
H	-3.52995300	-2.68452900	-0.13835400
H	-2.74343100	-4.18587000	0.42897600

Structures were optimized using the CAM-B3LYP[10] density functional. π-contribution of electron localization function (ELF_π) [3] analyses were conducted by the Multiwfn program.[11] And for large differences between some upper and lower bifurcation values, the average values were taken. The fuzzy atom bond orders (FBO) [12] are obtained through the Multiwfn program. Since the molecular orbitals (MOs) show that the ligand Cl at the equatorial plane has a lone pair of electrons contributing to the ring, so some orbitals were selected for ELF_π calculations in **7a′**, **8′**, **9′**, **10a′**, **11a′**, **12a′** and **13′**. The relevant selected orbitals are provided in Figures S44-S52.

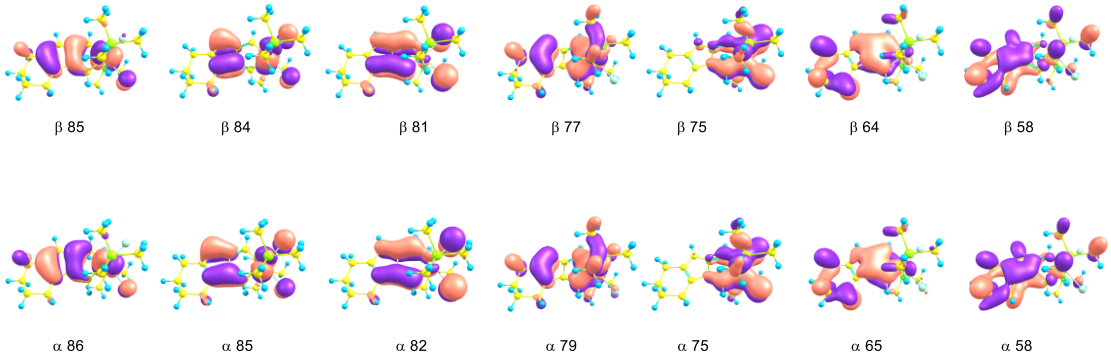


Figure S44. Key MOs of **7a′** are involved in ELF_π calculations.

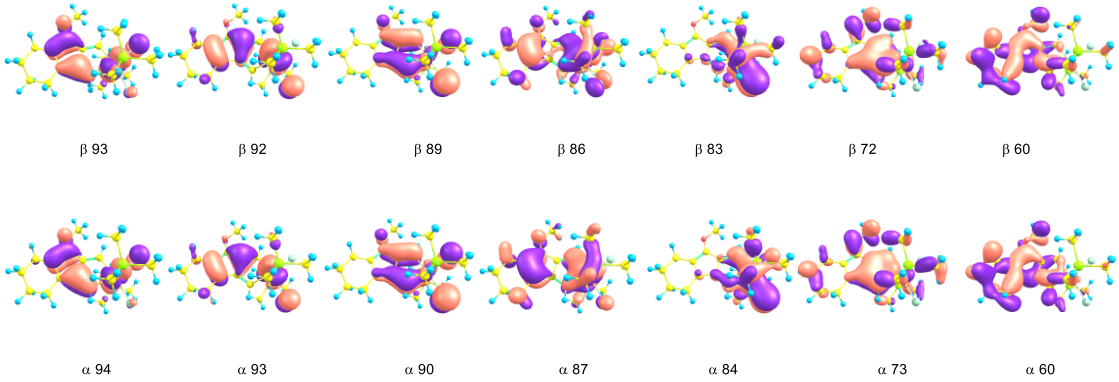


Figure S45. Key MOs of **8′** are involved in ELF$_\pi$ calculations.

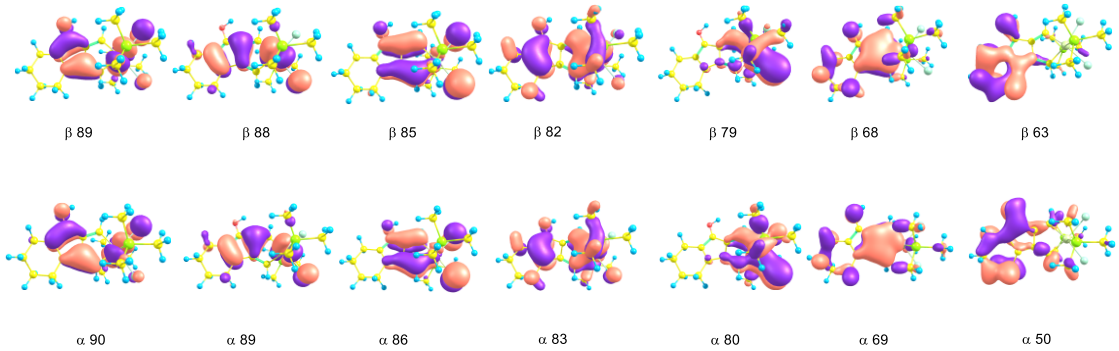


Figure S46. Key MOs of **9′** are involved in ELF$_\pi$ calculations.

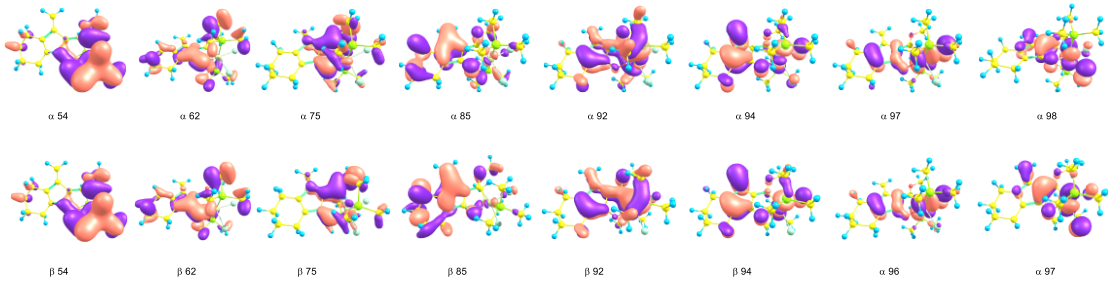


Figure S47. Key MOs of **10a′** are involved in ELF$_\pi$ calculations.

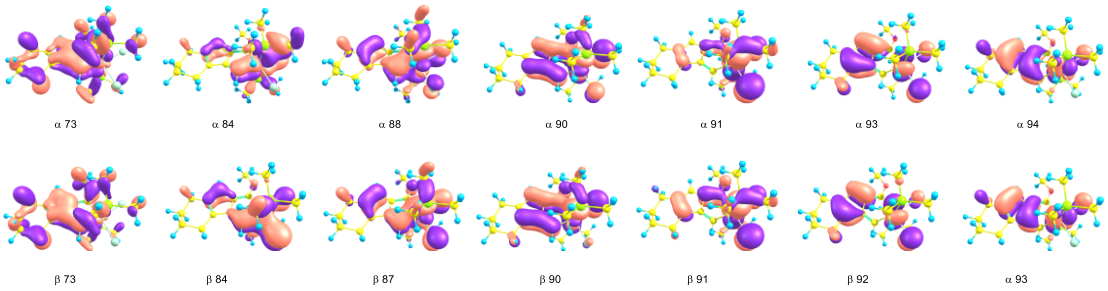


Figure S48. Key MOs of **11a′** are involved in ELF$_\pi$ calculations.

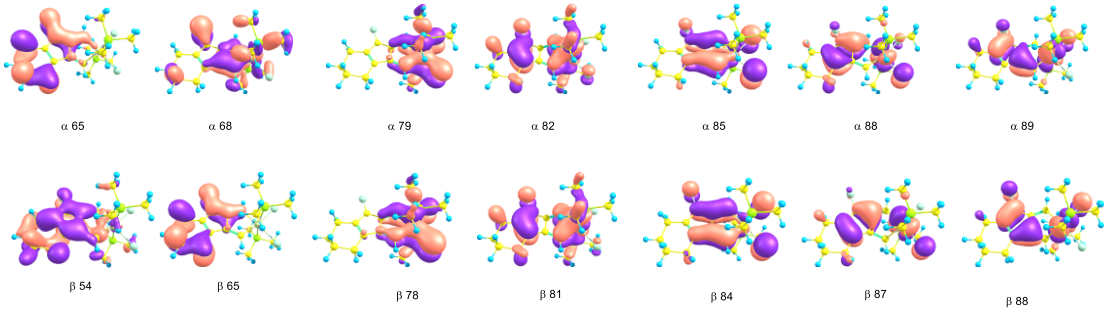


Figure S49. Key MOs of **12a′** are involved in ELF$_\pi$ calculations.

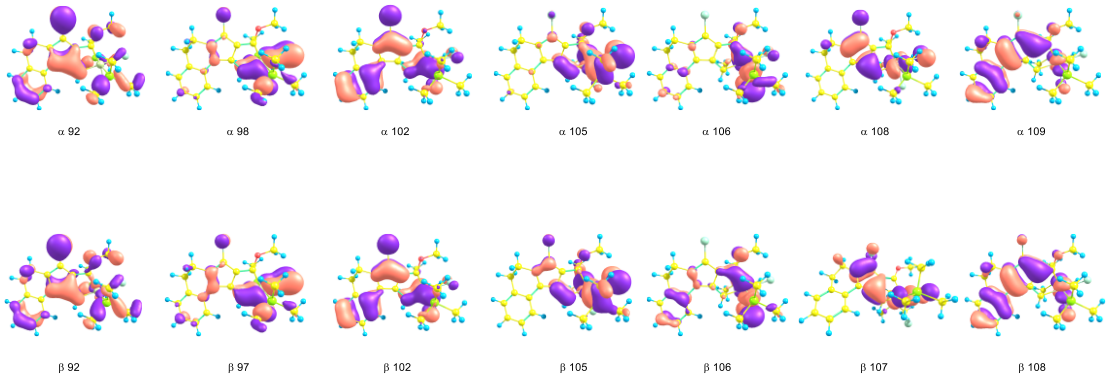


Figure S50. Key MOs of **13′** are involved in ELF$_\pi$ calculations.

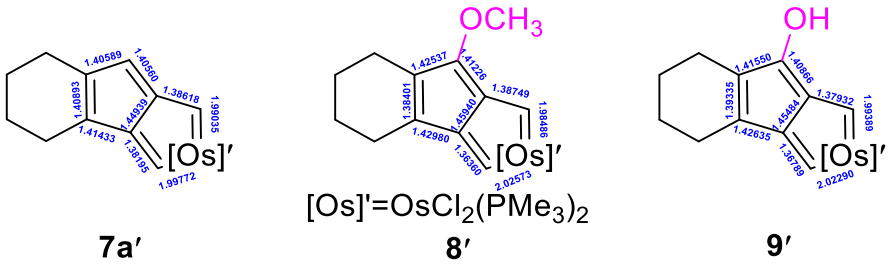


Figure S51. More precise bond lengths (Å, blue) of **7a′, 8′** and **9′**.

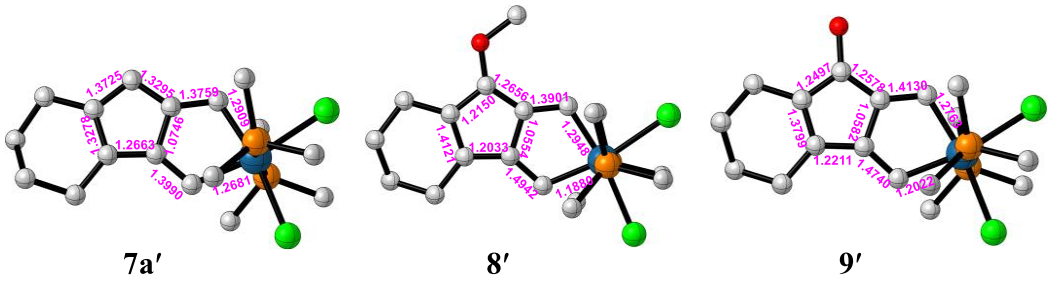
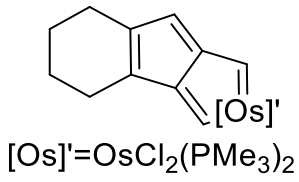


Figure S52. More precise bond orders (pink) of **7a′, 8′** and **9′**. Hydrogen atoms were omitted for clarity.

Cartesian coordinates

Osmapentalene(7a')

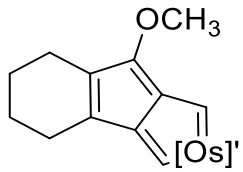


Os	4.307768361	0.000000000	0.000000000
Cl	5.318888901	-2.247795191	0.014690779
Cl	6.337333098	1.395704017	-0.009261960
P	4.485226324	-0.065300640	-2.402542625
P	4.485838525	-0.035453883	2.403240328
C	3.368438210	-1.259678548	-3.244624998
C	4.163885054	1.530257685	-3.258826790
C	6.157972051	-0.544591819	-2.983558327

C	3.372762015	-1.223076999	3.259695321
C	2.487078172	-0.822151323	0.005994744
H	2.321230523	-1.900206663	0.017718070
C	6.160007577	-0.502957081	2.989734278
C	3.176032038	1.637249742	-0.009460584
H	3.584110792	2.648733765	-0.017490324
C	1.803398298	1.443984028	-0.006197077
C	1.413513346	0.048028051	-0.000789340
C	-2.788023542	0.468035674	-0.374612217
H	-2.705150567	0.301041615	-1.454506489
H	-3.840646850	0.676343670	-0.168497695
C	0.000000000	0.000000000	0.000000000
C	0.625471456	2.210925897	-0.004910105
H	0.558100090	3.291708877	-0.007352508
C	-0.469030723	1.328563572	0.000000000
C	-0.911354200	-1.185432025	-0.023651777
H	-0.530920429	-1.973284109	0.632531986
H	-0.911387756	-1.612073901	-1.034663509
C	-1.930927245	1.674130870	0.021810677
H	-2.214355058	2.001404946	1.029611078
H	-2.133442826	2.520391841	-0.640603499
C	-2.341909928	-0.795916293	0.361570426
H	-3.021496186	-1.623690801	0.145414132
H	-2.393581611	-0.619403166	1.441663319
C	4.159575822	1.569147634	3.240522091
H	4.844692397	2.313540019	2.833626431
H	3.136954865	1.886325476	3.034281462
H	4.305842943	1.490137380	4.319124342
H	6.878569340	0.209310267	2.586021411
H	6.202431619	-0.507549695	4.080312919
H	6.400674736	-1.490150728	2.597179354
H	3.542076904	-1.218141923	4.337791730
H	2.334547035	-0.961338574	3.053541161
H	3.566876012	-2.220966980	2.865186220
H	6.395681558	-1.528045815	-2.579988215
H	6.200569188	-0.561369783	-4.074007442
H	6.878575147	0.170007151	-2.587641916
H	4.851041298	2.277318767	-2.860341097
H	4.310424541	1.438124453	-4.336352179
H	3.142109109	1.852876151	-3.056851341
H	3.559529213	-2.253377865	-2.838247114
H	2.331081638	-0.992397739	-3.041275025

H	3.537426187	-1.268167617	-4.322759668

Osmapentalene(8')

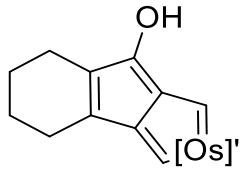


[Os]'=$OsCl_2(PMe_3)_2$

Os	5.328632101	0.612132793	0.017576622
P	5.477727857	0.466275946	2.409997851
P	5.502784457	0.526926780	-2.376169748
Cl	7.490103082	1.812675224	0.043328815
Cl	6.109260028	-1.728958698	-0.007951988
O	1.810369875	4.529519522	0.027806171
C	7.122426385	-0.098241894	2.996821929
C	4.385711170	2.358651301	0.033132172
H	4.932168361	3.299153541	0.046742153
C	3.397686665	0.000000000	0.000000000
H	3.103560835	-1.049730230	-0.018534280
C	4.307623236	-0.714687448	3.197376600
C	7.152269829	-0.026391236	-2.960239112
C	1.885391538	3.202938507	0.022121622
C	2.998467633	2.333724398	0.025508930
C	2.450723211	0.981109311	0.009518741
C	5.245108473	2.120589715	-3.261213873
C	5.206771081	2.036084768	3.332850500
C	4.338297134	-0.630071886	-3.206461690
C	0.687928300	2.429886727	0.010245997
C	3.021403437	5.273336516	0.048861247
H	2.732351472	6.321238143	0.054878067
H	3.619563395	5.057263238	-0.838928681
H	3.598671909	5.040980096	0.946332805
C	1.024908840	1.087557225	0.002085140
C	0.000000000	0.000000000	0.000000000
H	-0.048863223	-0.439690182	1.003834760
H	0.309405748	-0.810088920	-0.665947763
C	-0.716049544	2.951655414	0.000000000
H	-0.815627172	3.788912741	0.696078134
H	-0.953843684	3.356667703	-0.991229162
C	-1.703514550	1.834484829	0.353531299
H	-1.662491052	1.642929396	1.431585223

H	-2.723527741	2.155834142	0.130126057
C	-1.378650632	0.539979395	-0.394120478
H	-1.397940276	0.733002878	-1.472353657
H	-2.142470640	-0.215757007	-0.196423697
H	4.513926577	-0.665095065	-4.283061708
H	4.482464860	-1.622967329	-2.779604283
H	3.312992419	-0.313145196	-3.014124583
H	7.905089547	0.657433356	-2.570079570
H	7.346988507	-1.017132298	-2.551211124
H	7.190750180	-0.053214157	-4.050718539
H	5.966454172	2.845060652	-2.881599260
H	5.380616098	2.003595623	-4.337851024
H	4.238597273	2.488816789	-3.060368797
H	7.149593969	-0.153690679	4.086561881
H	7.323967453	-1.077412752	2.563920328
H	7.877499214	0.597335039	2.632682331
H	4.472197874	-0.777956318	4.274435157
H	3.283573725	-0.395094127	3.002809276
H	4.458624828	-1.695482630	2.745653456
H	5.930966720	2.771278097	2.980230884
H	4.201946769	2.407807284	3.130016684
H	5.330264542	1.891640946	4.407596921

Osmapentalene(9')

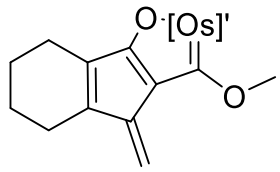


[Os]'=$OsCl_2(PMe_3)_2$

Os	3.446740098	1.547293516	0.009522104
Cl	5.663989813	0.473963389	0.011230464
P	3.636267425	1.601148344	-2.385063130
P	3.630689805	1.595385724	2.404552157
Cl	4.096482916	3.929465607	0.012146240
O	-1.758175921	1.821943631	-0.015544245
H	-1.367688588	2.702658568	-0.006662895
C	5.193114848	2.358891827	2.990720626
C	5.202353603	2.361326976	-2.965787836
C	0.601918836	1.067366500	0.003705338
C	1.182960870	-0.266404698	0.006191151
C	3.616549491	-0.040673149	-3.214719491

C	1.528004097	2.089564739	0.006191151
H	1.211130253	3.134744766	0.005792648
C	-0.795704359	0.891685028	-0.006457782
C	2.550847709	-0.266404698	0.006191151
H	3.103438847	-1.206297831	0.001699661
C	2.337671491	2.559413670	-3.270247753
C	2.326987730	2.547036328	3.289373327
C	3.614603031	-0.048903576	3.229250629
C	-1.094383802	-0.491939433	-0.005701823
C	0.105208454	-1.200707399	0.002263114
C	0.152184509	-2.693929240	0.021169195
H	0.419447506	-3.022804268	1.033097893
H	0.951926073	-3.055368369	-0.630839379
C	-2.451140409	-1.127680963	-0.020815973
H	-3.125787357	-0.601085311	0.659573780
H	-2.894466742	-1.029412644	-1.019135170
C	-2.352257681	-2.609603926	0.355817963
H	-2.193819882	-2.699459640	1.436264685
H	-3.296318543	-3.112432170	0.133796377
C	-1.198703198	-3.298240754	-0.375628988
H	-1.341938805	-3.189652011	-1.456303057
H	-1.199798746	-4.370142546	-0.164693308
H	2.333316308	3.569964713	2.911429833
H	1.351483727	2.104243712	3.086100601
H	2.503971127	2.556520502	4.366269224
H	5.245861880	3.376791887	2.606418973
H	5.240786682	2.361136444	4.081131610
H	6.028141851	1.794689236	2.577062529
H	3.760842929	0.045730396	4.306635780
H	2.663600219	-0.544518969	3.032595952
H	4.416848394	-0.652022017	2.803130847
H	5.257324152	3.378101754	-2.578822703
H	6.034783324	1.793539987	-2.551823357
H	5.252346572	2.366207942	-4.056089364
H	2.345933581	3.581105231	-2.889025664
H	2.517733101	2.571788377	-4.346603141
H	1.360356931	2.118719070	-3.071181920
H	3.764225066	0.056922812	-4.291642437
H	4.416731180	-0.647368357	-2.789777344
H	2.663919736	-0.534196255	-3.020675974

Osmapentalene(10a')

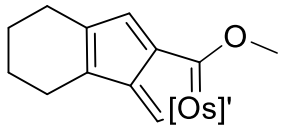


[Os]'=$OsCl_2(PMe_3)_2$

Os	1.06607899	-0.00383114	-0.13935407
Cl	1.98308926	-0.08192979	-2.40755578
P	1.15678024	-2.39559640	-0.17852570
Cl	3.19824773	0.02863315	0.92138984
P	1.16389998	2.38004840	-0.33307841
O	-0.79119561	-0.03429500	-1.12538910
O	-0.08124277	0.09529977	2.78128398
C	-1.76948108	-0.00531625	-0.32039593
C	-0.24007611	0.05165203	1.45837025
C	-0.08731199	-3.15446463	-1.30033588
C	2.75726620	-3.07423707	-0.76715649
C	-3.84722879	-0.08112867	-1.96670154
H	-3.32210620	-0.80061229	-2.60069003
H	-3.74160988	0.88773574	-2.46903360
C	0.89017644	-3.27864312	1.41811658
C	-0.09124037	3.07230431	-1.48524930
C	2.75952721	3.01349928	-0.98210980
C	-1.57382559	0.04031141	1.06351378
C	0.92007839	3.36289112	1.20793344
C	-3.20176327	-0.01820342	-0.62110427
C	-2.89679093	0.06196398	1.69492410
C	1.19896027	0.11542398	3.40871909
H	1.76708931	-0.77937964	3.16513113
H	0.99236357	0.15465081	4.47665899
H	1.77073204	0.98770361	3.10071620
C	-3.85783980	0.02468541	0.55920346
C	-3.23109954	0.10548604	2.98544688
H	-4.26945754	0.11904984	3.29430765
H	-2.47365463	0.12772533	3.75663556
C	-5.34954251	0.02462682	0.66347238
H	-5.67719959	0.74822772	1.41522093
H	-5.68471332	-0.95614062	1.02250495
C	-5.32775263	-0.44802609	-1.82657436
H	-5.84930941	-0.26712461	-2.76920077
H	-5.41520001	-1.52002023	-1.61839566
C	-5.99180393	0.33648697	-0.69322045

H	-7.06155341	0.11788744	-0.65524950
H	-5.89655509	1.40852443	-0.89706725
H	-1.09079075	-2.93667572	-0.93392369
H	0.02361189	-2.70529825	-2.28716400
H	0.04776938	-4.23548401	-1.36493326
H	3.54983032	-2.72206683	-0.10760208
H	2.73639601	-4.16532470	-0.78119417
H	2.95007976	-2.68505044	-1.76586926
H	-0.07270607	-2.99275153	1.84250936
H	0.91571899	-4.36064026	1.27642543
H	1.67798434	-2.99529949	2.11686008
H	0.04732189	4.14644980	-1.61957582
H	0.00491879	2.56149178	-2.44321144
H	-1.09083219	2.88299534	-1.09325475
H	3.55852193	2.70004886	-0.31083447
H	2.93933555	2.56153074	-1.95648599
H	2.74241131	4.10163531	-1.06435944
H	-0.03859740	3.10854759	1.66098191
H	1.71548429	3.12046084	1.91344118
H	0.94777576	4.43372273	0.99817282

Osmapentalene(11a')

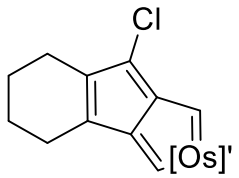


[Os]'=$OsCl_2(PMe_3)_2$

Os	1.00394471	-0.00061053	-0.17723597
Cl	2.15201372	-0.02779495	-2.34369475
P	1.18281743	2.39576488	-0.21998051
P	1.18689812	-2.39711090	-0.15809096
Cl	2.98553235	0.01930458	1.27837663
O	0.17980120	0.03522905	2.64464730
C	-0.28097178	0.01737369	1.41205004
C	0.81230428	3.23500817	1.37552028
C	-0.74443046	-0.01473628	-1.11736531
H	-0.82853137	-0.03307460	-2.20454132
C	2.87254045	-2.99877524	-0.56182505
C	0.10294675	3.25866437	-1.43458608
C	0.10876128	-3.29273212	-1.35034603
C	2.86740346	2.98949250	-0.63960752
C	0.81702856	-3.19555818	1.45830708

C	-1.66404592	0.00955465	1.08686414
C	-1.88486255	-0.00471842	-0.34418043
C	-3.28591913	-0.01033259	-0.56988209
C	-2.92678101	0.00914431	1.69367759
H	-3.15968394	0.01731161	2.74802087
C	-3.91046071	-0.00327806	0.67683785
C	-4.03606730	-0.00196229	-1.86497717
H	-3.56097954	-0.66970798	-2.58919556
H	-3.98599032	1.00215873	-2.30421040
C	-0.69299215	0.04798752	3.77134536
H	-0.04414947	0.06433446	4.64332986
H	-1.31433109	-0.84900214	3.78468553
H	-1.32340564	0.93859371	3.75771100
C	-5.40276266	-0.02395811	0.84799696
H	-5.72605318	-1.02660881	1.15416910
H	-5.70740587	0.65222753	1.65229476
C	-5.50289982	-0.38962799	-1.65169551
H	-6.07665570	-0.18414991	-2.55871482
H	-5.57180515	-1.46836303	-1.47237033
C	-6.10591312	0.35494715	-0.45938290
H	-7.17553046	0.14477701	-0.38176563
H	-6.00730623	1.43365690	-0.62543509
H	1.44095958	2.79377815	2.14934948
H	1.00495580	4.30734351	1.31224115
H	-0.23390502	3.07252515	1.63799187
H	3.56632038	2.59002217	0.09417652
H	3.13914730	2.59540912	-1.61808632
H	2.90495215	4.08027172	-0.64570520
H	0.26439825	4.33783562	-1.41337382
H	0.33199726	2.87681222	-2.43007362
H	-0.94206083	3.04214146	-1.21091040
H	1.44391376	-2.73278852	2.22090187
H	-0.22984901	-3.02891772	1.71543708
H	1.01233430	-4.26869991	1.42311124
H	-0.93662393	-3.07177696	-1.13284774
H	0.33793445	-2.93676283	-2.35536288
H	0.27154704	-4.37076994	-1.30086418
H	2.91120526	-4.08934946	-0.54170696
H	3.14468562	-2.62800491	-1.54925728
H	3.57042232	-2.58108646	0.16272936

Osmapentalene(12a')

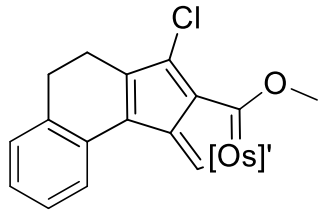


[Os]'=$OsCl_2(PMe_3)_2$

Os	1.17150181	0.00102128	-0.04905670
P	1.35714678	-2.40313872	-0.03525172
Cl	2.61715190	-0.01775256	-2.04026778
P	1.36278925	2.40444390	-0.07571469
Cl	2.87379563	0.01380474	1.72656349
Cl	-3.35864175	0.00732999	2.99170423
C	0.48776498	-3.27208491	-1.40332787
C	3.09008896	-2.98817961	-0.17330546
C	-1.56821403	0.00941679	0.84619241
C	3.09719638	2.98262269	-0.22391449
C	-1.67069792	0.00132425	-0.60030732
C	0.73551608	-3.22465440	1.48778724
C	-0.44131765	-0.00732884	-1.22979606
H	-0.38379897	-0.02135392	-2.31869199
C	0.49528022	3.25231417	-1.45810418
C	-0.26862872	0.01255586	1.32207645
H	-0.08558569	0.02110172	2.39671387
C	0.74355192	3.25284168	1.43348732
C	-3.04399222	-0.00058165	-0.94127133
C	-3.78698804	0.00280659	0.25265960
C	-2.88463918	0.00764090	1.32937373
C	-3.69082339	0.01180899	-2.28937873
H	-3.61452233	1.02262703	-2.70910086
H	-3.14678419	-0.64041117	-2.97792397
C	-5.28421405	-0.01462167	0.29929354
H	-5.62818502	-1.01328088	0.59435273
H	-5.64806557	0.66804026	1.07160547
C	-5.87470468	0.35008889	-1.06648071
H	-6.94415877	0.12783674	-1.07706832
H	-5.77595761	1.42915593	-1.22897033
C	-5.16604030	-0.39150898	-2.20073453
H	-5.66097110	-0.19193536	-3.15393993
H	-5.23927259	-1.47071763	-2.02710057
H	3.66651841	2.58363198	0.61474503
H	3.51919471	2.58199347	-1.14469150

H	3.14336500	4.07301758	-0.22824315
H	0.66087906	4.33054795	-1.42746579
H	0.87466796	2.85259849	-2.39905523
H	-0.57382399	3.04703968	-1.39685699
H	1.27243876	2.84663806	2.29617507
H	0.90933286	4.33006288	1.37815685
H	-0.32205005	3.05495445	1.55297374
H	3.13327474	-4.07862080	-0.15946166
H	3.51335538	-2.60416054	-1.10055435
H	3.66031673	-2.57684933	0.65874626
H	-0.58083745	-3.06314071	-1.34581897
H	0.86847575	-2.88945682	-2.35083075
H	0.65062587	-4.35004930	-1.35427839
H	-0.32965185	-3.02235601	1.60366537
H	0.89884895	-4.30302585	1.45051489
H	1.26516449	-2.80534451	2.34371231

Osmapentalene(13')



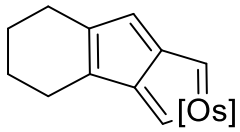
[Os]'=$OsCl_2(PMe_3)_2$

Os	-1.47754100	-0.28074507	0.05840287
Cl	-2.09399034	-2.62389131	0.46413236
Cl	-3.83347147	0.44285889	-0.02081281
P	-1.63185095	-0.80766605	-2.28890751
P	-1.53234413	-0.02211327	2.45462093
Cl	2.00691815	3.93285451	-0.61183241
O	-0.90797172	2.73732074	-0.44655243
C	0.90802674	1.38128415	-0.26480840
C	-1.24898683	1.67401130	3.11687747
C	2.84927328	0.12112698	-0.07933643
C	0.43545613	-0.89032506	0.12632269
H	0.68892091	-1.92806156	0.32911750
C	3.88295173	-0.90598889	0.01455190
C	-3.22842897	-1.56929522	-2.77542517
C	-3.12071304	-0.52945133	3.21969048
C	-0.38247480	-2.02562803	-2.87149447
C	-1.43980548	0.59383767	-3.46962205

C	-0.28468264	-1.03722288	3.34637487
C	1.41515097	0.04365818	-0.06774464
C	3.63076288	-2.26295843	-0.19480217
H	2.62851938	-2.58744884	-0.44194199
C	3.19422375	1.45577375	-0.25397025
C	2.00418756	2.21943662	-0.37485900
C	-0.51325161	1.49772858	-0.25444674
C	-2.27445996	3.15608459	-0.48333005
H	-2.23079587	4.22916436	-0.65533830
H	-2.77087241	2.93344853	0.45745697
H	-2.80872272	2.65538278	-1.28629817
C	5.47046332	0.97690453	0.55710485
H	5.24225329	1.18705868	1.60936612
H	6.53272976	1.18666915	0.41730905
C	4.65166430	-3.19655660	-0.11300892
H	4.43853280	-4.24560175	-0.27953263
C	4.61964791	1.90036949	-0.31795523
H	4.71985915	2.93684435	0.00919760
H	4.97384181	1.86321700	-1.35583657
C	5.19741875	-0.48597450	0.29418057
C	5.94536529	-2.78218539	0.17038968
H	6.74957194	-3.50575532	0.22999390
C	6.20945781	-1.43280500	0.36785074
H	7.22223766	-1.10944442	0.58355347
H	-3.31451557	-1.56681449	2.94845984
H	-3.07645043	-0.42556712	4.30520967
H	-3.92446181	0.08111021	2.81153187
H	-2.03223835	2.33947816	2.75286007
H	-1.26375382	1.67400625	4.20816247
H	-0.28535061	2.04845166	2.76976261
H	0.71838838	-0.72702154	3.05272763
H	-0.39528698	-0.93411651	4.42710597
H	-0.42559355	-2.08034853	3.06253729
H	-1.49730565	0.24474599	-4.50207320
H	-2.23433709	1.32042062	-3.29747500
H	-0.47878926	1.08328708	-3.30804985
H	-3.23028181	-1.81530252	-3.83871364
H	-3.37377265	-2.46997745	-2.17983972
H	-4.03692937	-0.87784482	-2.54368275
H	-0.53812680	-2.27581604	-3.92221623
H	0.61877759	-1.61445462	-2.74104006
H	-0.47447253	-2.92688252	-2.26473333

Cartesian coordinates together with the symmetry and electronic energies for neutral parent complexes **7a−b**, **10a−b**, **11a−b** and **12a−b** calculated in this study.

Osmapentalene(7a)



[Os]=$OsCl_2(PPh_3)_2$

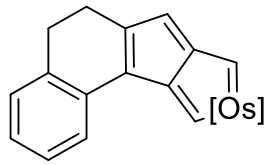
E(TD-HF/TD-KS) = -3509.85062476

Os	-0.00674	-0.51039	-0.00057
Cl	-0.01865	-1.62844	-2.22644
Cl	-0.0215	-2.42932	1.58708
P	2.46056	-0.65644	-0.00786
P	-2.47517	-0.61326	-0.00133
C	3.28769	0.64945	-1.02541
C	3.20234	-2.20166	-0.70272
C	4.51059	-2.18155	-1.21516
H	5.07194	-1.25308	-1.24161
C	-3.28404	0.69908	-1.02557
C	0.00713	1.2721	-0.93745
H	0.00235	1.36152	-2.02427
C	-3.24766	-2.14958	-0.68289
C	5.09929	-3.34995	-1.69832
H	6.1108	-3.31813	-2.09467
C	2.87513	0.77142	-2.36476
H	2.09705	0.11758	-2.74959
C	0.00736	0.74607	1.56798
H	0.00824	0.38278	2.59726
C	4.38959	-4.55238	-1.67572
H	4.84703	-5.46243	-2.05537
C	2.49536	-3.41245	-0.68415
H	1.48842	-3.44185	-0.28777
C	-4.56298	-2.11057	-1.17608
H	-5.11113	-1.17402	-1.1946
C	0.01912	2.11026	1.28704
C	0.02094	2.40663	-0.13908
C	0.46856	6.63653	-0.01358
H	1.55141	6.52088	-0.16343
H	0.28099	7.70866	0.12095
C	-2.86863	0.80979	-2.36502

H	-2.09743	0.14537	-2.74545
C	3.46734	1.71482	-3.20283
H	3.14155	1.79278	-4.23679
C	3.09101	-4.57974	-1.16644
H	2.53069	-5.51055	-1.14853
C	-2.55787	-3.37026	-0.6756
H	-1.5457	-3.4146	-0.29453
C	-3.45007	1.75492	-3.20877
H	-3.12248	1.82391	-4.24282
C	-4.48282	-4.48249	-1.63936
H	-4.95879	-5.38568	-2.01257
C	4.47578	2.55339	-2.71905
H	4.93456	3.29033	-3.37308
C	-5.1756	-3.27004	-1.65068
H	-6.19233	-3.22345	-2.03192
C	0.03796	3.81739	-0.28863
C	4.31054	1.48234	-0.55266
H	4.65997	1.39341	0.47008
C	-3.17723	-4.52858	-1.14986
H	-2.62992	-5.46722	-1.14094
C	0.03226	3.3464	1.97495
H	0.03403	3.49026	3.05118
C	0.0433	4.3815	1.01385
C	0.07662	4.64229	-1.54167
H	-0.60089	4.22261	-2.2969
H	1.0856	4.58127	-1.97959
C	-4.45078	2.6059	-2.73075
H	-4.90098	3.34427	-3.3891
C	4.89594	2.43277	-1.39502
H	5.68544	3.0737	-1.01123
C	-4.29908	1.54473	-0.55858
H	-4.6506	1.46461	0.46419
C	-4.8741	2.49626	-1.40683
H	-5.65767	3.14706	-1.02755
C	0.04259	5.86975	1.25303
H	-0.96677	6.19731	1.54831
H	0.69884	6.12729	2.09495
C	-0.27025	6.11648	-1.25733
H	-0.02481	6.73006	-2.13247
H	-1.35369	6.21216	-1.09859
C	-3.22794	-0.4653	1.67875
C	-3.85186	-1.56218	2.28999

C	-3.12256	0.73896	2.39721
C	-4.36483	-1.45576	3.58462
H	-3.93295	-2.50458	1.76053
C	-3.64586	0.84445	3.68587
H	-2.62888	1.59691	1.9539
C	-4.26781	-0.25356	4.28452
H	-4.83957	-2.31868	4.04371
H	-3.56266	1.78563	4.22309
H	-4.67026	-0.17199	5.29072
C	3.22193	-0.53412	1.67044
C	3.83738	-1.64345	2.2676
C	3.13267	0.66382	2.40166
C	4.35745	-1.55554	3.56079
H	3.90611	-2.58128	1.72844
C	3.66307	0.75075	3.68881
H	2.64577	1.53149	1.96978
C	4.27626	-0.35968	4.27338
H	4.82522	-2.42803	4.00882
H	3.59205	1.68722	4.23594
H	4.6841	-0.29262	5.27848

Osmapentalene(7b)



[Os]=$OsCl_2(PPh_3)_2$

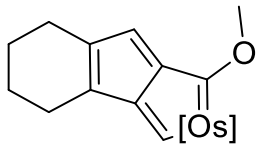
E(TD-HF/TD-KS) = -3662.28247293

Os	0.45366	0.67539	0.02565
Cl	1.63428	2.53046	1.1818
Cl	0.81558	1.19644	-2.38596
P	2.59239	-0.56885	-0.02053
P	-1.56475	2.10274	-0.07256
C	-0.8104	-1.26275	1.8038
C	-0.5927	-0.94371	-0.53645
H	-0.76457	-1.15834	-1.5914
C	-1.1098	-1.75965	0.46824
C	1.82236	-3.07174	-1.08792
H	1.21203	-3.17578	-0.19732
C	4.05874	1.61036	-1.11109
H	3.1002	2.00229	-1.42523
C	-1.90819	-2.93315	0.62081
C	2.6257	-1.93111	-1.26543

C	-1.42371	-2.13169	2.73985
H	-1.39617	-2.04059	3.82064
C	3.38723	-1.81851	-2.43737
H	4.00356	-0.94199	-2.60178
C	3.05073	-1.35853	1.58986
C	-0.18298	4.34421	-1.13553
H	0.55238	3.62965	-1.48257
C	-2.24526	4.84274	0.0285
H	-3.11217	4.52042	0.59616
C	-0.06015	-0.09361	1.81037
H	0.22069	0.37199	2.75561
C	1.80003	-4.08138	-2.05074
H	1.17748	-4.95786	-1.89248
C	-0.96984	6.63094	-0.98313
H	-0.84013	7.68747	-1.20325
C	5.37508	-0.09355	-0.007
H	5.44397	-1.02267	0.54982
C	6.47252	1.80587	-1.02438
H	7.38181	2.35181	-1.26245
C	-2.63974	-4.83579	-2.57141
H	-2.29901	-4.87477	-3.60247
C	-1.29705	3.90192	-0.40765
C	3.35392	-2.82607	-3.40409
H	3.9475	-2.71881	-4.30792
C	5.23113	2.30362	-1.42035
H	5.16715	3.24002	-1.96786
C	-3.42734	0.3558	-1.28583
H	-3.2559	-0.29096	-0.43244
C	3.42522	-1.05084	3.97151
H	3.42168	-0.40206	4.84347
C	3.82202	-3.20767	2.96521
H	4.12584	-4.24798	3.04757
C	6.54218	0.60345	-0.3174
H	7.50419	0.20825	-0.00177
C	2.56557	-3.9604	-3.21308
H	2.54459	-4.74498	-3.9648
C	-0.02575	5.70191	-1.42149
H	0.84393	6.0307	-1.98387
C	-3.90266	1.89011	1.59072
H	-4.46437	1.62237	0.70262
C	-3.00321	2.40058	-2.50129
H	-2.50092	3.3561	-2.59954

C	3.45129	-2.6956	1.71811
H	3.48171	-3.34364	0.84916
C	-4.29997	-0.06169	-2.2907
H	-4.79718	-1.02384	-2.20223
C	3.80816	-2.38917	4.09389
H	4.09888	-2.78838	5.06206
C	-2.87565	-4.31253	2.52705
H	-3.28975	-4.11688	3.52294
H	-2.21554	-5.18841	2.62827
C	-3.64277	-5.70058	-2.1274
H	-4.09025	-6.41764	-2.81047
C	3.04665	-0.53744	2.73197
H	2.75986	0.50696	2.64397
C	-4.52354	0.74733	-3.40705
H	-5.19886	0.41921	-4.19277
C	-4.00467	-4.64254	1.53323
H	-4.50839	-5.57319	1.81837
H	-4.7623	-3.84566	1.59101
C	4.12078	0.40245	-0.4022
C	-2.06564	-3.92593	-1.68729
H	-1.2643	-3.279	-2.02786
C	-2.77197	1.59681	-1.37572
C	-2.4869	-3.85793	-0.34567
C	-2.08945	-3.13529	2.02317
C	-2.5292	2.15401	1.50597
C	-3.5061	-4.73978	0.10351
C	-4.0653	-5.64761	-0.79661
H	-4.84526	-6.32318	-0.45173
C	-2.08181	6.19792	-0.25808
H	-2.8223	6.91372	0.08908
C	-1.83367	2.52459	2.67137
H	-0.77237	2.75191	2.61659
C	-3.87159	1.97583	-3.50934
H	-4.03341	2.60983	-4.37692
C	-4.56528	1.97583	2.8191
H	-5.6302	1.76392	2.86843
C	-2.50066	2.6166	3.89179
H	-1.95067	2.90907	4.78239
C	-3.86776	2.33672	3.97102
H	-4.38534	2.40541	4.92424

Osmapentalene(11a)



[Os]=$OsCl_2(PPh_3)_2$

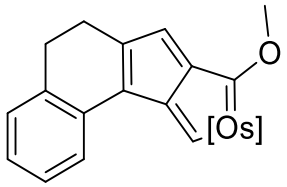
E(TD-HF/TD-KS) = -3624.38427732

Os	0.00628	-0.56557	-0.1003
Cl	0.04328	-1.79788	-2.2633
P	2.46851	-0.64881	-0.10045
P	-2.45478	-0.67618	-0.10768
Cl	0.00176	-2.47072	1.49271
O	-0.01105	0.30743	2.72471
C	-0.00997	0.76305	1.48585
C	3.21946	-0.28443	1.54823
C	-0.01055	1.18786	-1.06681
H	-0.01545	1.25586	-2.1557
C	-3.262	-2.31033	-0.44641
C	3.71772	-1.32062	2.3509
H	3.70333	-2.34184	1.98706
C	3.28126	0.53819	-1.27244
C	-3.30032	0.39961	-1.36222
C	3.28504	-2.24085	-0.58492
C	-3.18728	-0.18441	1.51461
C	-0.02043	2.14314	1.13526
C	-0.02233	2.34325	-0.30689
C	-3.28601	1.16977	1.8793
H	-2.97946	1.94568	1.18566
C	-4.5664	1.87756	-3.39661
H	-5.05339	2.45069	-4.18125
C	4.64815	-2.23655	-0.92974
H	5.20509	-1.30495	-0.94262
C	-5.09103	1.87002	-2.10437
H	-5.99053	2.4358	-1.87564
C	2.58671	-3.45568	-0.59062
H	1.53899	-3.47595	-0.32286
C	-2.78632	0.40336	-2.67066
H	-1.90366	-0.18452	-2.90412
C	3.23002	1.02695	2.05501
H	2.82884	1.8435	1.46362
C	-4.46697	1.13239	-1.09513
H	-4.8963	1.13482	-0.09936
C	-4.66367	-2.3709	-0.54517

H	-5.25891	-1.47007	-0.43105
C	-2.51803	-3.48493	-0.61313
H	-1.43999	-3.45496	-0.54088
C	5.29857	-3.42241	-1.26677
H	6.35216	-3.40111	-1.53287
C	2.80697	0.56315	-2.59608
H	1.98064	-0.0806	-2.88352
C	-3.78494	1.53277	3.13167
H	-3.87472	2.58542	3.38835
C	4.37505	1.34767	-0.93288
H	4.77673	1.3317	0.07408
C	4.23038	-1.0507	3.62166
H	4.60974	-1.86757	4.22957
C	4.59588	-4.62974	-1.26831
H	5.1013	-5.55447	-1.5349
C	-3.56014	-1.16316	2.44797
H	-3.46836	-2.21364	2.19577
C	-0.03756	3.74635	-0.55842
C	3.24331	-4.64162	-0.92968
H	2.68764	-5.57543	-0.93125
C	4.96504	2.18196	-1.88677
H	5.80901	2.80558	-1.60337
C	-0.03464	3.42312	1.7249
H	-0.03845	3.66945	2.77943
C	-3.16663	-4.69669	-0.86779
H	-2.57551	-5.59937	-0.99587
C	-3.41619	1.13667	-3.67657
H	-3.00667	1.12344	-4.68326
C	4.47927	2.21011	-3.19353
H	4.94031	2.85795	-3.93453
C	-4.55648	-4.7498	-0.95846
H	-5.05627	-5.69443	-1.1572
C	-0.04497	4.39481	0.68753
C	3.40292	1.3922	-3.54599
H	3.02556	1.39508	-4.56524
C	-0.02454	4.47601	-1.87143
H	-0.69245	3.98639	-2.59242
H	0.98341	4.41792	-2.31155
C	3.75764	1.29548	3.31873
H	3.77727	2.31879	3.68569
C	-4.16824	0.55021	4.04779
H	-4.55767	0.83362	5.02217

C	-5.30601	-3.58143	-0.79596
H	-6.39007	-3.61094	-0.8685
C	-0.03132	1.19173	3.85233
H	-0.03407	0.54178	4.72756
H	-0.93647	1.80489	3.83609
H	0.86277	1.8214	3.85619
C	4.25959	0.25666	4.10666
H	4.669	0.46633	5.09138
C	-4.04534	-0.79669	3.70488
H	-4.3296	-1.56914	4.41431
C	-0.07678	5.89518	0.8316
H	-1.08737	6.22224	1.12397
H	0.58878	6.22353	1.64158
C	-0.41766	5.9544	-1.68777
H	-0.19916	6.51359	-2.60563
H	-1.5025	6.02548	-1.52531
C	0.31259	6.58443	-0.49052
H	0.09147	7.65705	-0.43002
H	1.39737	6.49296	-0.64326

Osmapentalene(11b)



$[Os]=OsCl_2(PPh_3)_2$

E(TD-HF/TD-KS) = -3776.81397297

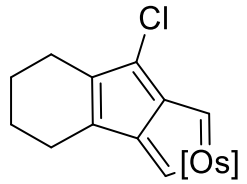
Os	0.43916	-0.66559	-0.06655
Cl	0.7434	-1.11551	-2.49178
Cl	1.61742	-2.60404	0.93328
P	-1.60419	-2.0482	-0.19258
P	2.60161	0.52982	-0.14208
O	0.35183	-0.54083	2.8921
C	-0.03823	0.09124	1.79437
C	4.09862	-0.44949	-0.62243
C	-0.58527	0.97234	-0.56155
H	-0.77663	1.20964	-1.60758
C	-1.39324	-3.83287	-0.63915
C	-2.38959	-4.75834	-0.28337
H	-3.25533	-4.43556	0.28606
C	-2.54451	-2.18737	1.39647
C	-1.87506	2.96298	0.57886

C	-0.79288	1.29648	1.7997
C	-0.28354	-4.27635	-1.37208
H	0.48748	-3.57392	-1.65962
C	-3.08231	-2.17299	-2.61177
H	-2.59236	-3.12553	-2.77702
C	-2.82717	-1.44551	-1.44027
C	-2.07075	3.1868	1.96166
C	3.99346	-1.64811	-1.34085
H	3.01782	-2.03378	-1.60378
C	2.62137	1.94068	-1.33445
C	3.15712	1.24113	1.47648
C	3.50069	2.58621	1.67053
H	3.4316	3.29271	0.85108
C	-1.84544	-2.69628	2.50625
H	-0.79514	-2.95417	2.40881
C	-1.07882	1.77826	0.45758
C	-2.27743	-6.0982	-0.65325
H	-3.05554	-6.80147	-0.36823
C	-3.46542	4.76084	0.01224
C	-3.4669	-0.20543	-1.2645
H	-3.27695	0.3862	-0.37605
C	-1.41479	2.18697	2.70547
H	-1.42156	2.14176	3.78634
C	0.04108	-0.04258	4.19827
H	0.45671	0.95991	4.33369
H	0.51301	-0.73833	4.89316
H	-1.04161	-0.03653	4.35366
C	3.74618	0.79063	3.79077
H	3.8519	0.08311	4.60926
C	-3.84617	-2.53882	3.86351
H	-4.35011	-2.67668	4.81668
C	3.95003	3.03086	2.91765
H	4.2109	4.07761	3.05035
C	3.28893	0.34329	2.55176
H	3.03494	-0.70328	2.41416
C	4.07294	2.13653	3.98022
H	4.42837	2.48229	4.94749
C	-3.90187	-1.86778	1.5373
H	-4.46661	-1.49437	0.69034
C	3.36171	1.87029	-2.52343
H	3.96575	0.99572	-2.73542
C	5.14433	-2.34081	-1.72454

H	5.04596	-3.27051	-2.27834
C	-0.17656	-5.61931	-1.74057
H	0.69099	-5.94884	-2.30584
C	-3.9587	-1.67624	-3.57903
H	-4.13861	-2.25256	-4.48258
C	-2.49526	-2.87205	3.72754
H	-1.94516	-3.27607	4.5736
C	-1.16821	-6.53246	-1.38214
H	-1.07825	-7.5775	-1.66746
C	-4.34693	0.28487	-2.2295
H	-4.8289	1.24625	-2.0744
C	-4.01549	5.6578	-0.90414
H	-4.80041	6.33576	-0.5751
C	-2.43956	3.8747	-0.41289
C	-2.0015	3.93218	-1.7488
H	-1.19331	3.28674	-2.0744
C	1.83148	3.08006	-1.09817
H	1.2319	3.15134	-0.19739
C	-3.97992	4.68232	1.43791
H	-4.73473	3.88277	1.49946
H	-4.49025	5.61514	1.704
C	6.52125	-0.65603	-0.68057
H	7.50088	-0.26544	-0.41774
C	-2.86051	4.36943	2.44749
H	-2.20428	5.24878	2.54594
H	-3.28561	4.18471	3.44125
C	6.4078	-1.85047	-1.39565
H	7.30041	-2.3952	-1.6925
C	-4.54597	-2.03759	2.76662
H	-5.59869	-1.78338	2.85902
C	-4.59485	-0.44948	-3.39118
H	-5.27579	-0.06475	-4.14576
C	-3.57762	5.69804	-2.2305
H	-4.01833	6.40648	-2.92688
C	5.37573	0.03918	-0.29539
H	5.47958	0.96314	0.26466
C	-2.56704	4.8313	-2.65059
H	-2.21191	4.85929	-3.67722
C	1.80387	4.12951	-2.01761
H	1.19036	5.00286	-1.814
C	3.32264	2.91721	-3.44706
H	3.8995	2.84131	-4.36483

C	2.54963	4.05042	-3.19604
H	2.52408	4.86565	-3.91428

Osmapentalene(12a)



[Os]=$OsCl_2(PPh_3)_2$

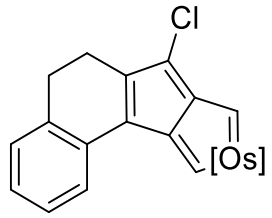
E(TD-HF/TD-KS) = -3969.44493496

Os	-0.01404	-0.63623	-0.03046
P	-2.48482	-0.72866	-0.01848
Cl	-0.03993	-2.0267	-2.08561
P	2.45452	-0.81081	-0.02313
Cl	-0.0401	-2.33063	1.78911
Cl	0.06613	3.9262	3.04775
C	-3.2824	0.48109	-1.16922
C	-3.25698	-2.32384	-0.54502
C	0.03735	2.12721	0.88682
C	3.17044	-2.42659	-0.56364
C	0.04211	2.23502	-0.5657
C	-3.23936	-0.40945	1.63714
C	-2.88795	0.43718	-2.51898
H	-2.14237	-0.28628	-2.83807
C	0.01657	1.0022	-1.20135
H	0.01379	0.94601	-2.29025
C	3.28419	0.38026	-1.17069
C	4.31359	-4.88297	-1.30121
H	4.75357	-5.83394	-1.59029
C	-4.54487	-2.33137	-1.10634
H	-5.07443	-1.39876	-1.27179
C	4.45358	-2.47427	-1.13377
H	5.01372	-1.55923	-1.29705
C	0.01135	0.81758	1.35504
H	0.00788	0.60633	2.42539
C	-5.15559	-3.53456	-1.46035
H	-6.15096	-3.52362	-1.89663
C	-2.59349	-3.54328	-0.34484
H	-1.60232	-3.55234	0.09085
C	2.46657	-3.6237	-0.36708
H	1.47802	-3.60064	0.07414
C	3.22809	-0.52604	1.63036

C	3.11348	0.72803	2.25563
H	2.59754	1.54106	1.75659
C	3.65758	0.94327	3.52161
H	3.56156	1.92075	3.98644
C	4.31261	-0.09365	4.18982
H	4.73047	0.0725	5.17915
C	4.42215	-1.34394	3.5822
H	4.92352	-2.15947	4.09633
C	3.88688	-1.56016	2.31048
H	3.97796	-2.53907	1.85419
C	0.07426	3.61154	-0.90961
C	3.04008	-4.84304	-0.73237
H	2.4819	-5.76227	-0.57718
C	0.08873	4.35992	0.29258
C	5.02005	-3.69528	-1.50013
H	6.01217	-3.71559	-1.94343
C	-4.48906	-4.74453	-1.25802
H	-4.96352	-5.68173	-1.53737
C	2.8894	0.34881	-2.52068
H	2.12782	-0.35687	-2.84191
C	-3.21107	-4.74455	-0.69801
H	-2.68382	-5.68139	-0.53984
C	-3.45976	1.30296	-3.44992
H	-3.15025	1.2521	-4.49056
C	0.06432	3.45267	1.37525
C	-4.42887	2.22777	-3.04956
H	-4.87192	2.9041	-3.77588
C	3.47881	1.20585	-3.44857
H	3.16792	1.16544	-4.48923
C	0.11179	4.25411	-2.26535
H	1.12068	4.13355	-2.69038
H	-0.5667	3.73168	-2.95211
C	-4.26516	1.3999	-0.77902
H	-4.59837	1.43829	0.25214
C	-4.28774	0.07123	4.20295
H	-4.69165	0.25598	5.19477
C	4.46633	2.10959	-3.0448
H	4.92341	2.77909	-3.76881
C	0.10957	5.86261	0.33277
H	-0.88746	6.23848	0.61053
H	0.7895	6.2173	1.11777
C	4.86825	2.14079	-1.71004

H	5.64135	2.83354	-1.38795
C	4.28561	1.27712	-0.77712
H	4.61905	1.30522	0.25431
C	-4.83015	2.27185	-1.71506
H	-5.58888	2.98141	-1.39544
C	-3.91275	-1.42257	2.33428
H	-4.02903	-2.40396	1.88918
C	-3.09138	0.848	2.2486
H	-2.56295	1.64455	1.73613
C	-4.43001	-1.18241	3.60914
H	-4.94303	-1.982	4.13665
C	-3.61776	1.08733	3.51776
H	-3.49606	2.06698	3.97184
C	0.51311	6.44303	-1.03642
H	0.32187	7.52254	-1.04946
H	1.5944	6.3115	-1.18321
C	-0.23797	5.75252	-2.18632
H	-0.00373	6.23785	-3.1412
H	-1.31997	5.86618	-2.03073

Osmapentalene(12b)



$[Os]=OsCl_2(PPh_3)_2$

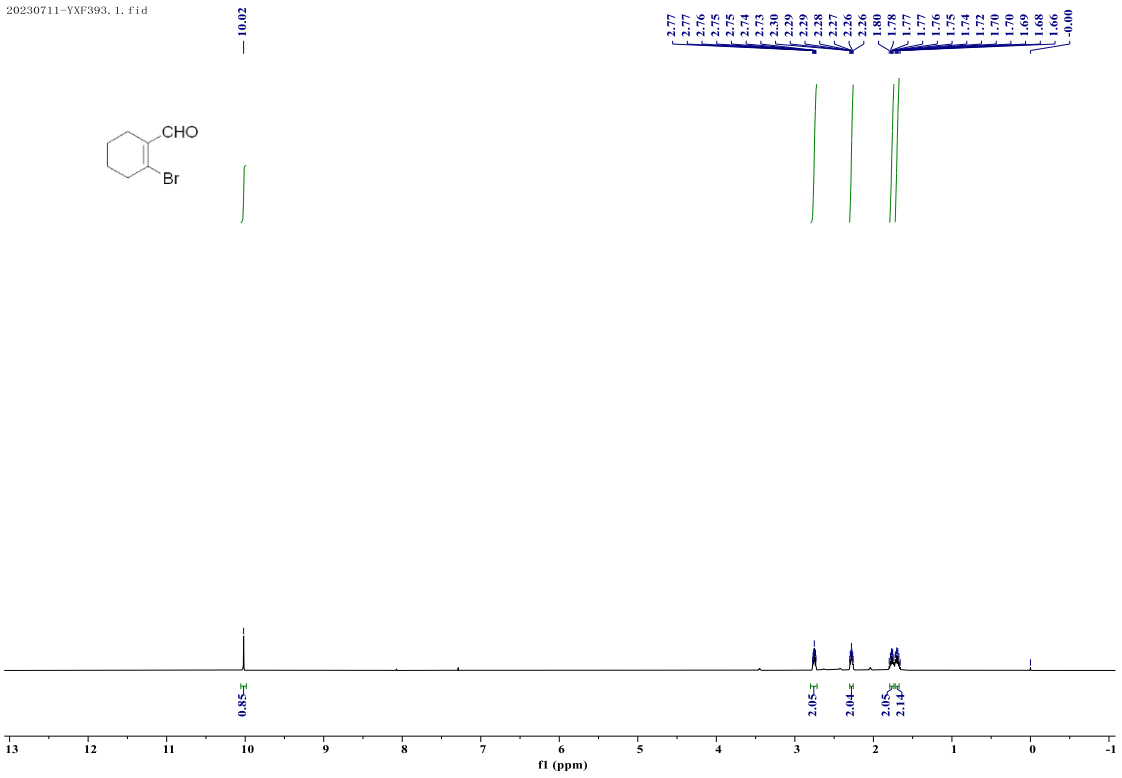
E(TD-HF/TD-KS) = -4121.87455128

Os	-0.76083	0.44962	-0.07607
Cl	-1.49504	0.85813	-2.4155
Cl	-2.51502	1.58654	1.2676
P	0.43279	2.61954	-0.14731
C	4.44365	2.99298	-1.22234
H	5.36501	3.36955	-0.78569
C	3.25887	3.04724	-0.48165
H	3.27576	3.4732	0.51542
C	2.34956	-1.32864	2.34753
C	4.44346	2.46509	-2.51273
H	5.36542	2.42403	-3.08658
C	1.71043	-1.10492	0.14759
C	1.33123	-0.79555	1.51934
C	0.79105	3.31493	1.52435

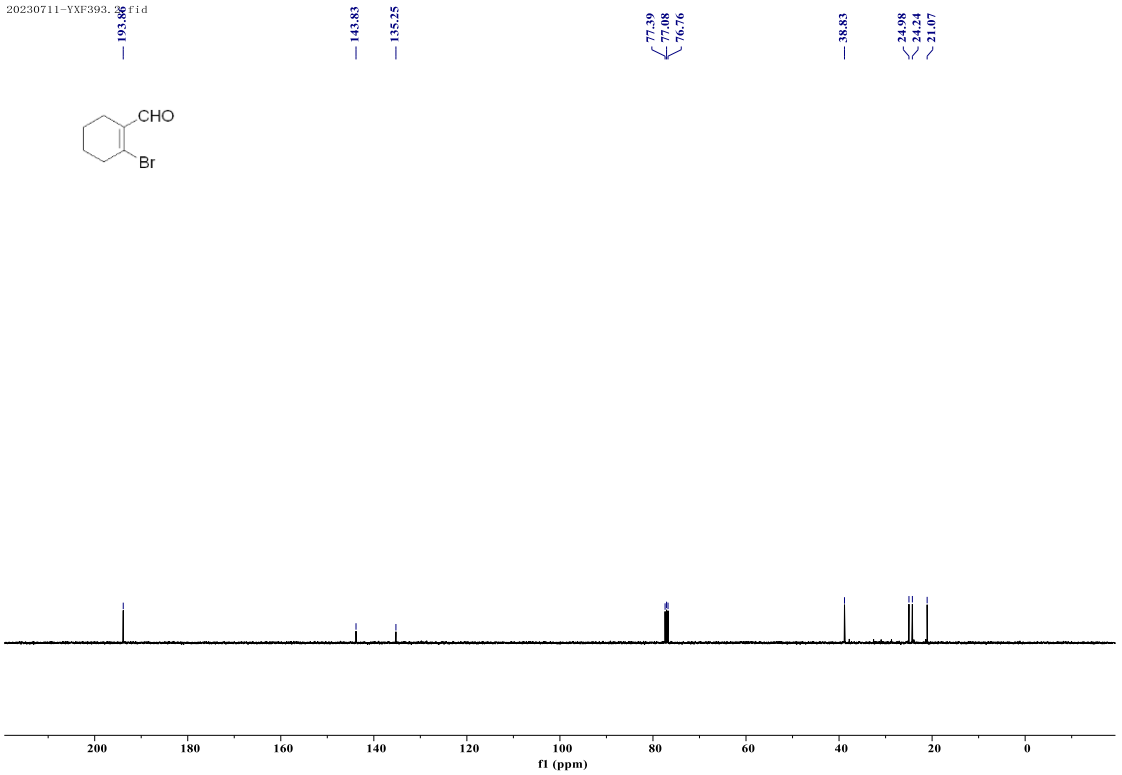
C	5.10327	-2.75862	-0.5422
C	-0.27611	6.16505	-2.1445
H	0.32666	6.98286	-2.53058
C	-0.41395	4.01332	-1.02121
C	-1.80923	4.04906	-1.15369
H	-2.40847	3.23474	-0.76799
C	1.7029	2.66803	2.37703
H	2.23274	1.78473	2.0378
C	0.82583	-0.56465	-0.78063
H	1.01079	-0.67453	-1.84861
C	0.11104	4.44606	1.99792
H	-0.60663	4.95397	1.36387
C	2.06098	2.56216	-1.02362
C	1.2567	4.28008	4.12506
H	1.43551	4.65299	5.13003
C	2.94069	-1.82599	0.1859
C	0.15685	-0.06327	1.63551
H	-0.22755	0.22123	2.61563
C	3.7618	-2.42055	-0.86086
C	5.41343	-3.59655	-2.80369
H	6.05612	-4.05402	-3.55114
C	5.90774	-3.34071	-1.52234
H	6.93634	-3.59884	-1.27977
C	1.93786	3.15123	3.66414
H	2.64837	2.63861	4.3068
C	3.32939	-1.93911	1.5529
C	-1.66637	6.19367	-2.27235
H	-2.15195	7.03539	-2.75941
C	0.34271	4.92232	3.29019
H	-0.1977	5.79699	3.64182
C	4.08946	-3.27722	-3.11424
H	3.69277	-3.49018	-4.10319
C	0.34689	5.08262	-1.52404
H	1.42852	5.072	-1.43591
C	3.24982	1.99404	-3.06612
H	3.23795	1.58964	-4.0747
C	-2.42795	5.13628	-1.77445
H	-3.51004	5.14859	-1.87243
C	3.26993	-2.69898	-2.14894
H	2.22905	-2.49434	-2.37567
C	2.06734	2.03964	-2.3297
H	1.14109	1.68129	-2.77083

C	5.64824	-2.43995	0.83699
C	4.5961	-2.63914	1.94436
P	-2.1837	-1.57158	-0.03373
C	-0.80577	-5.36292	-1.08946
H	-0.71602	-6.34518	-0.63307
C	-1.33546	-4.30383	-0.34529
H	-1.65895	-4.48159	0.6744
C	-0.40161	-5.16296	-2.40836
H	0.00673	-5.98798	-2.98589
C	-2.57526	-2.16	1.67124
C	-5.76635	-2.5647	-1.82977
H	-6.25876	-3.48087	-2.14491
C	-3.84281	-1.45266	-0.84305
C	-4.48147	-0.21774	-1.02144
H	-3.99095	0.69301	-0.70418
C	-1.5562	-2.66978	2.49551
H	-0.54264	-2.75857	2.11966
C	-3.87013	-2.03916	2.19582
H	-4.66862	-1.63523	1.58396
C	-1.45306	-3.02774	-0.91161
C	-3.12725	-2.94373	4.31554
H	-3.34085	-3.24638	5.33717
C	-1.83313	-3.06475	3.80418
H	-1.03348	-3.46017	4.42457
C	-6.39654	-1.33053	-2.00421
H	-7.38372	-1.28169	-2.45651
C	-4.14139	-2.42706	3.50969
H	-5.14963	-2.32078	3.90066
C	-4.49772	-2.6263	-1.25459
H	-4.01664	-3.59146	-1.13122
C	-0.5309	-3.89631	-2.98587
H	-0.23257	-3.73414	-4.01846
C	-5.75247	-0.1619	-1.59793
H	-6.23419	0.80269	-1.73271
C	-1.04827	-2.83437	-2.24514
H	-1.15245	-1.85405	-2.70281
H	4.40427	-3.71497	2.07979
H	4.97212	-2.2662	2.9032
H	5.97826	-1.38997	0.85578
H	6.53525	-3.05044	1.03985
Cl	2.40198	-1.23498	4.08259

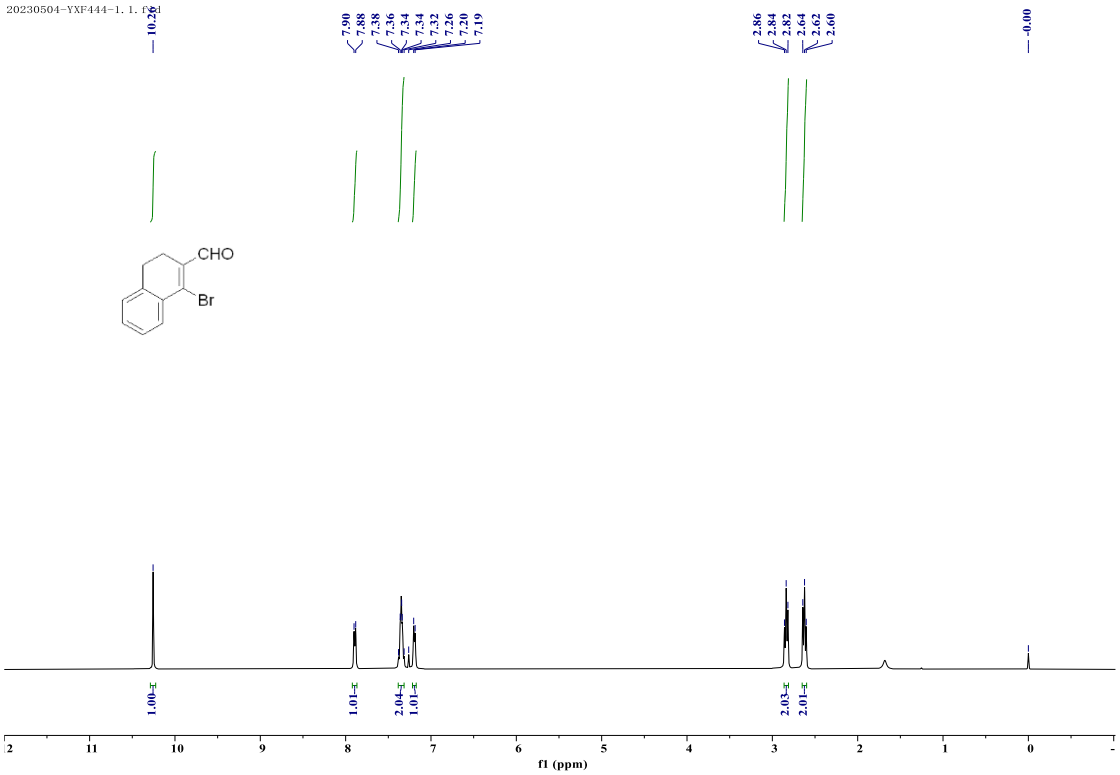
12. NMR and HRMS Spectra



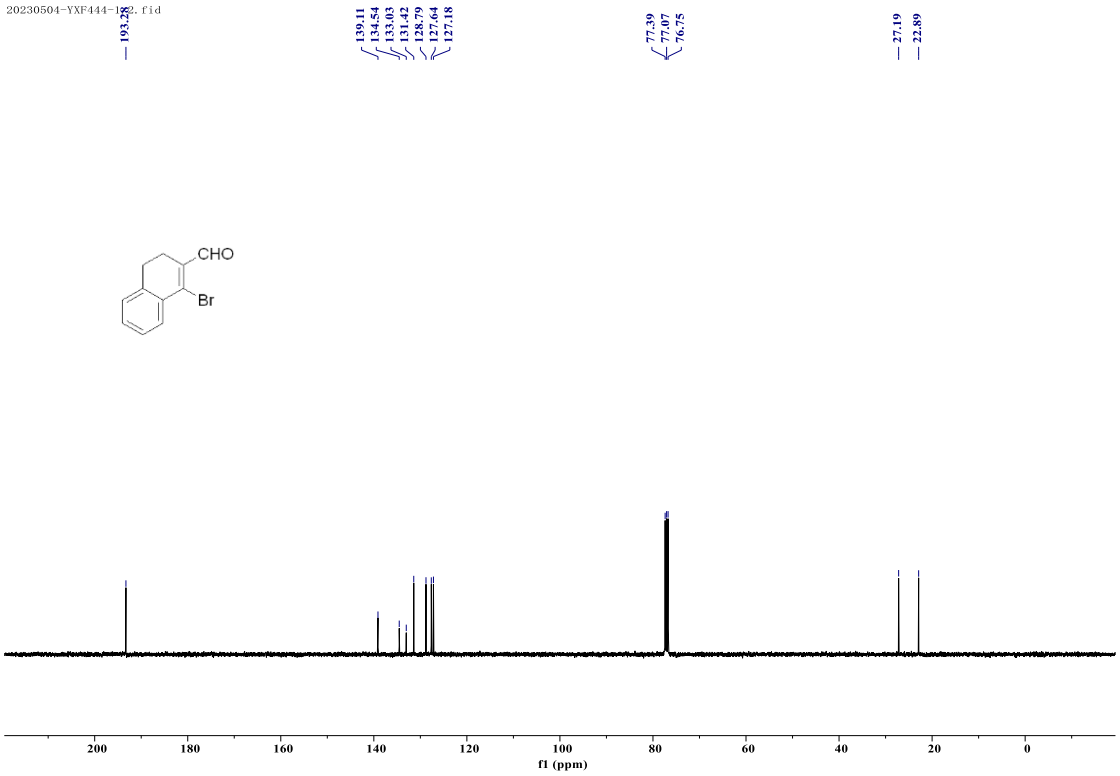
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**.



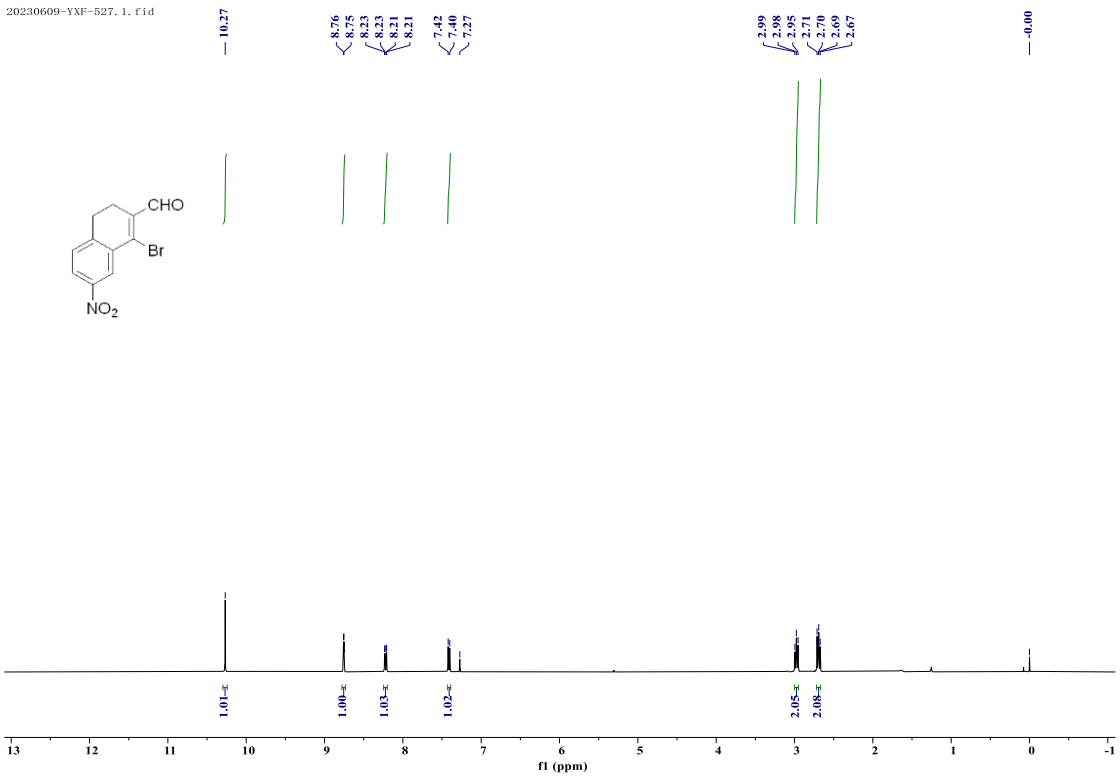
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2a**.



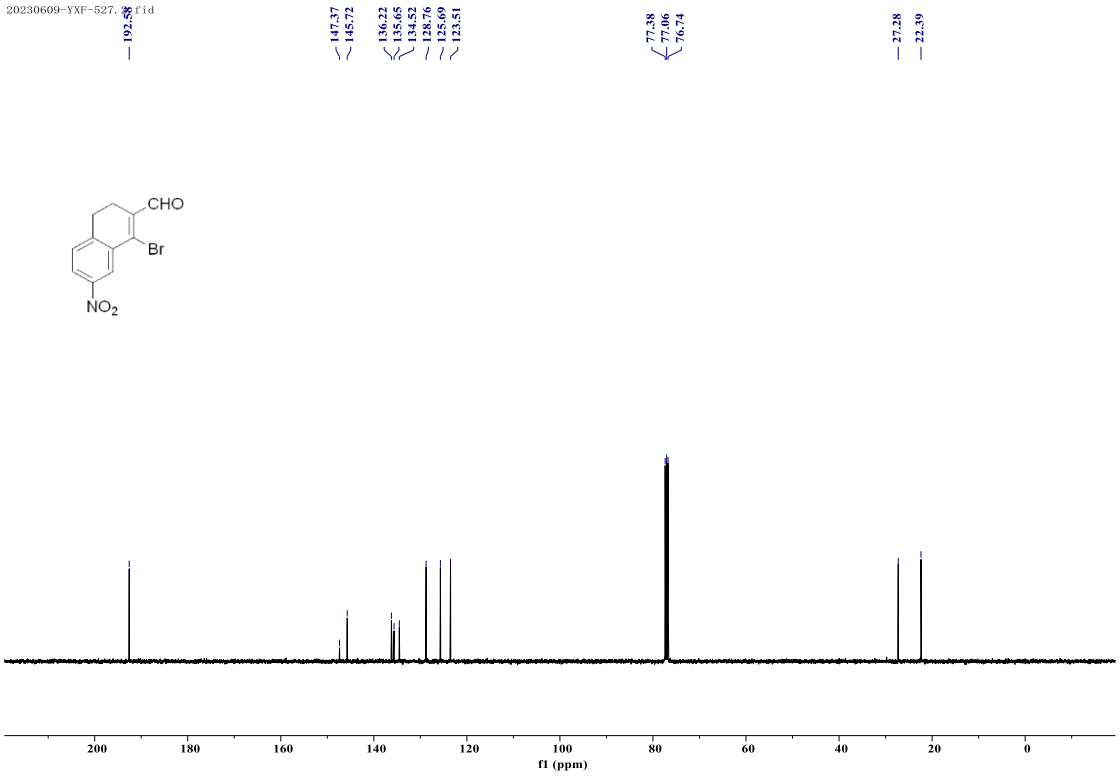
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b**.



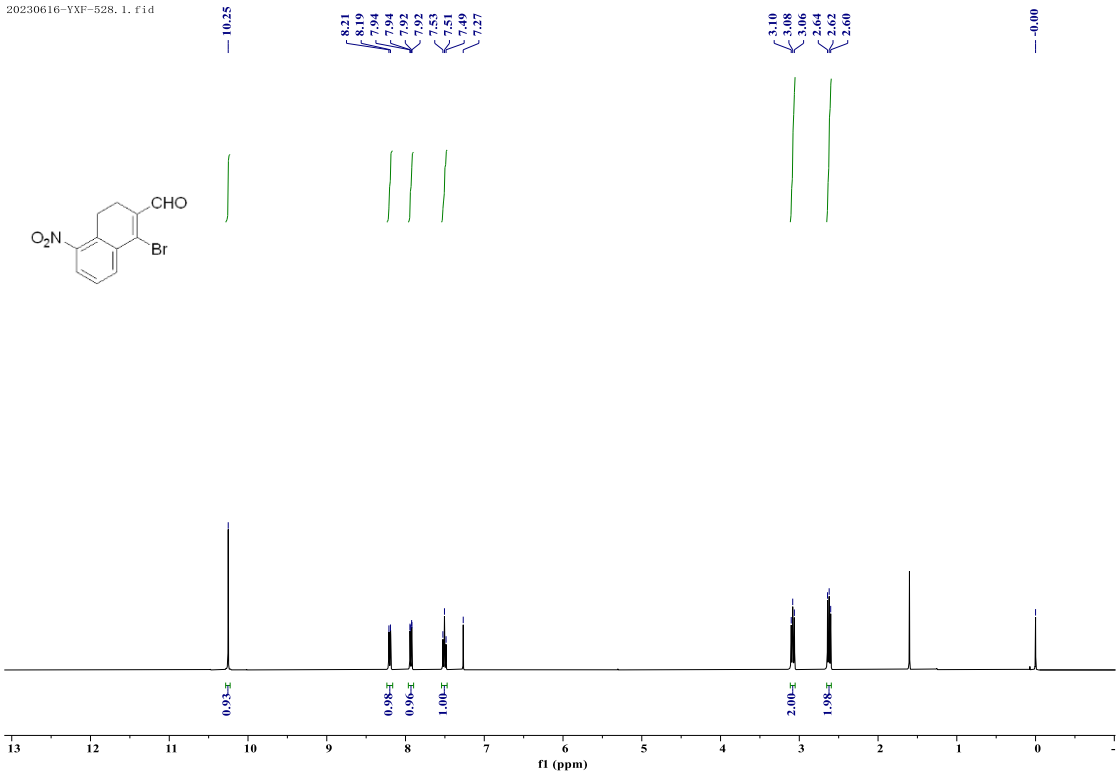
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2b**.



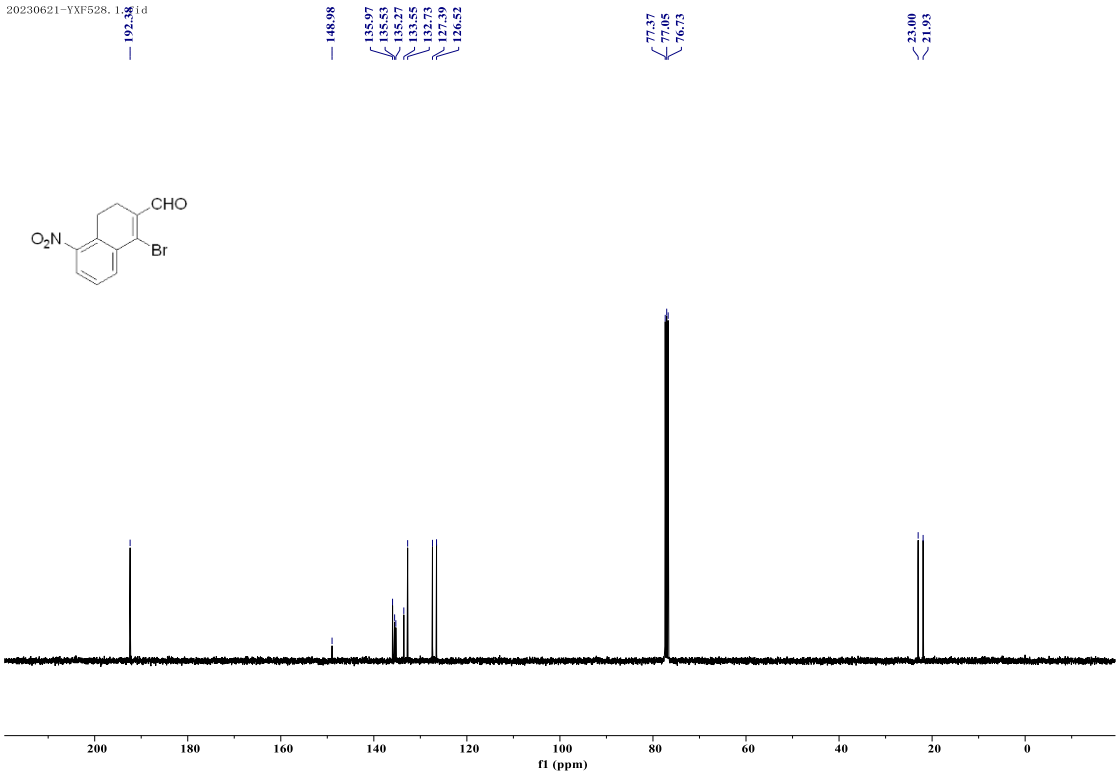
The ^{1}H NMR (400 MHz, $CDCl_3$) of **2c**.



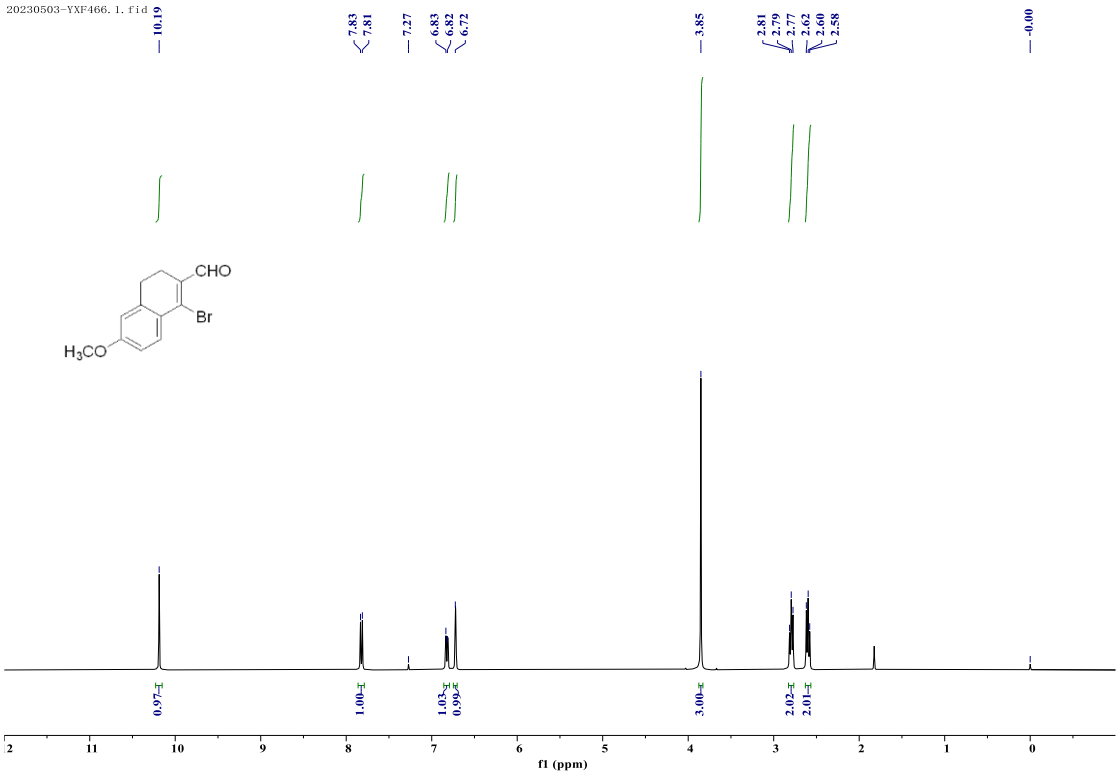
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2c**.



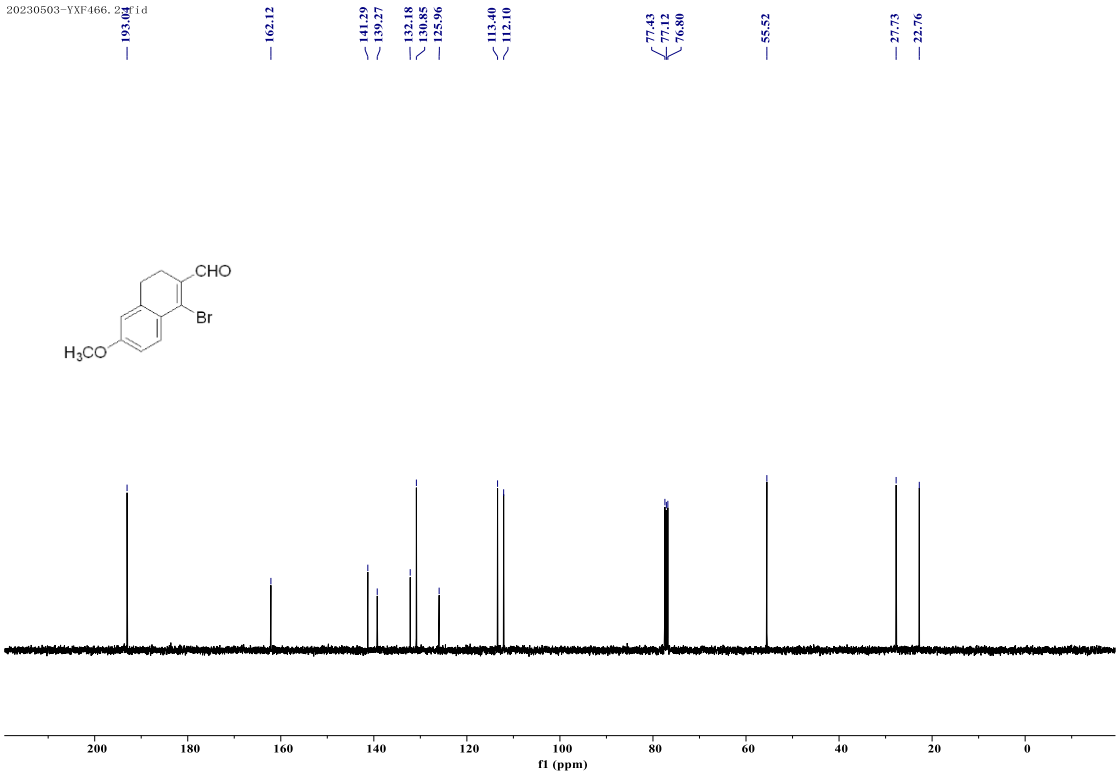
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**.



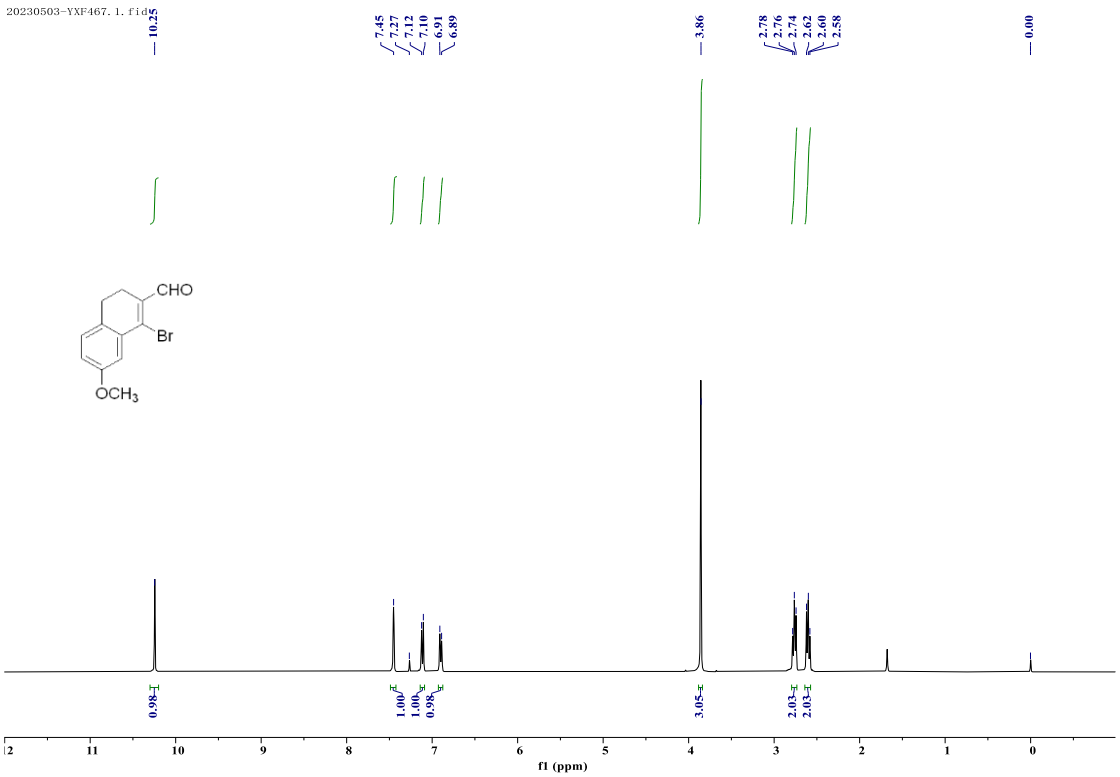
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2d**.



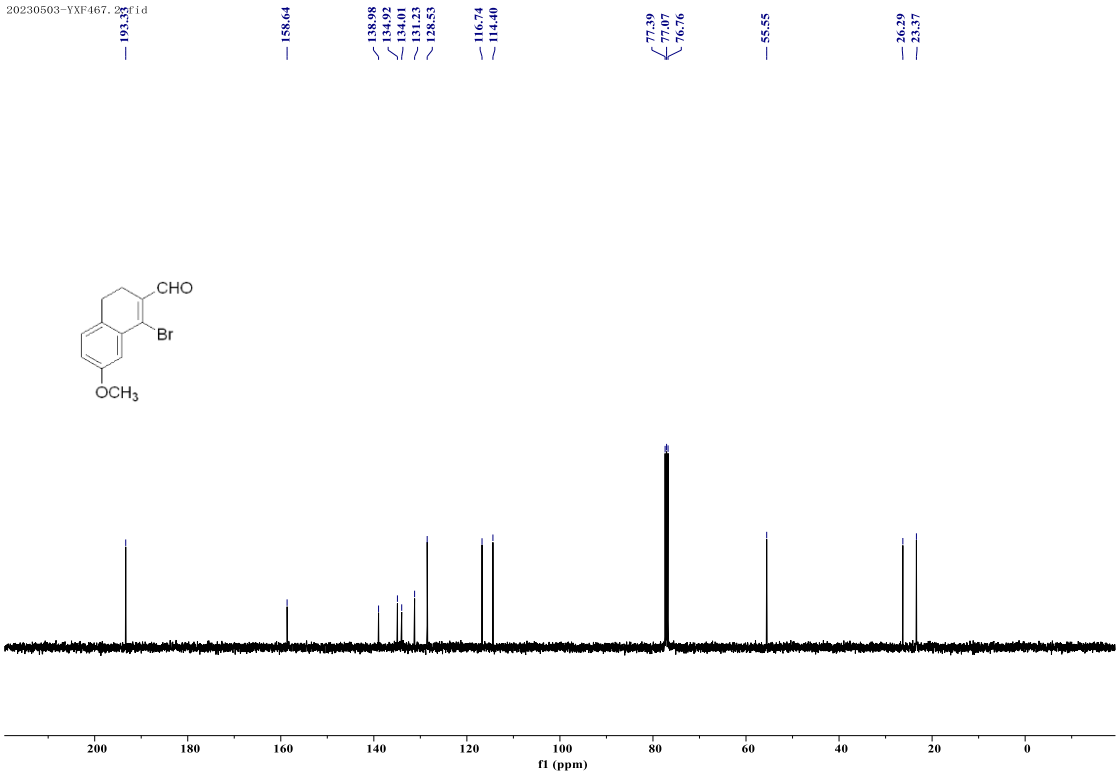
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2e**.



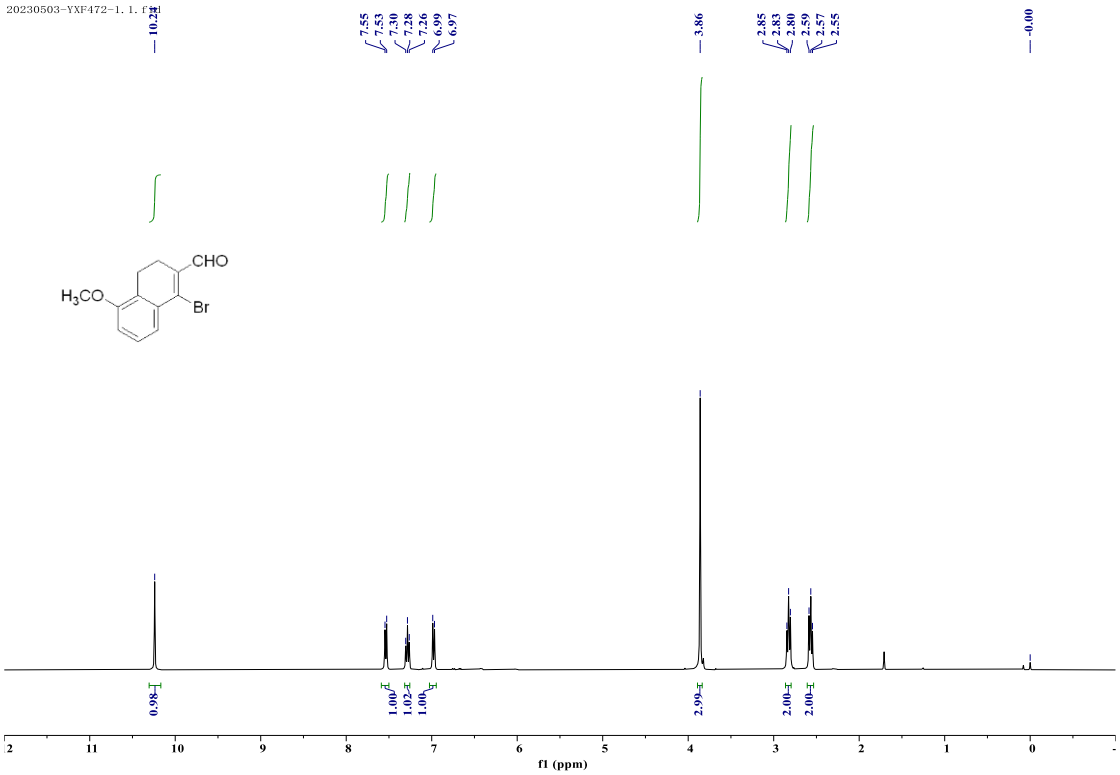
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2e**.



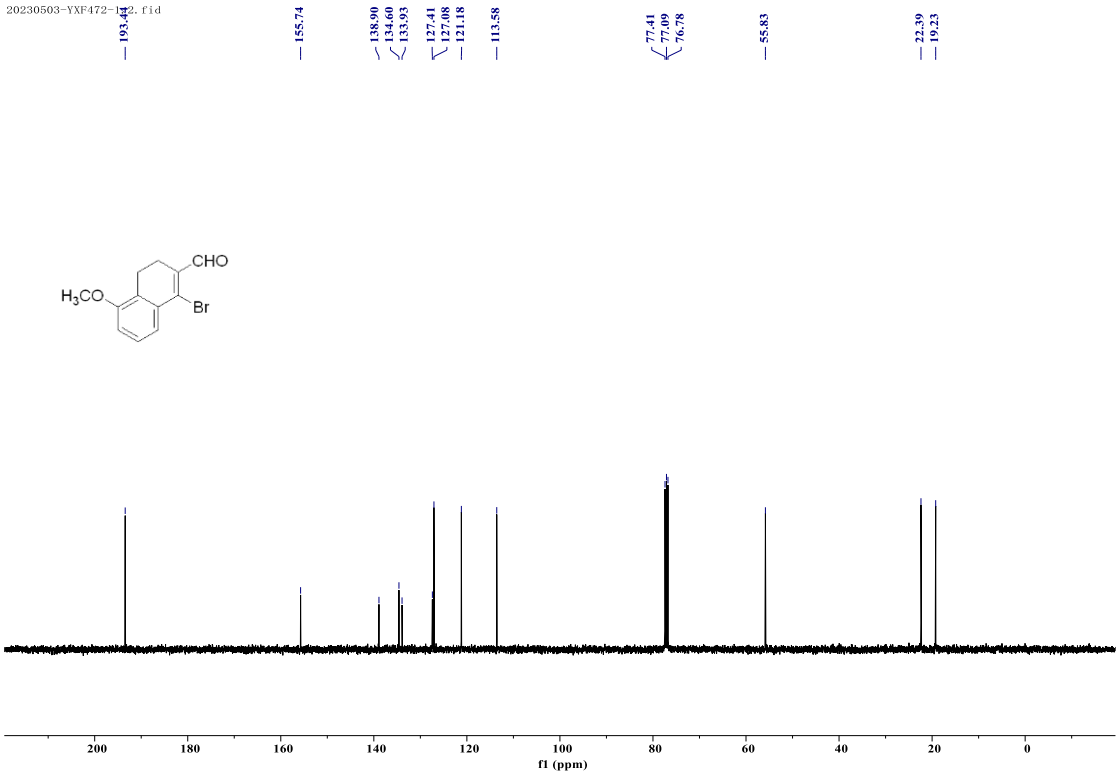
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2f**.



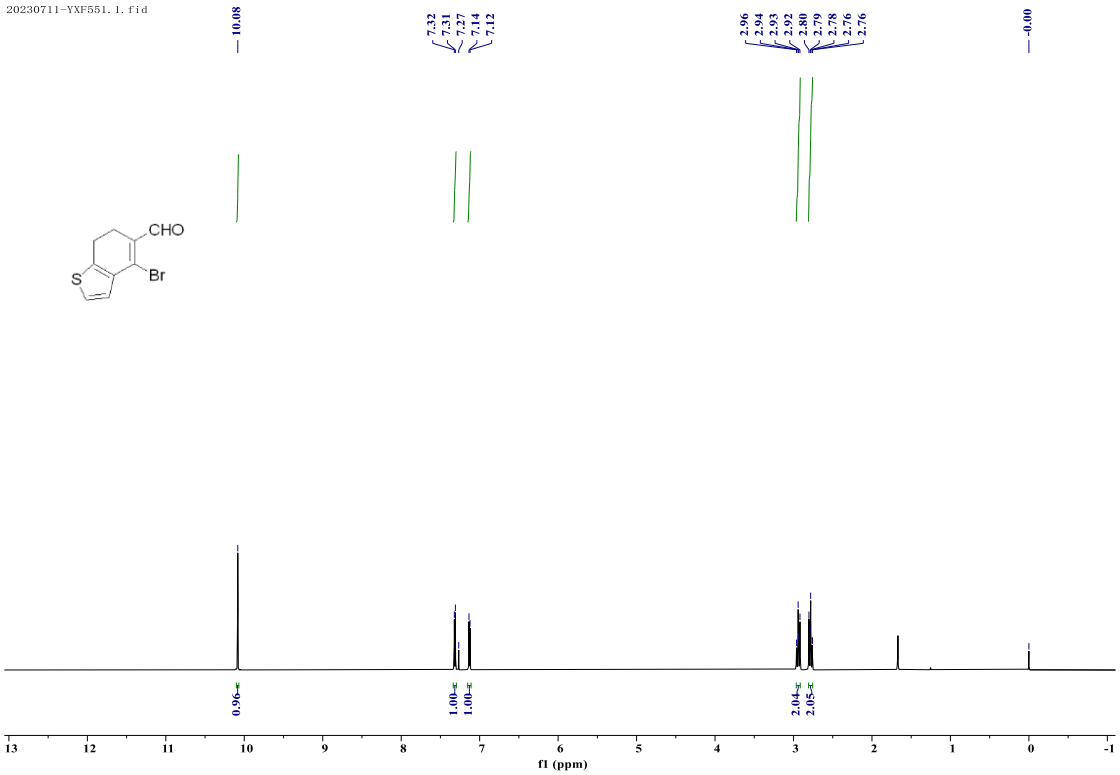
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2f**.



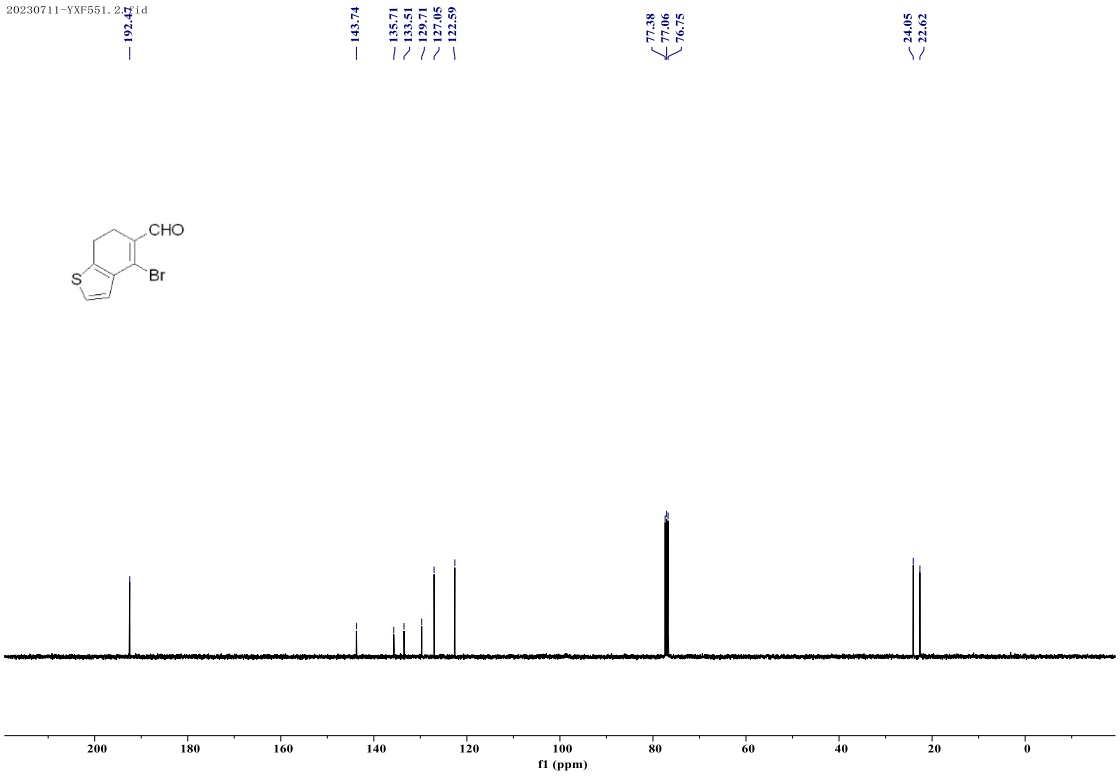
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2g**.



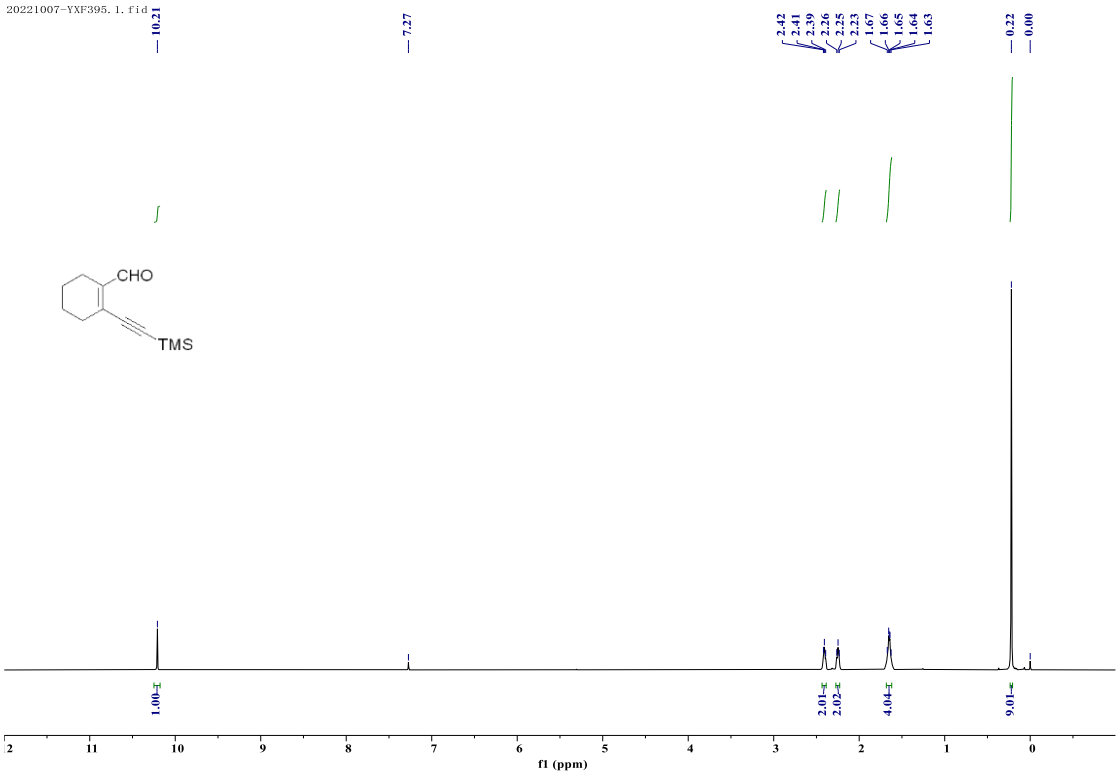
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2g**.



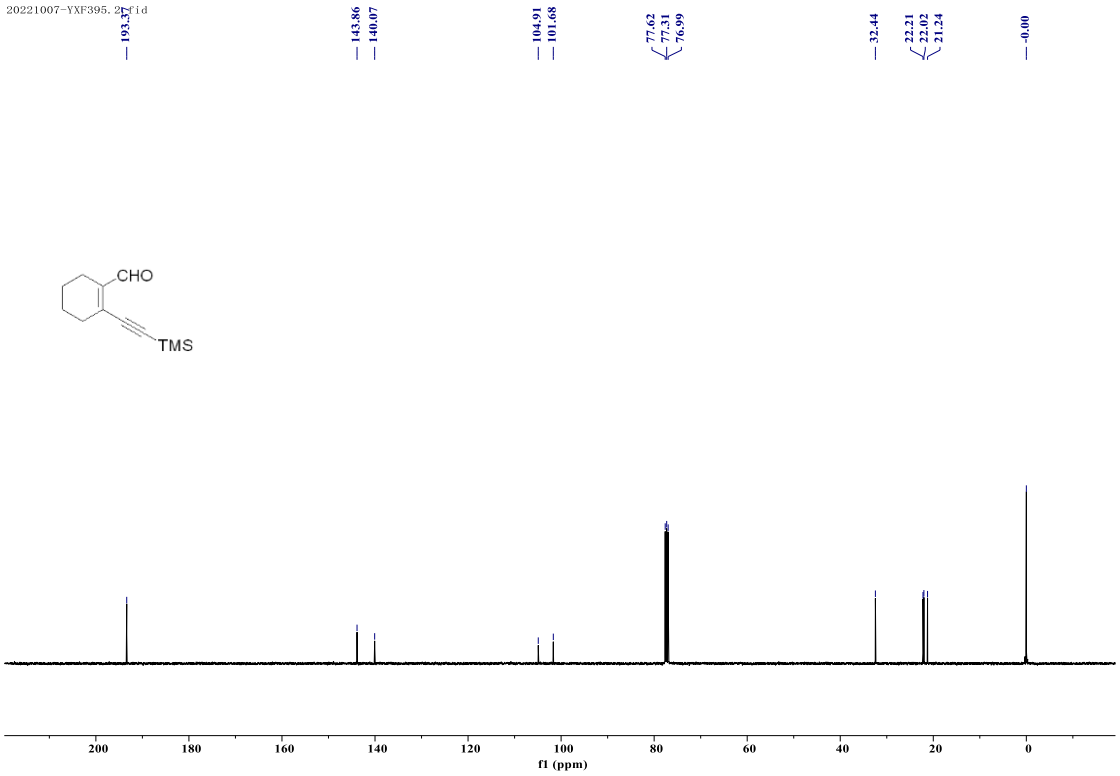
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2h**.



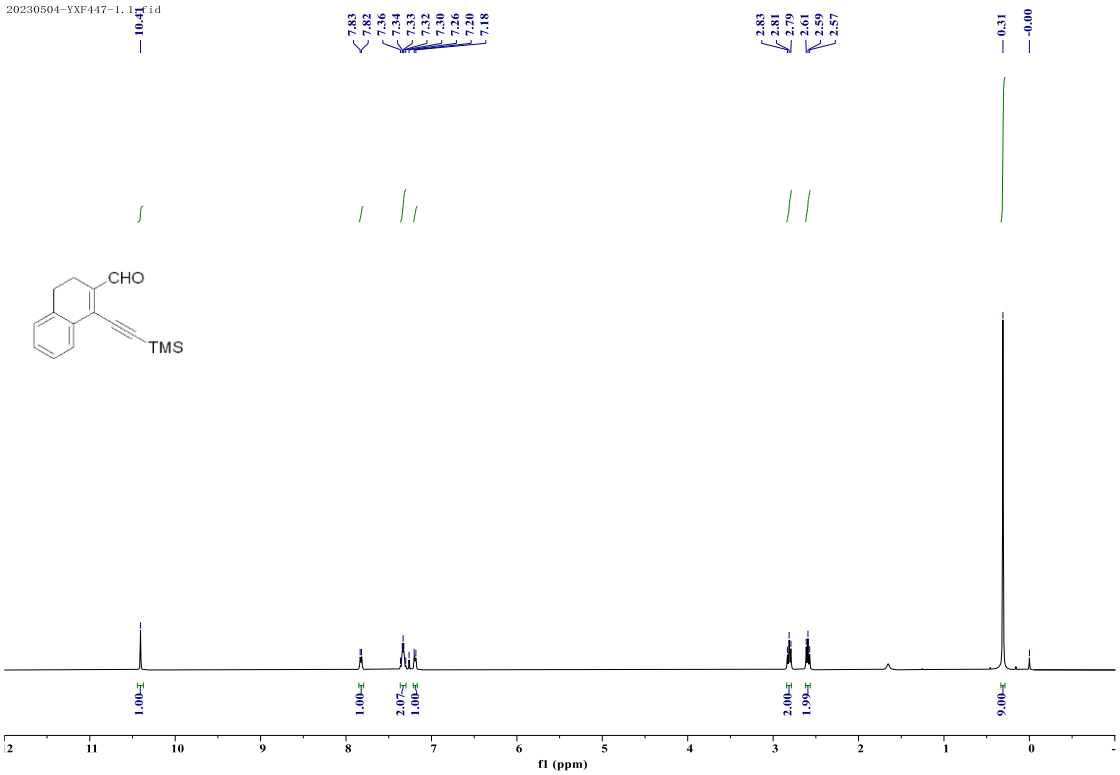
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2h**.



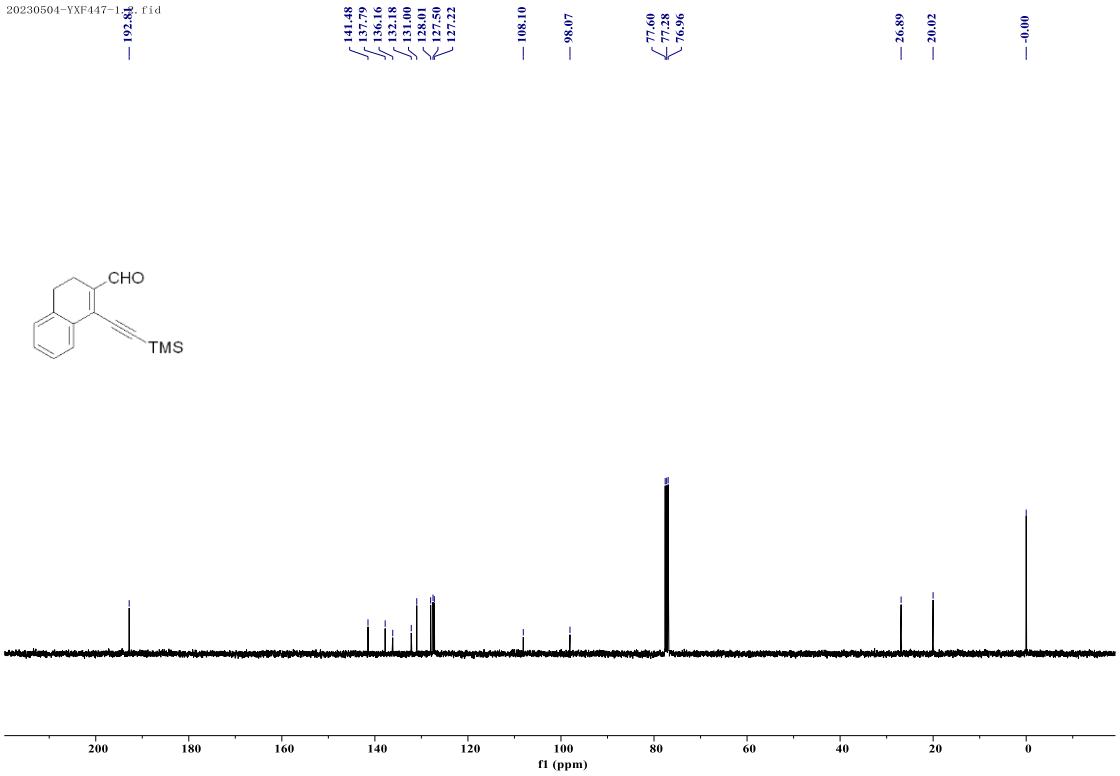
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**.



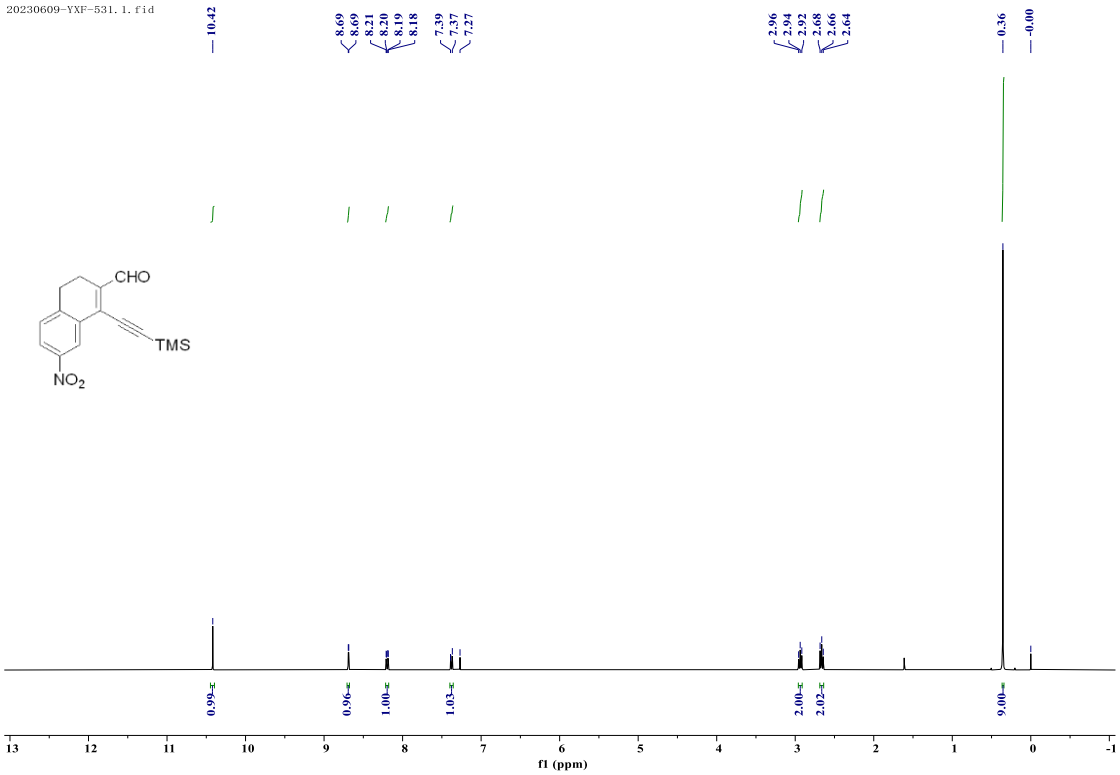
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3a**.



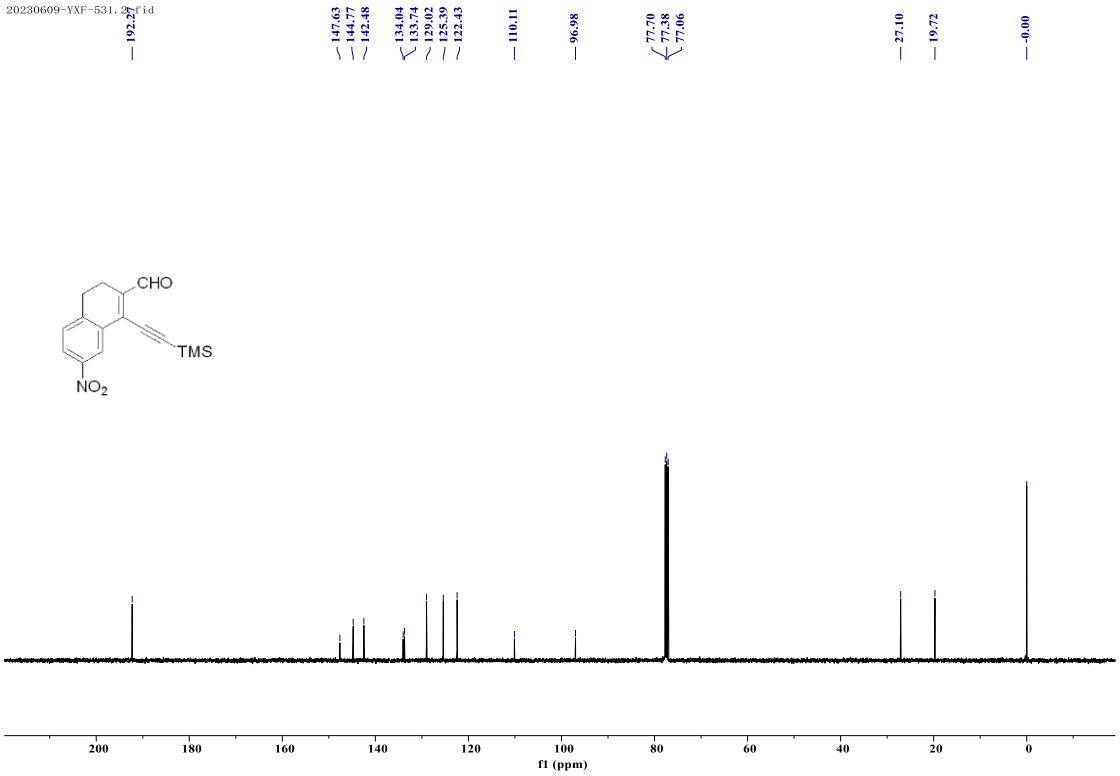
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**.



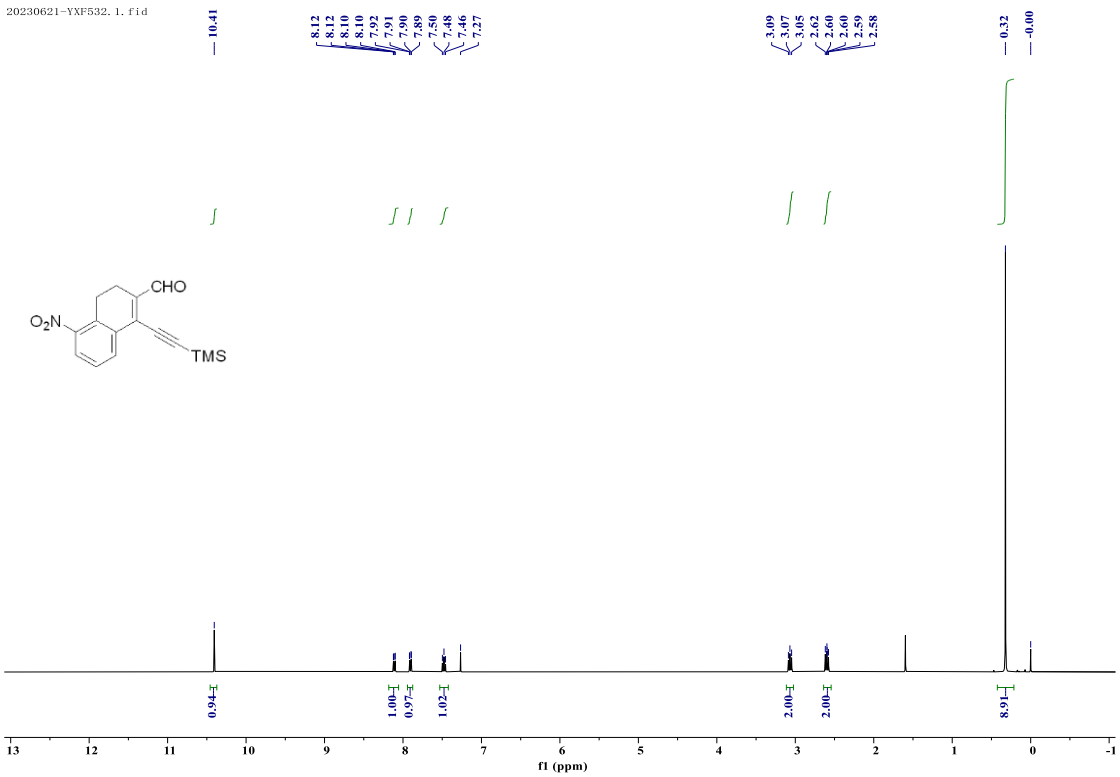
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3b**.



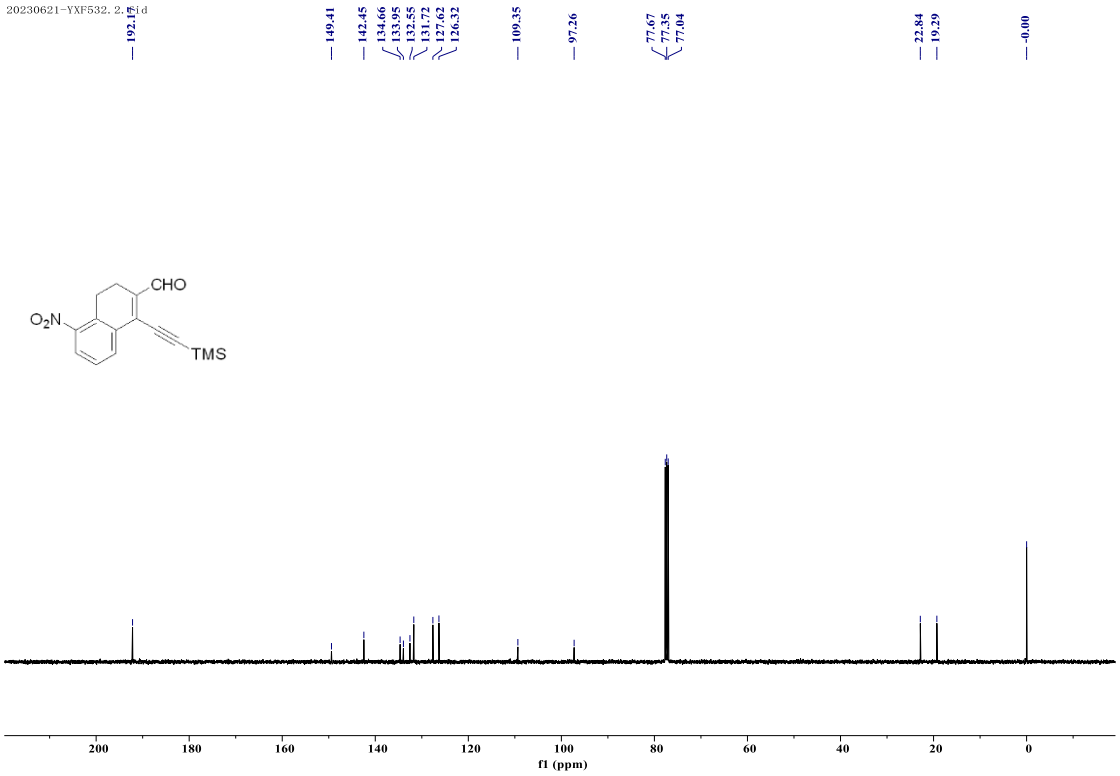
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**.



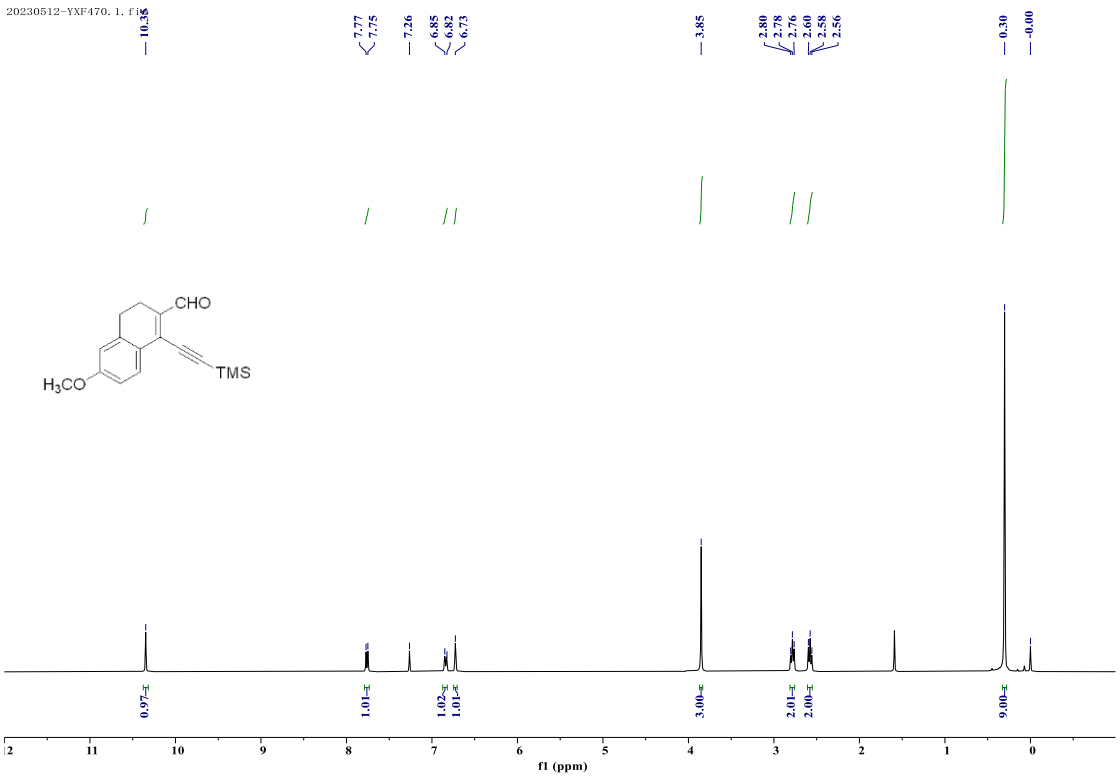
The $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3c**.



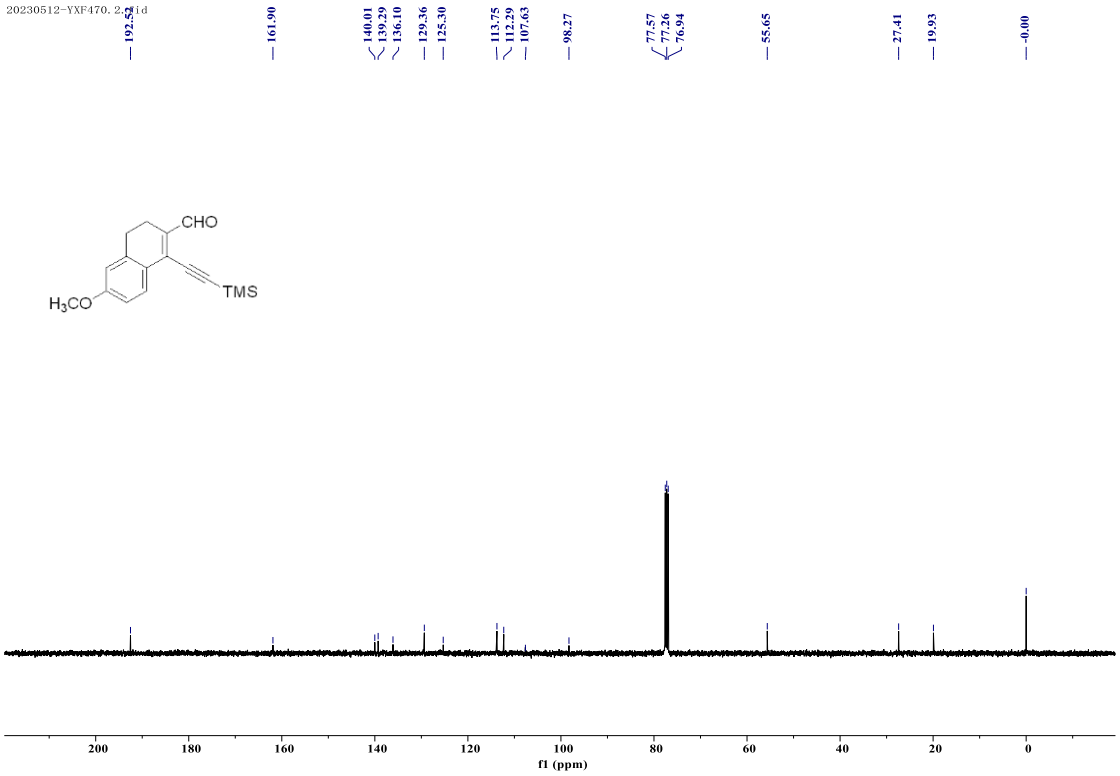
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3d**.



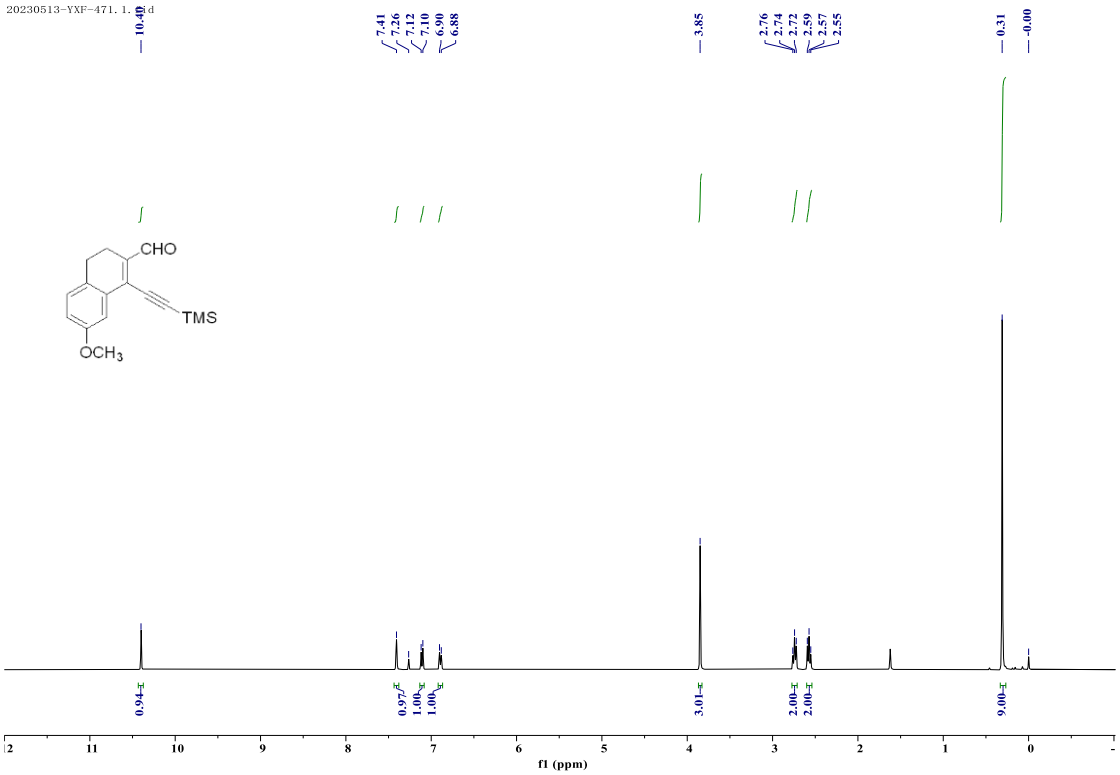
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3d**.



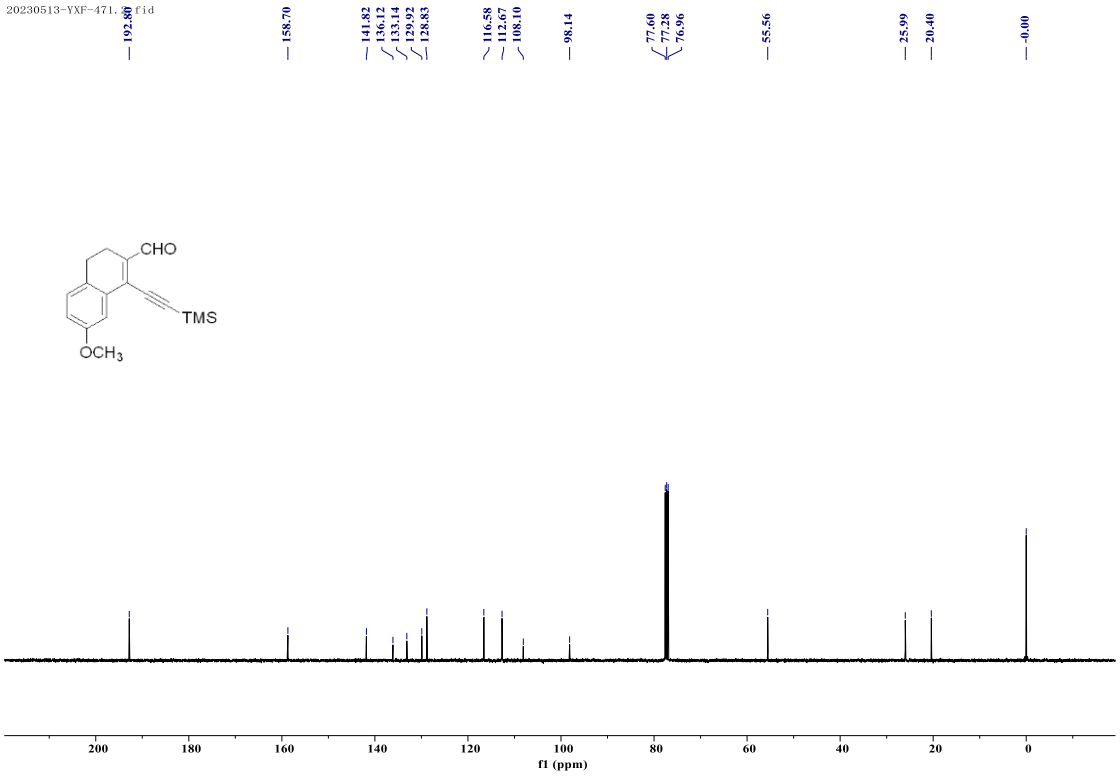
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3e**.



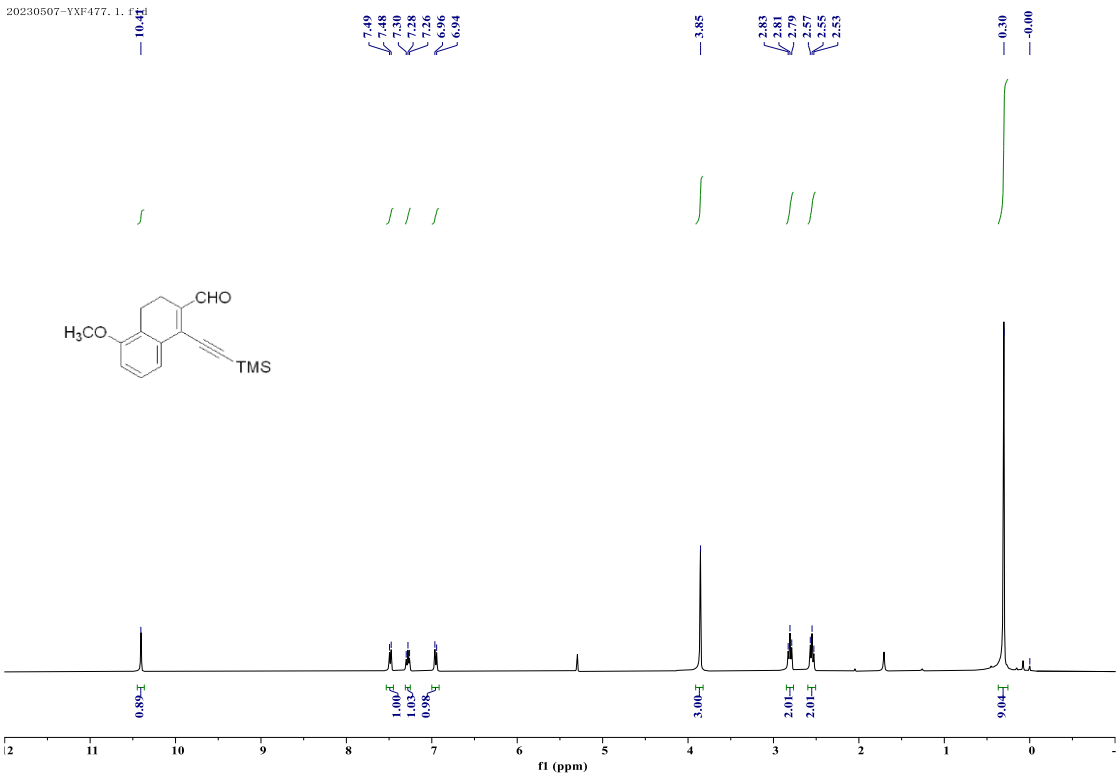
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3e**.



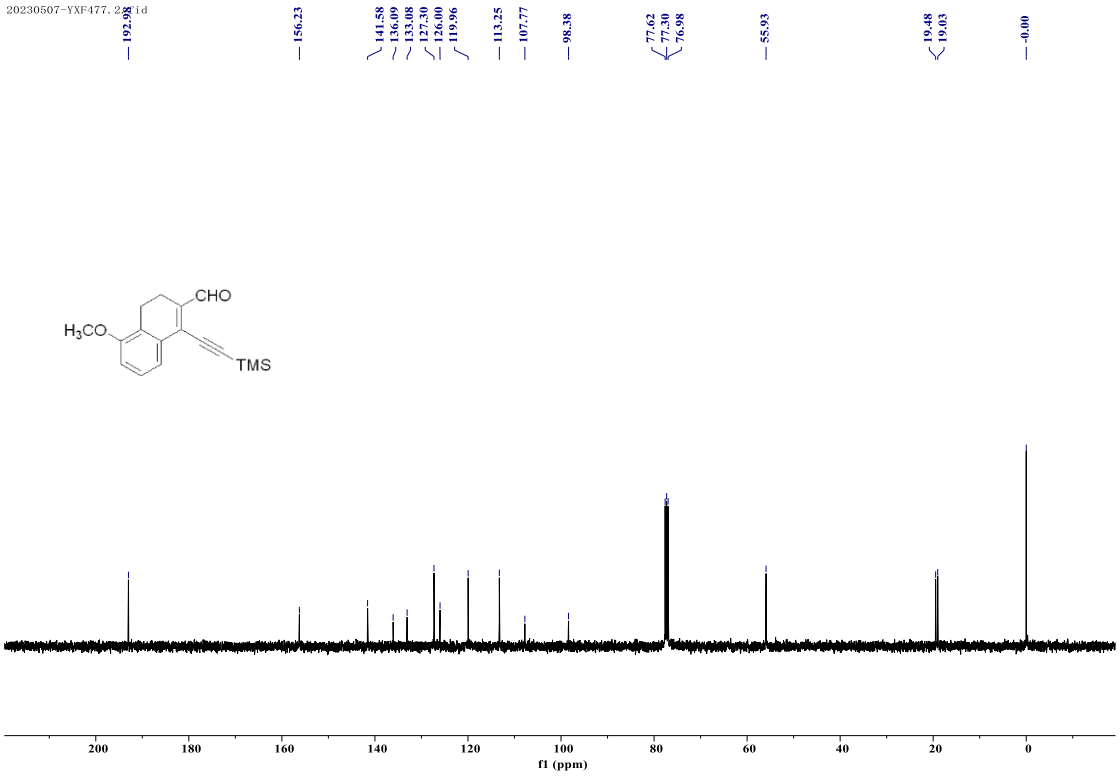
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3f**.



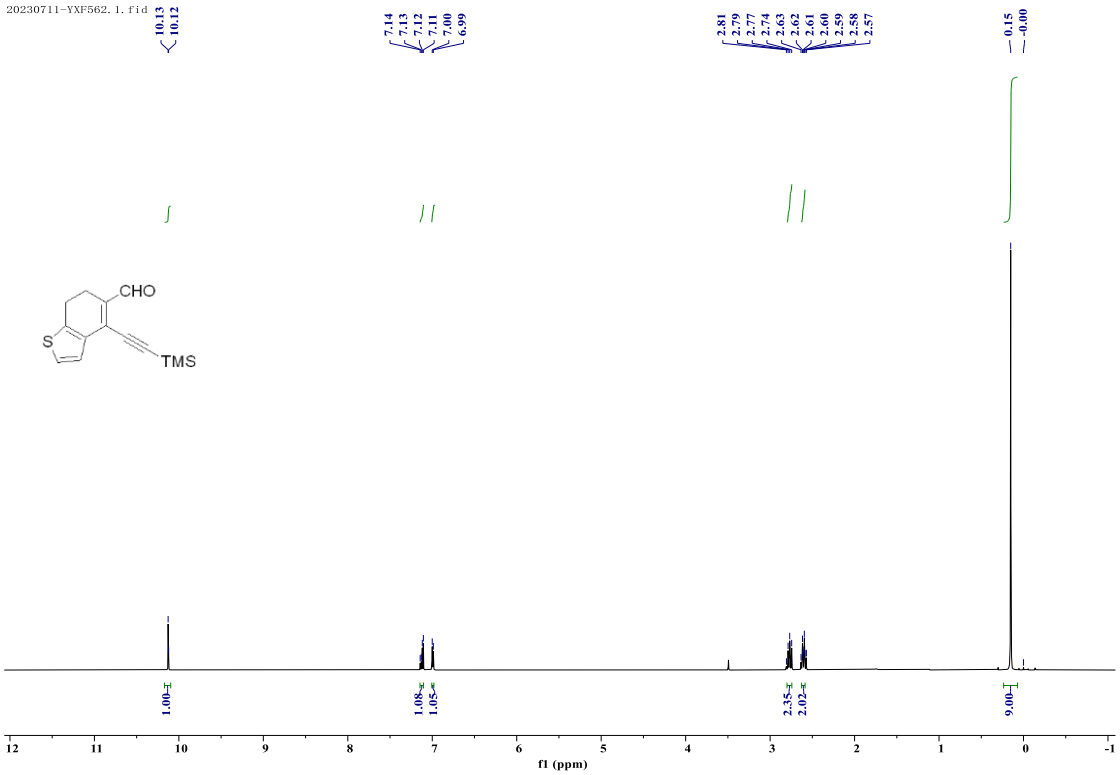
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3f**.



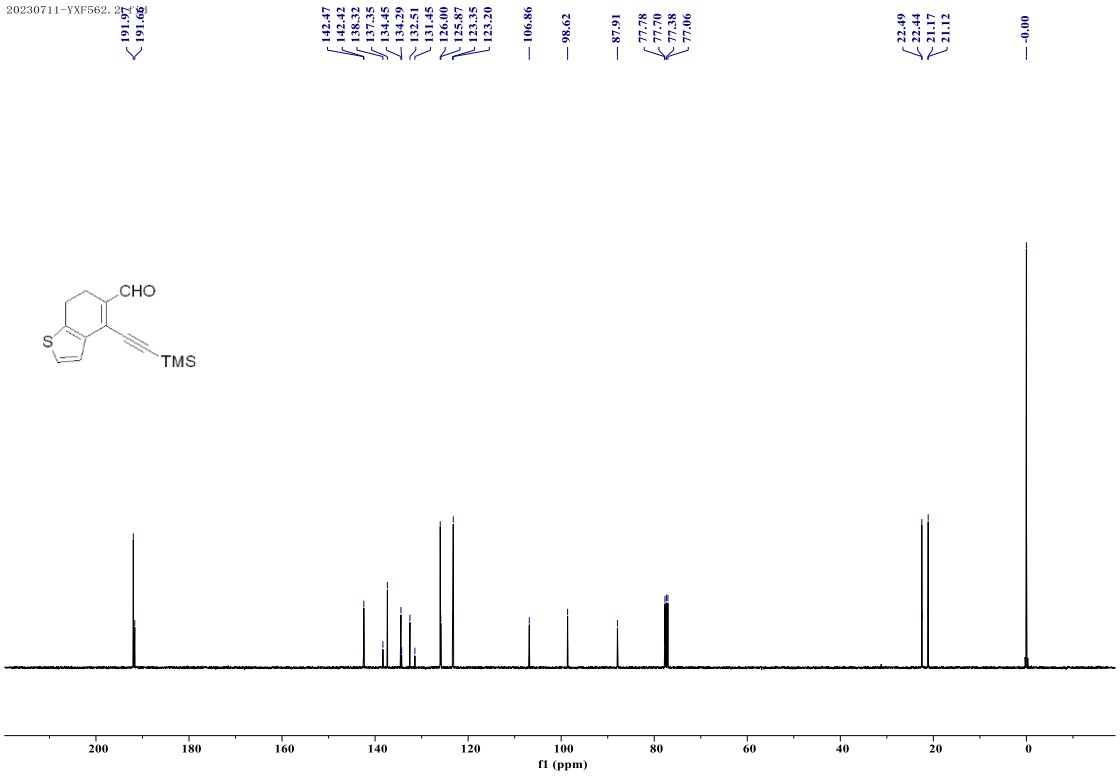
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**.



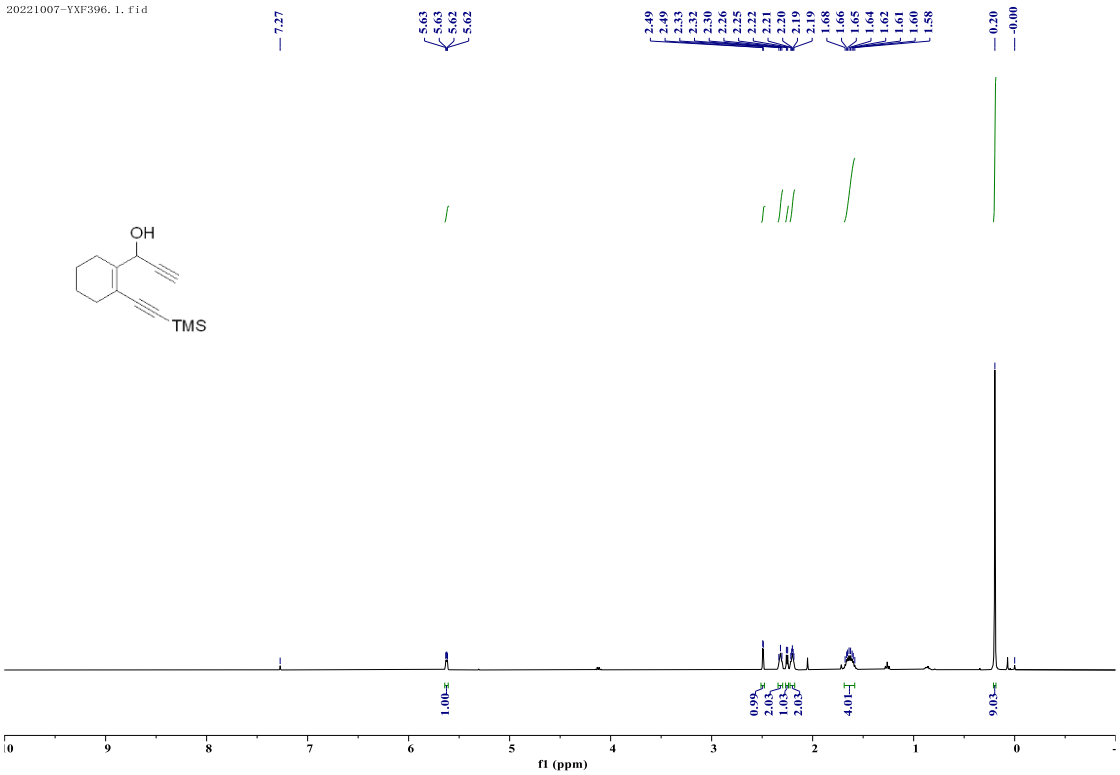
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3g**.



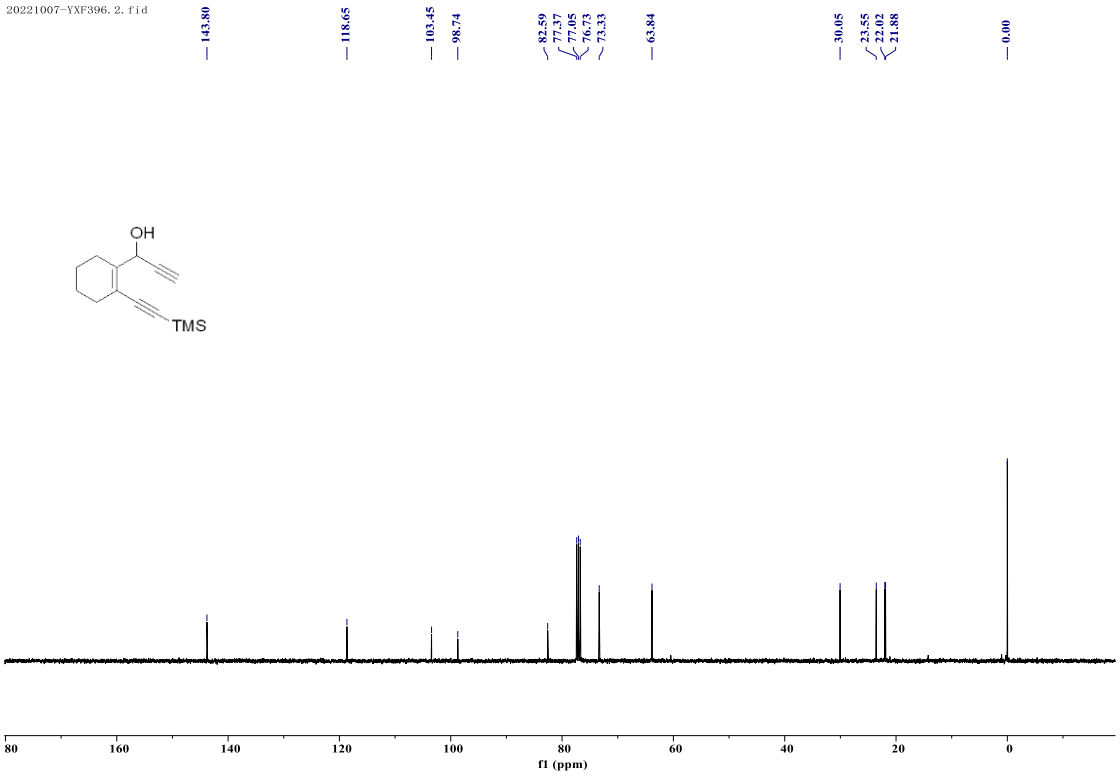
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**.



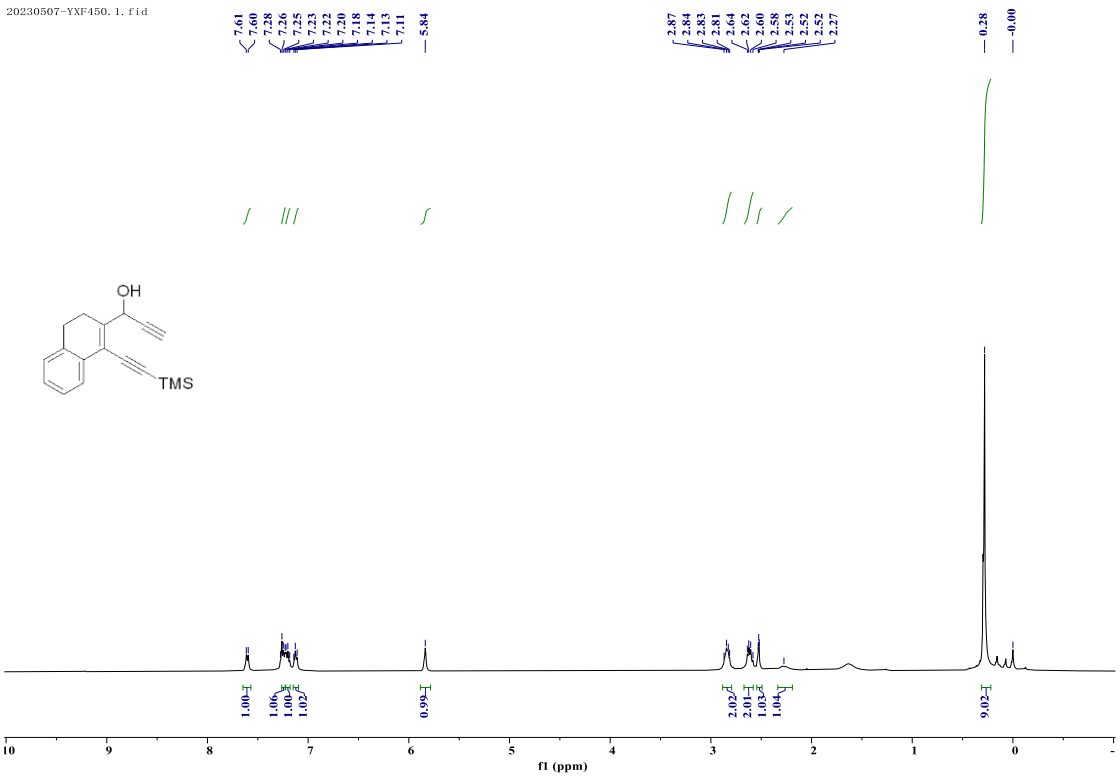
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3h**.



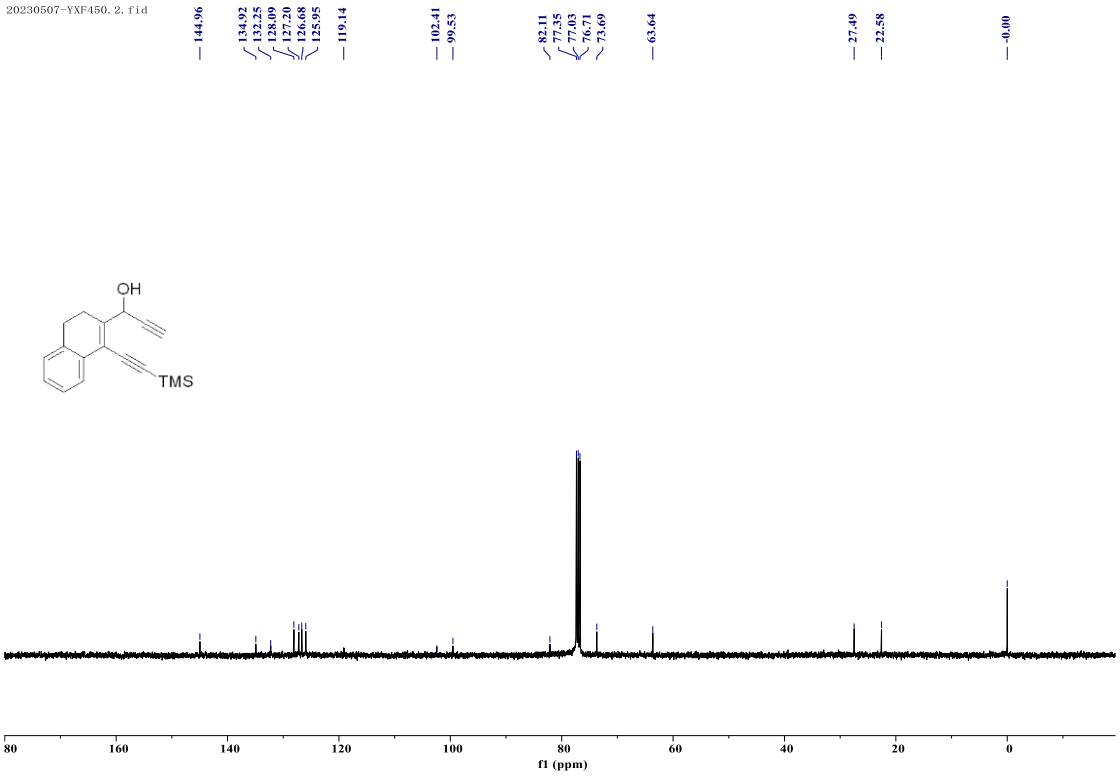
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**.



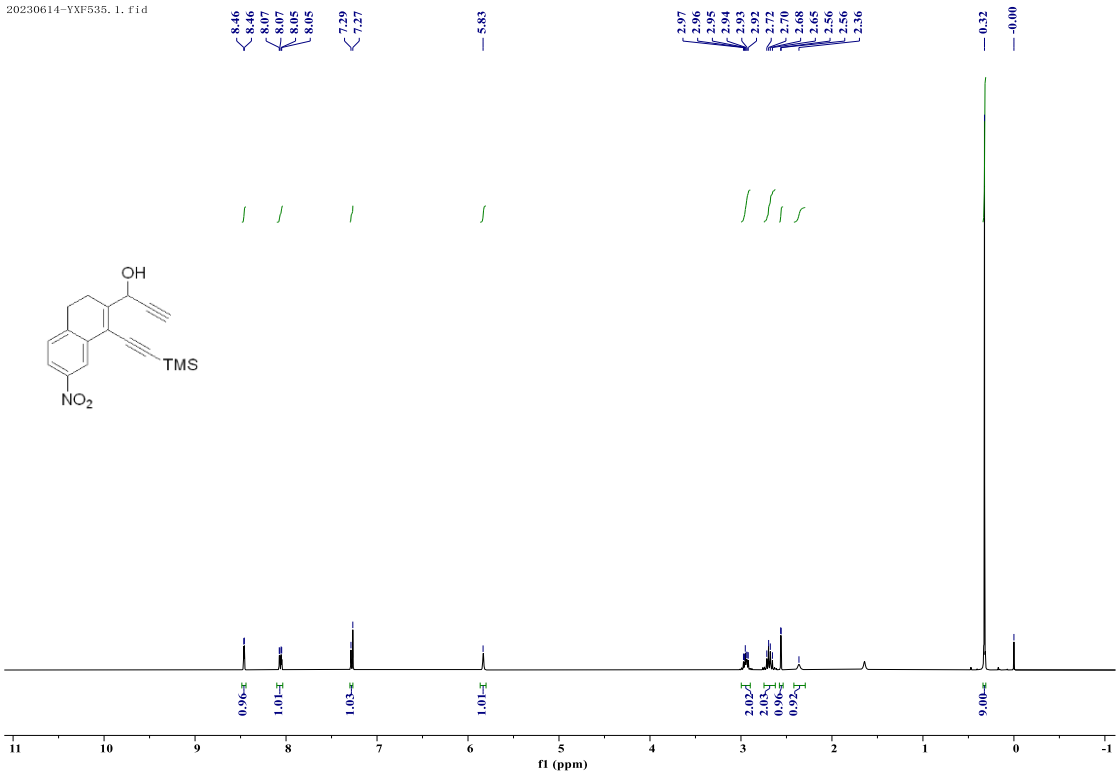
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **4a**.



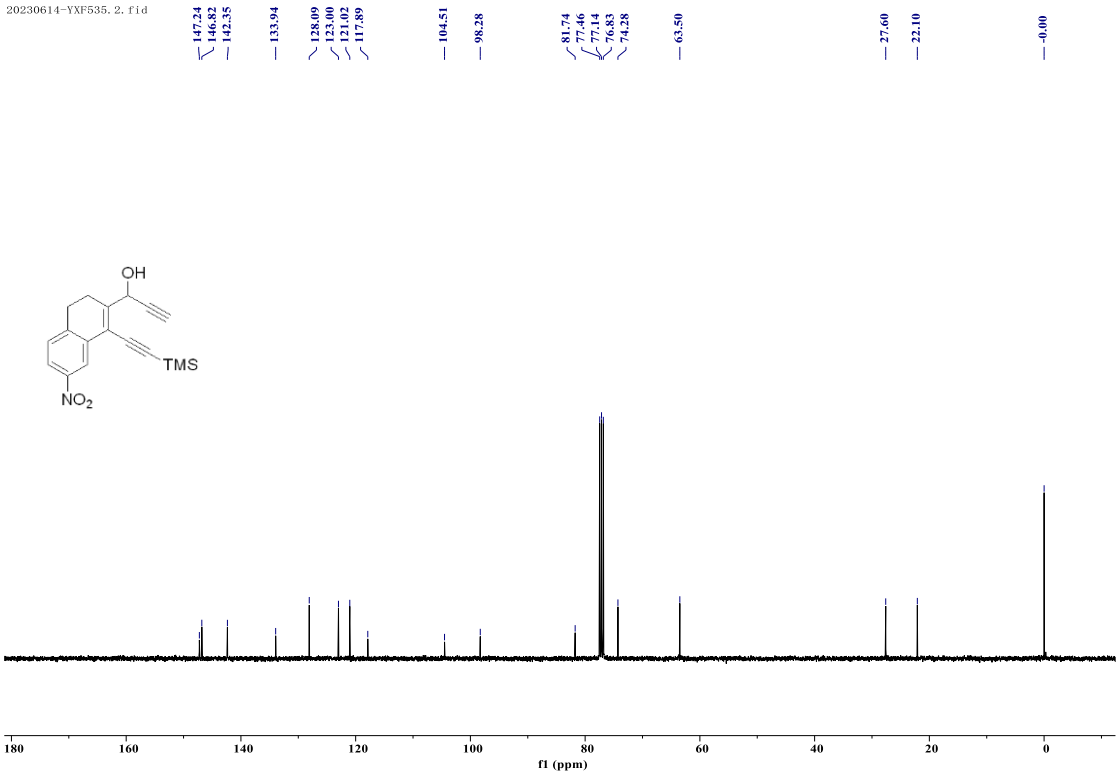
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**.



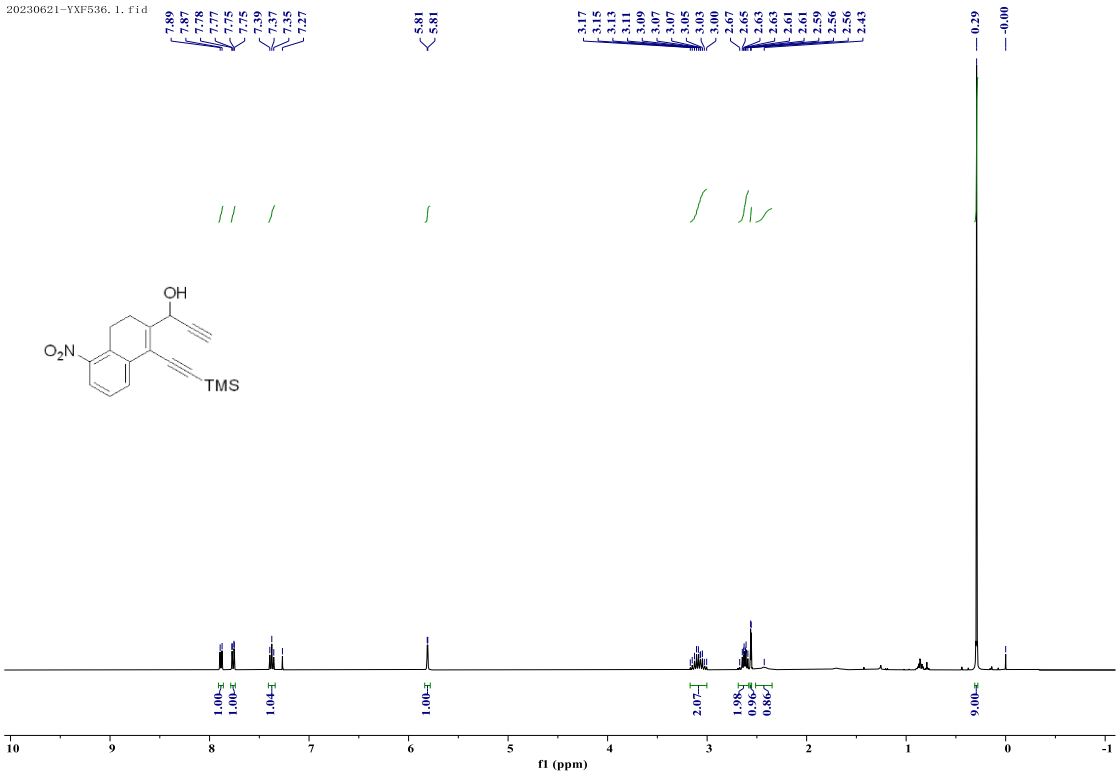
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **4b**.



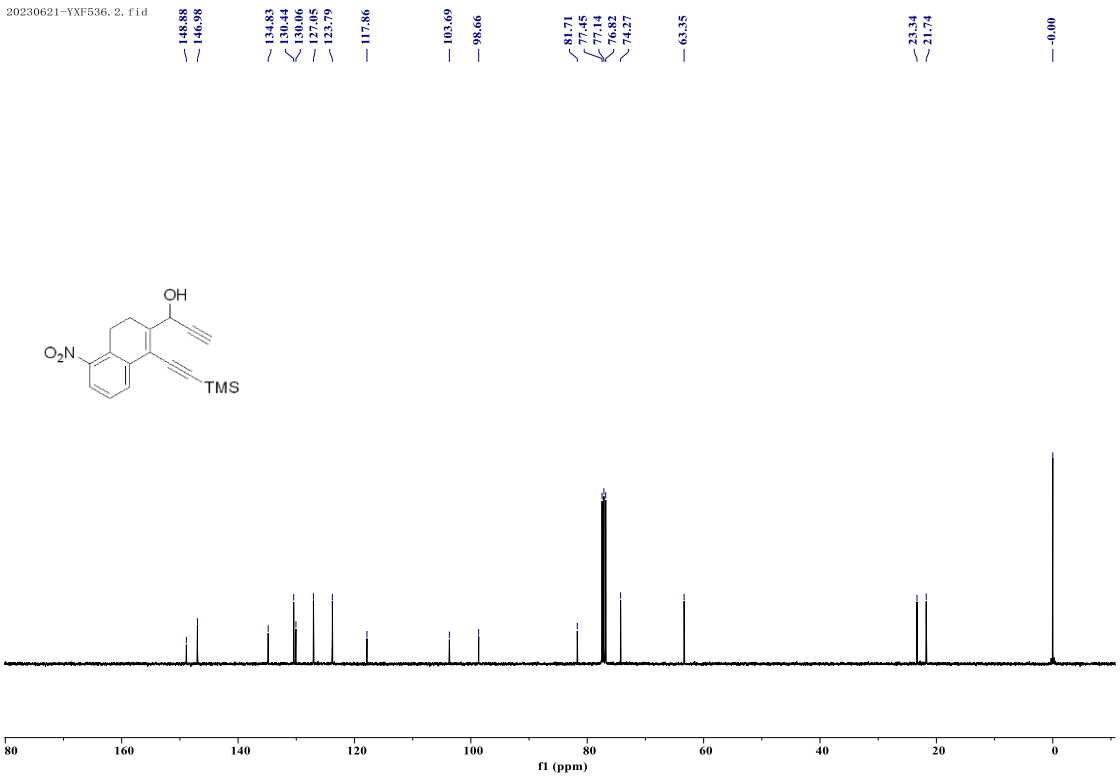
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4c**.



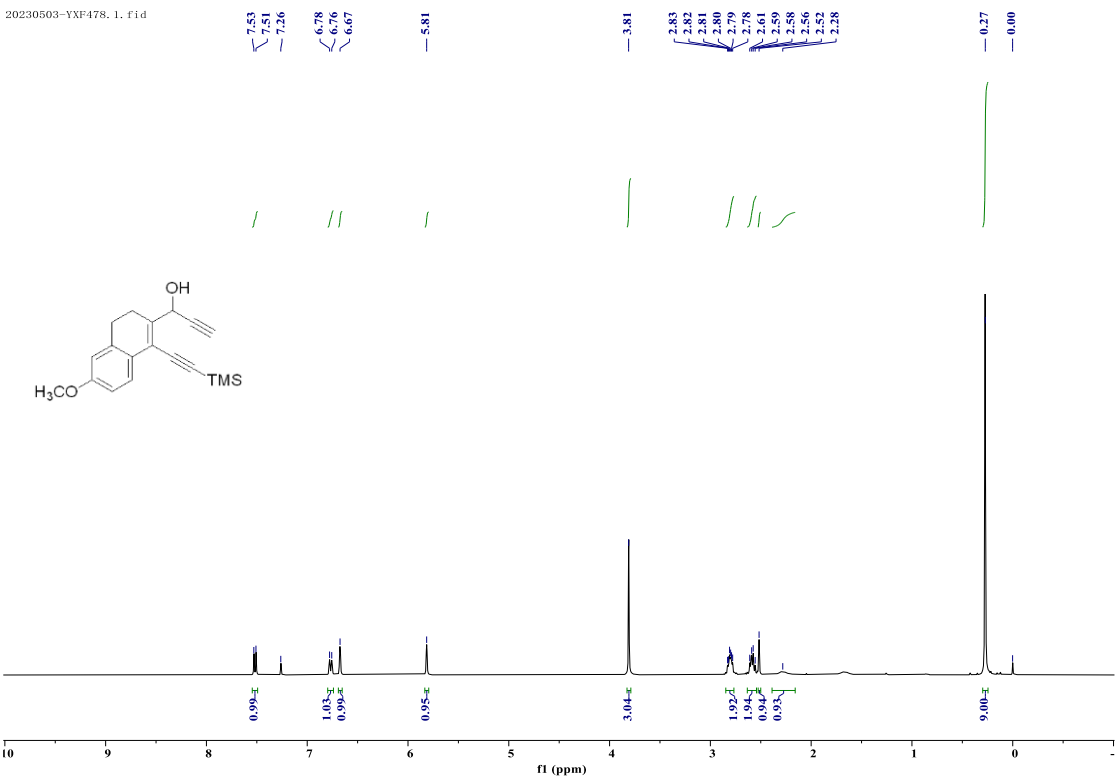
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **4c**.



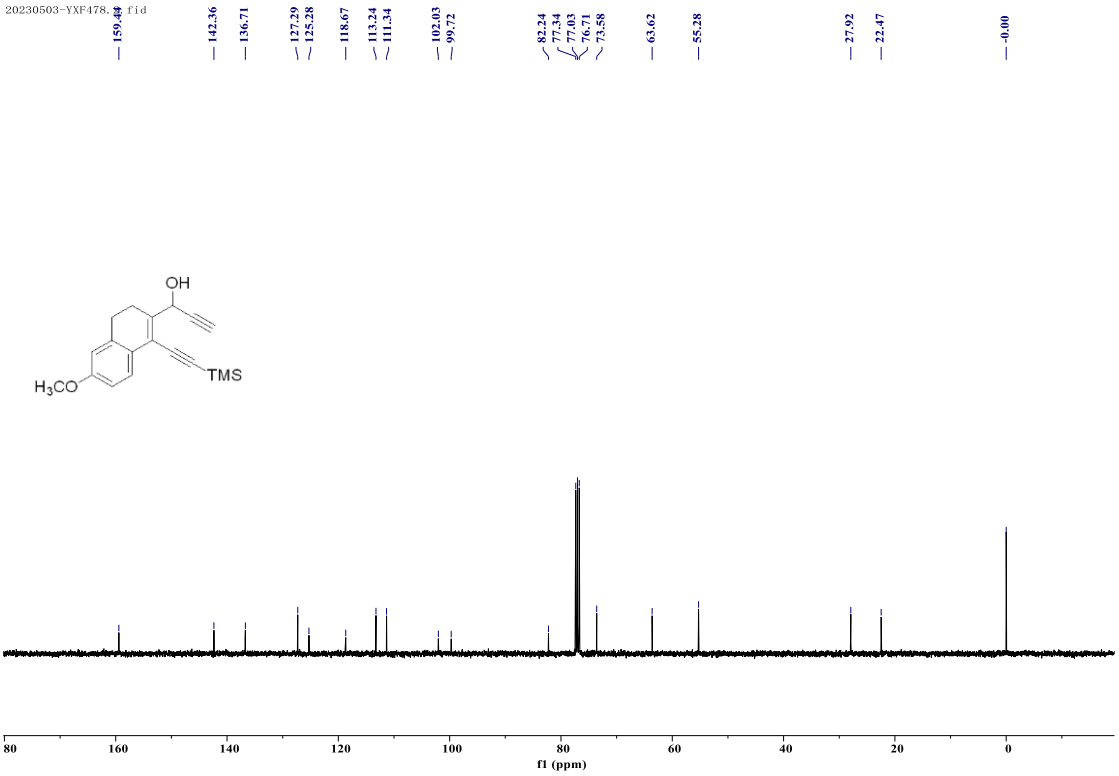
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4d**.



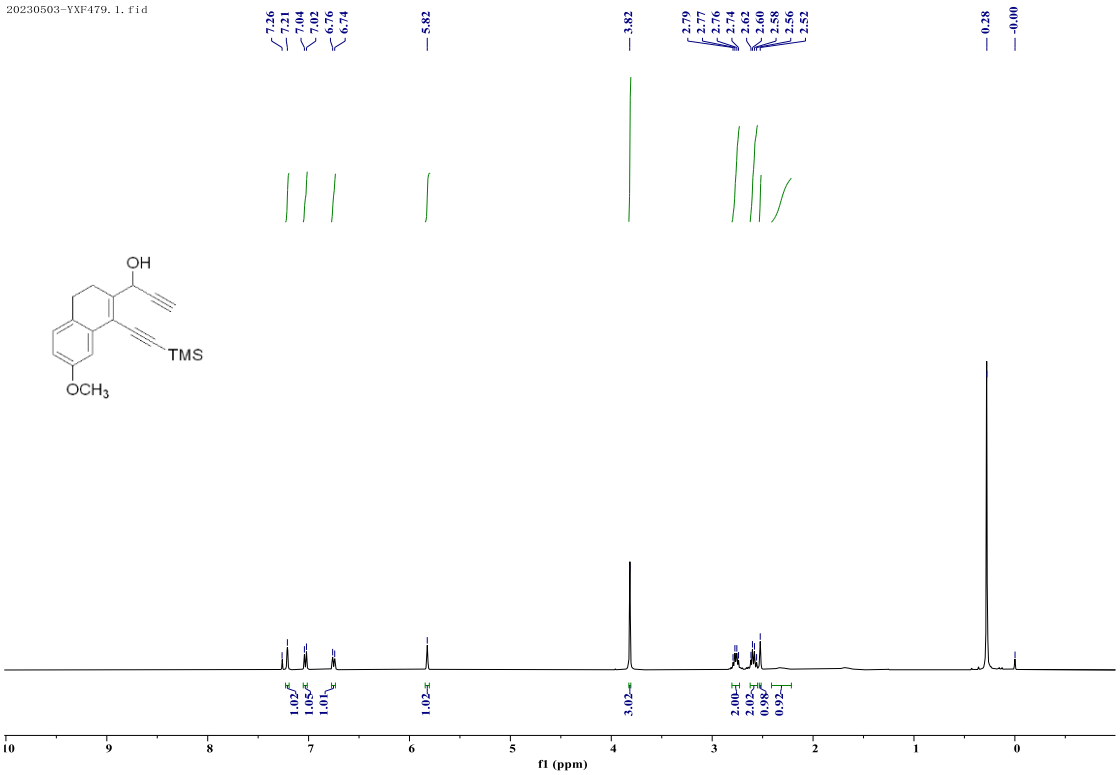
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **4d**.



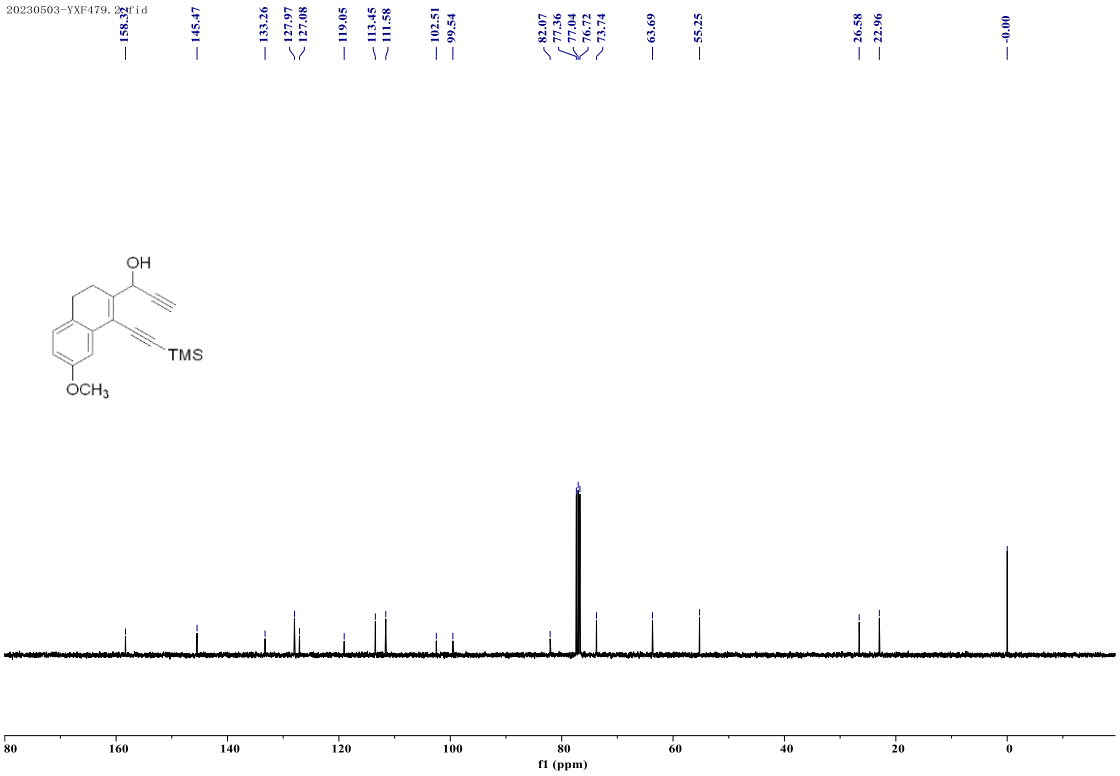
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4e**.



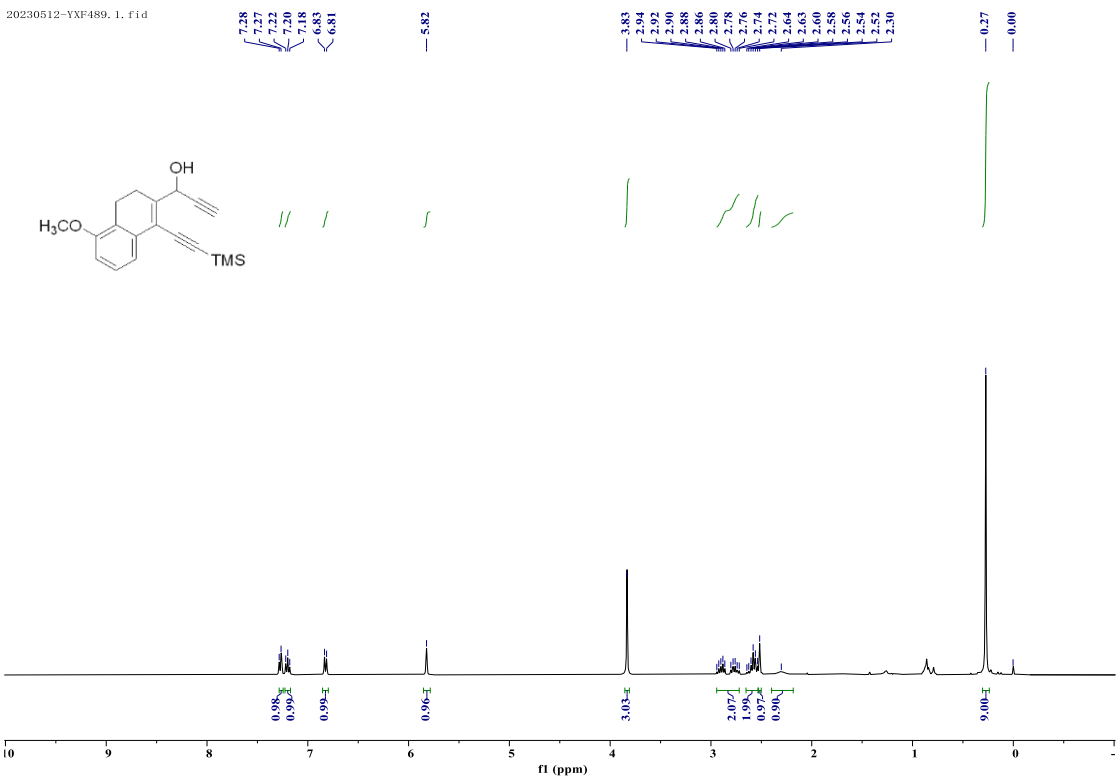
The $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4e**.



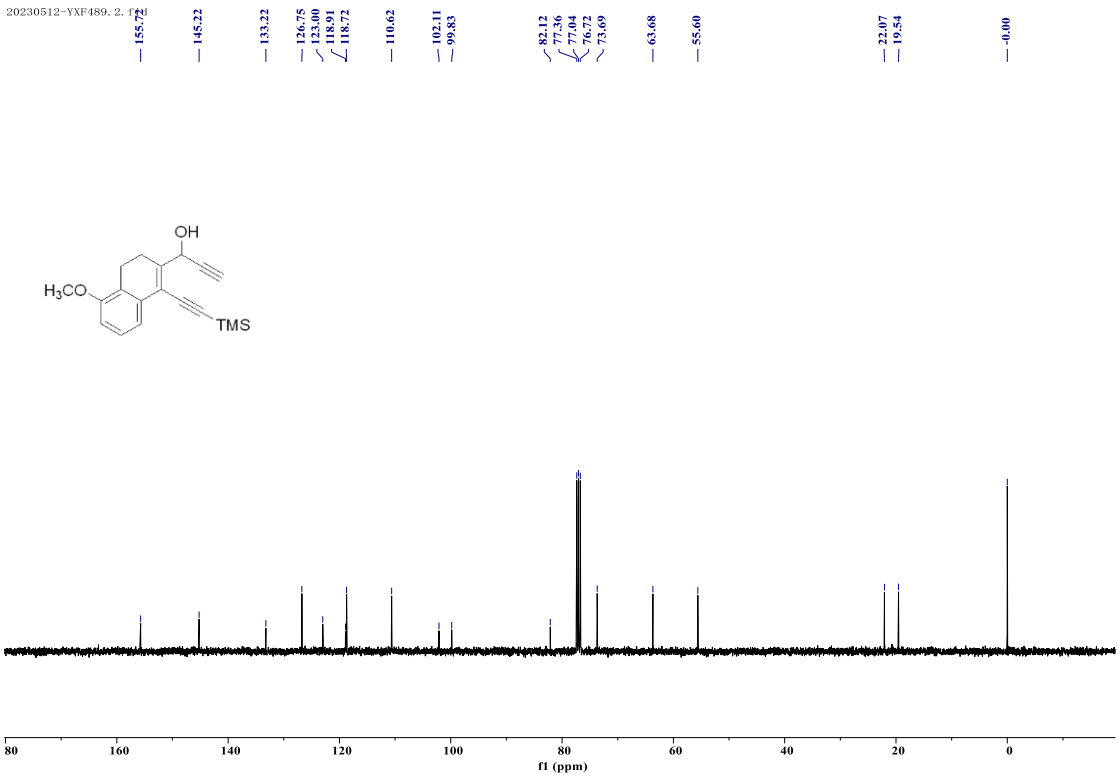
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4f**.



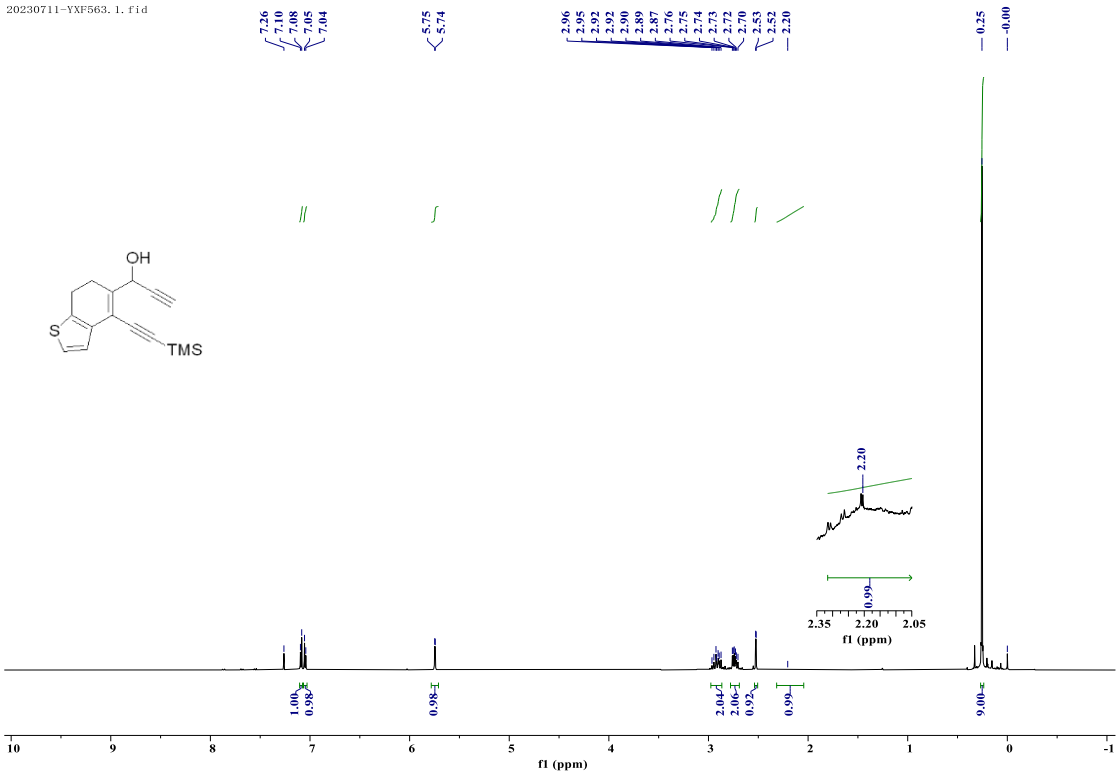
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **4f**.



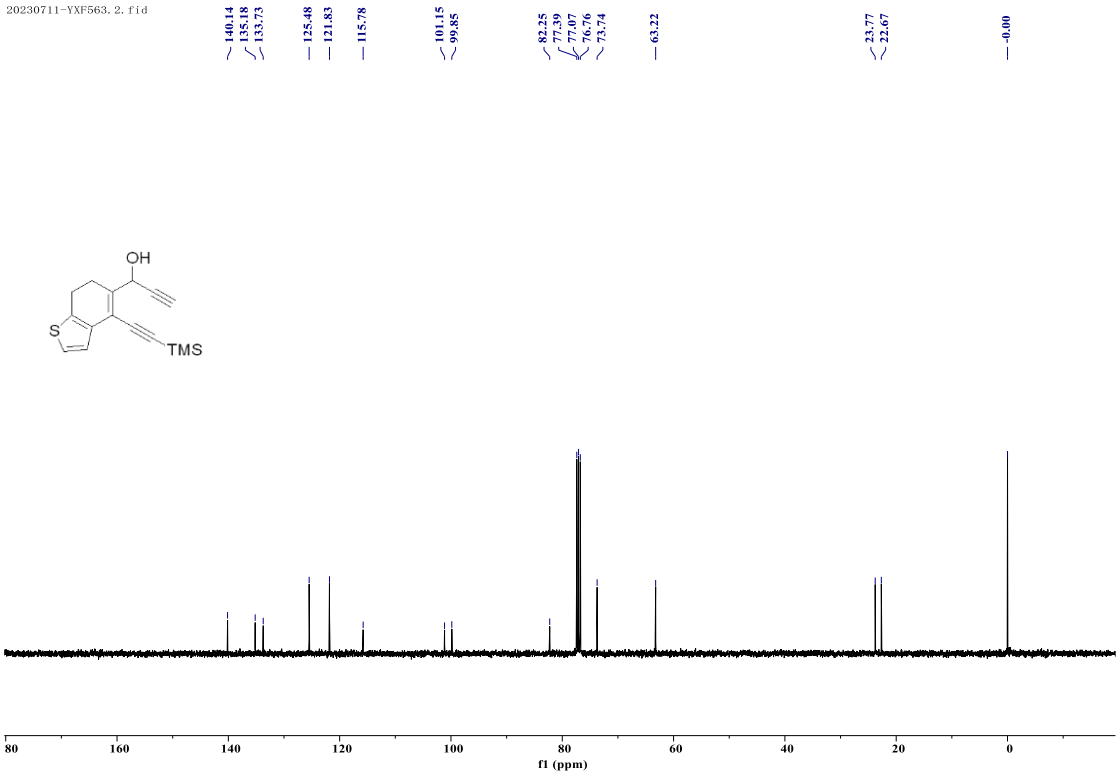
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4g**.



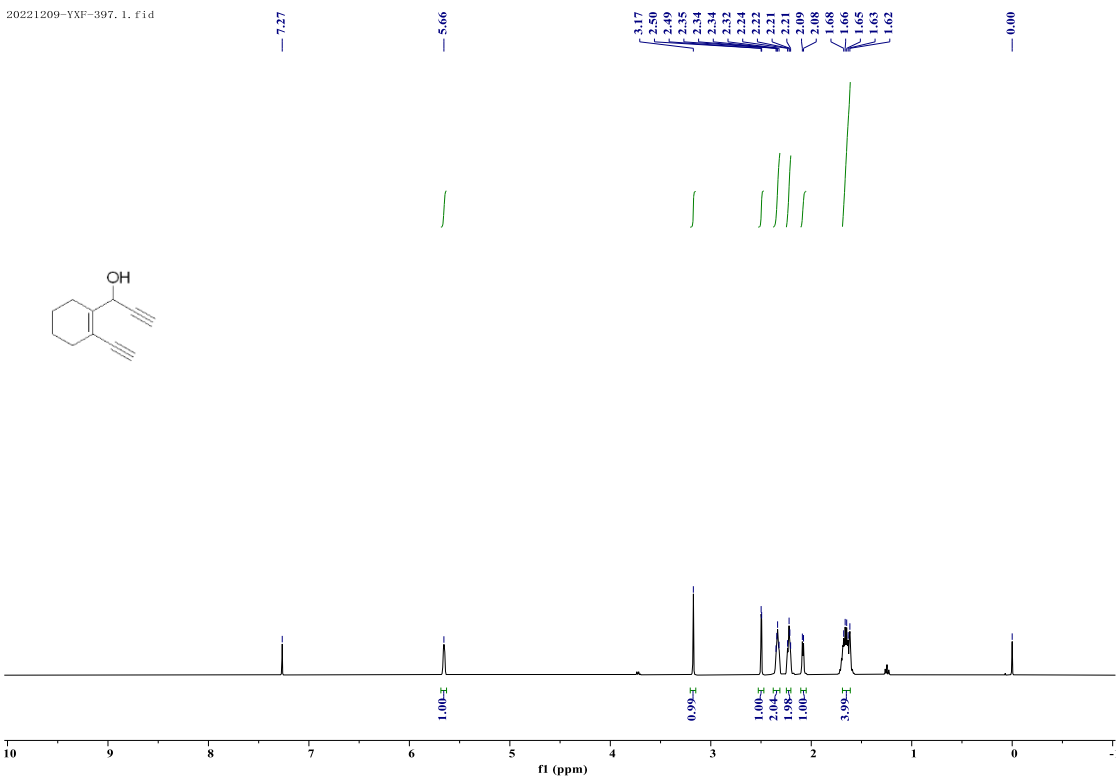
The $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4g**.



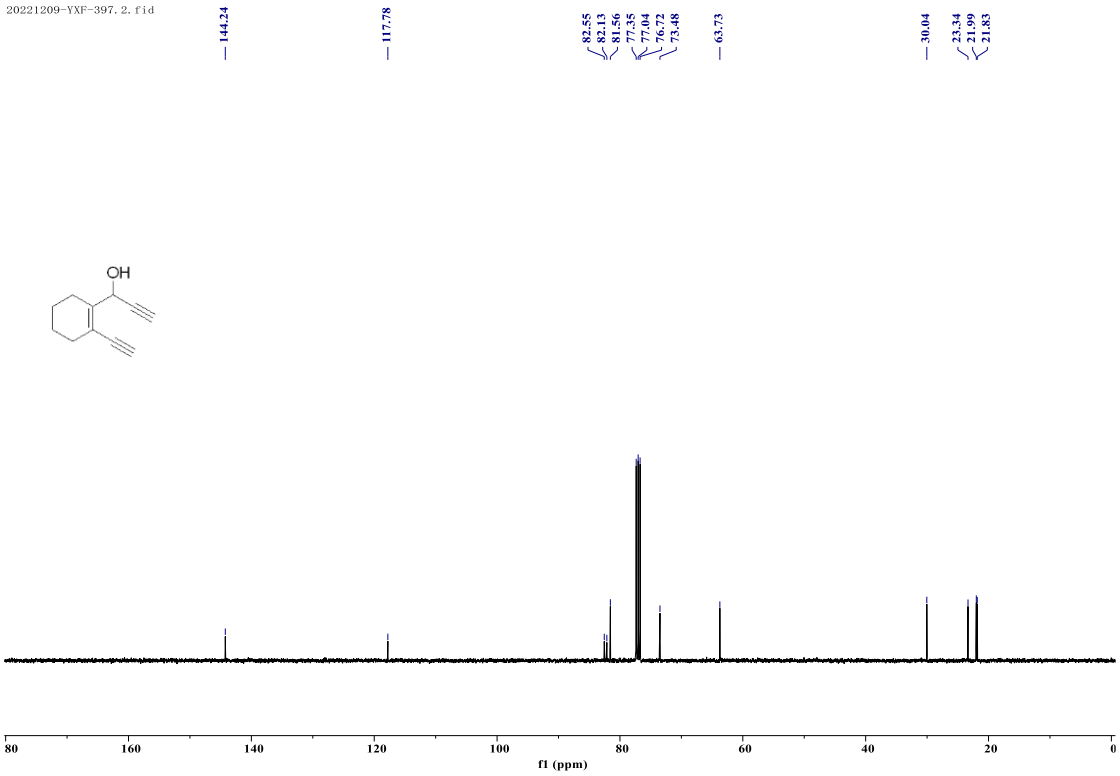
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4h**.



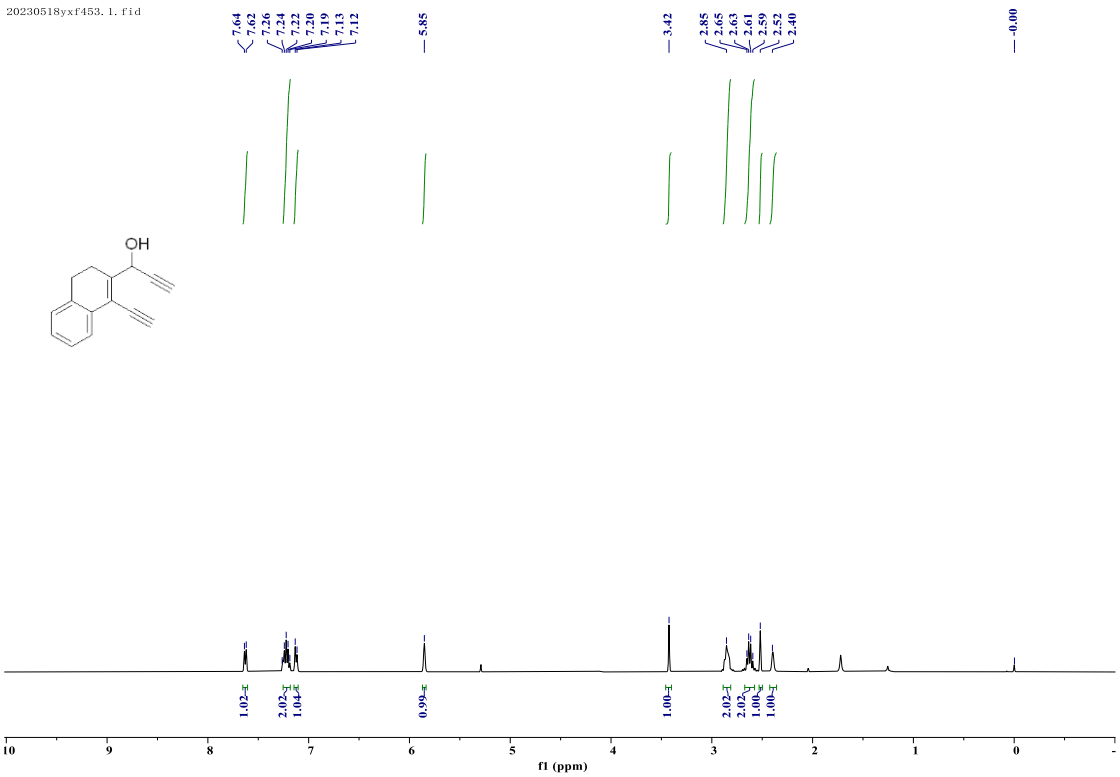
The $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4h**.



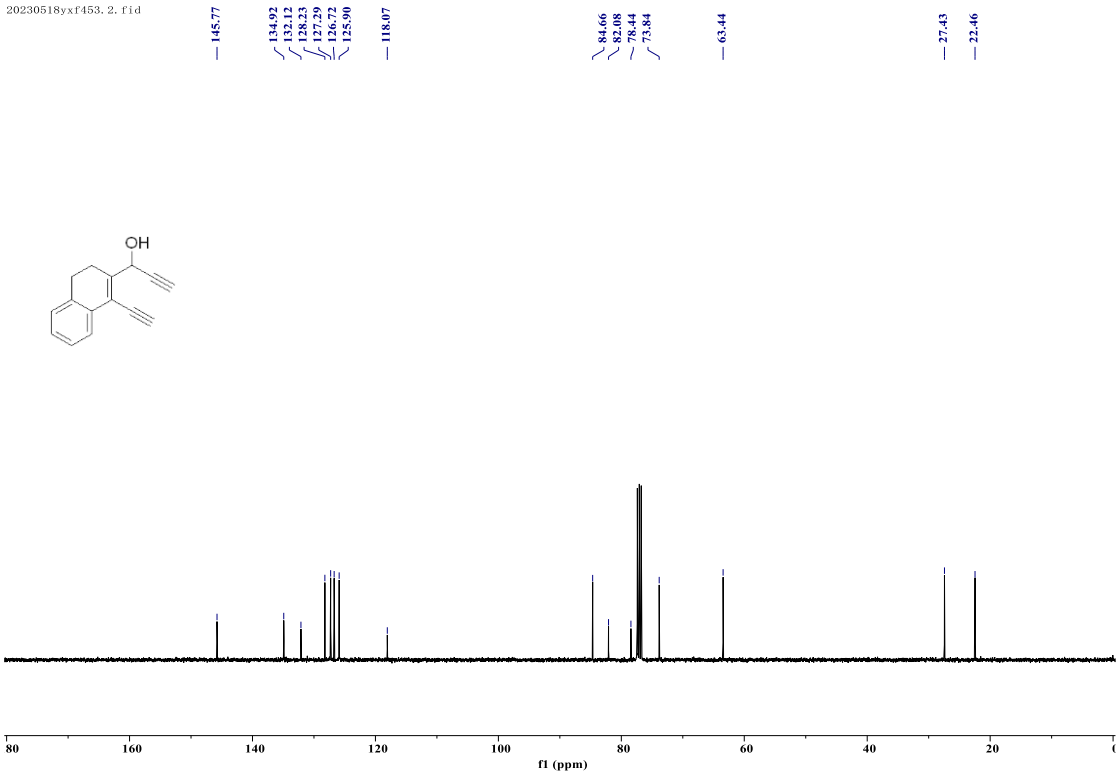
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a**.



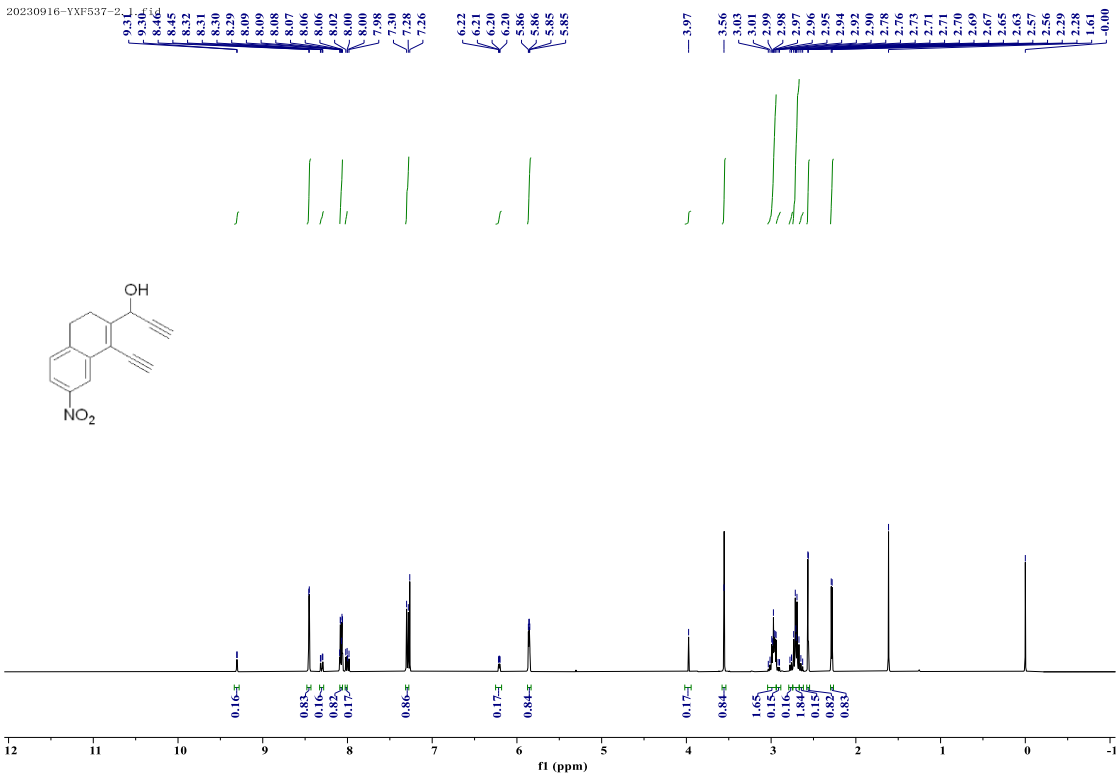
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5a**.



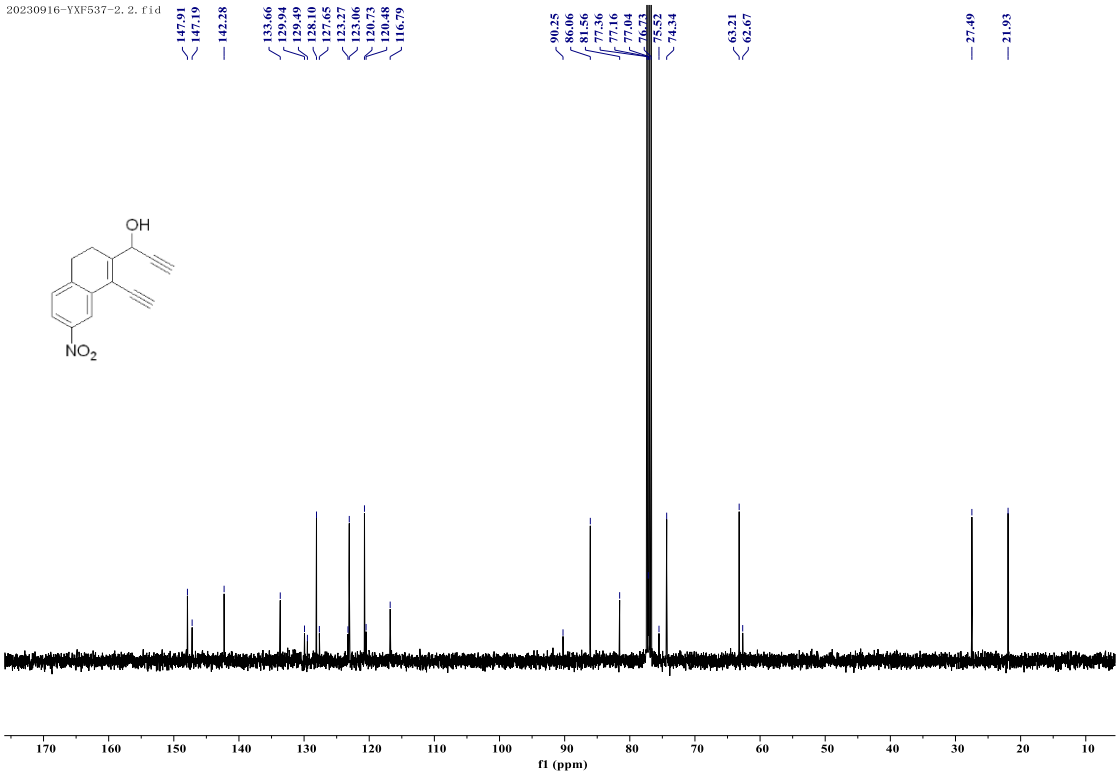
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**.



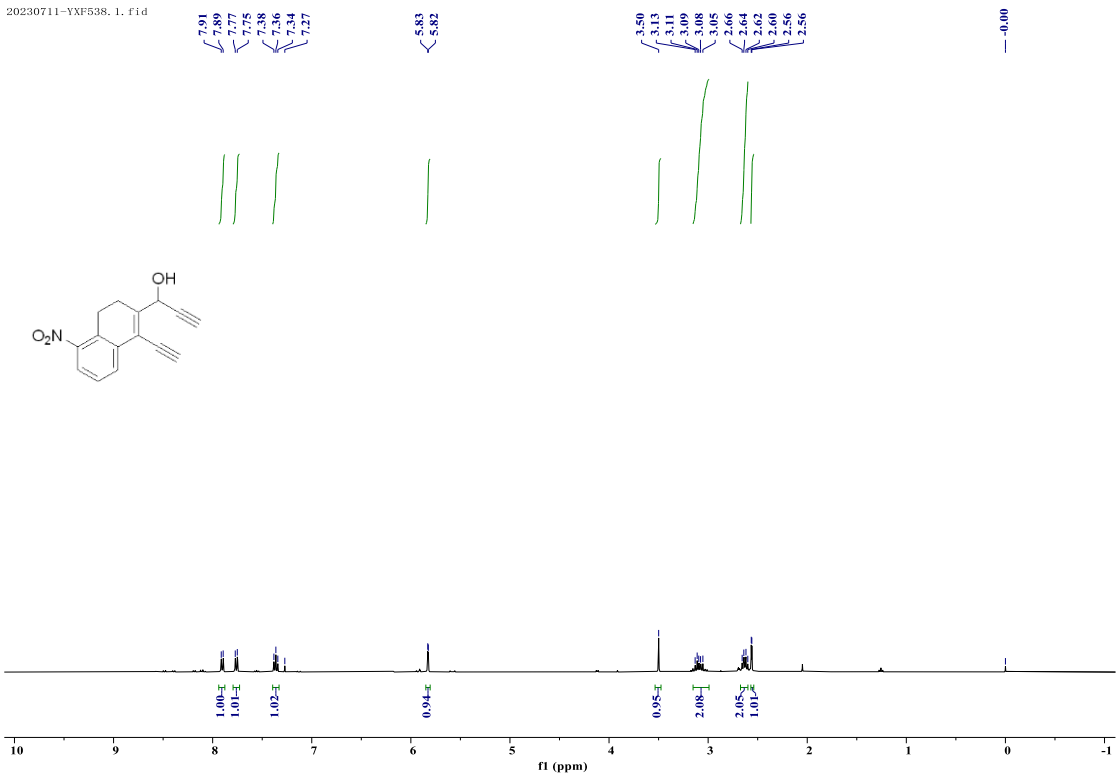
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5b**.



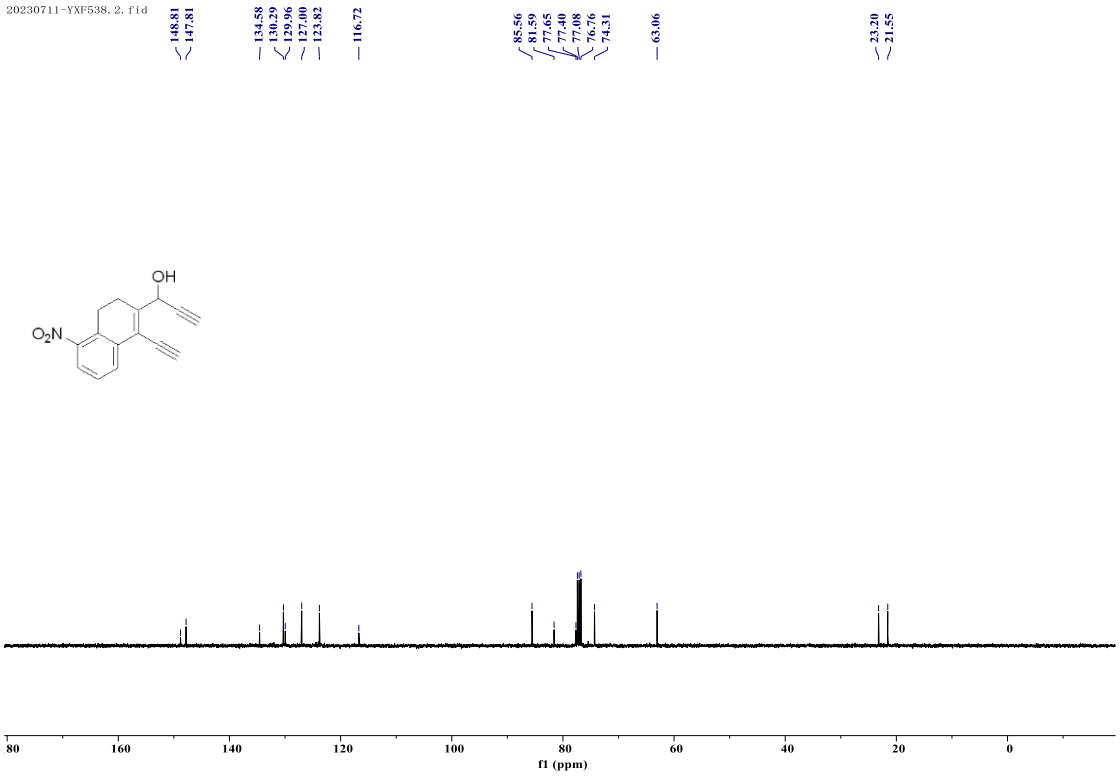
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c**.



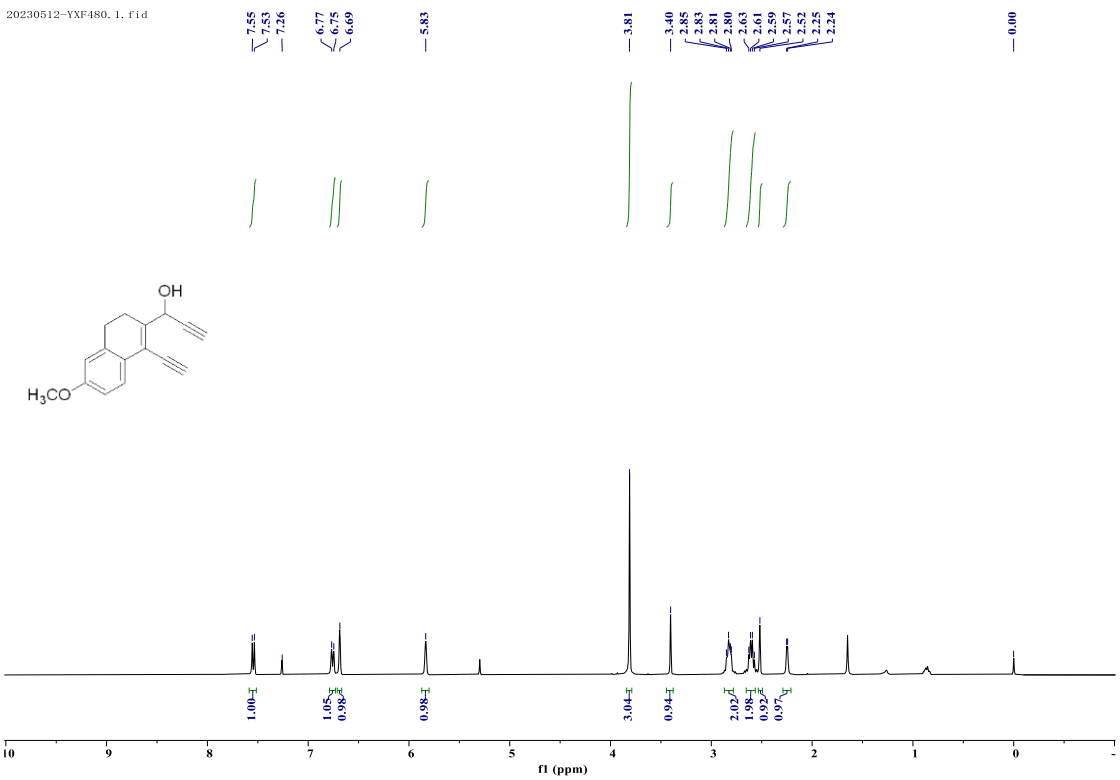
The $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5c**.



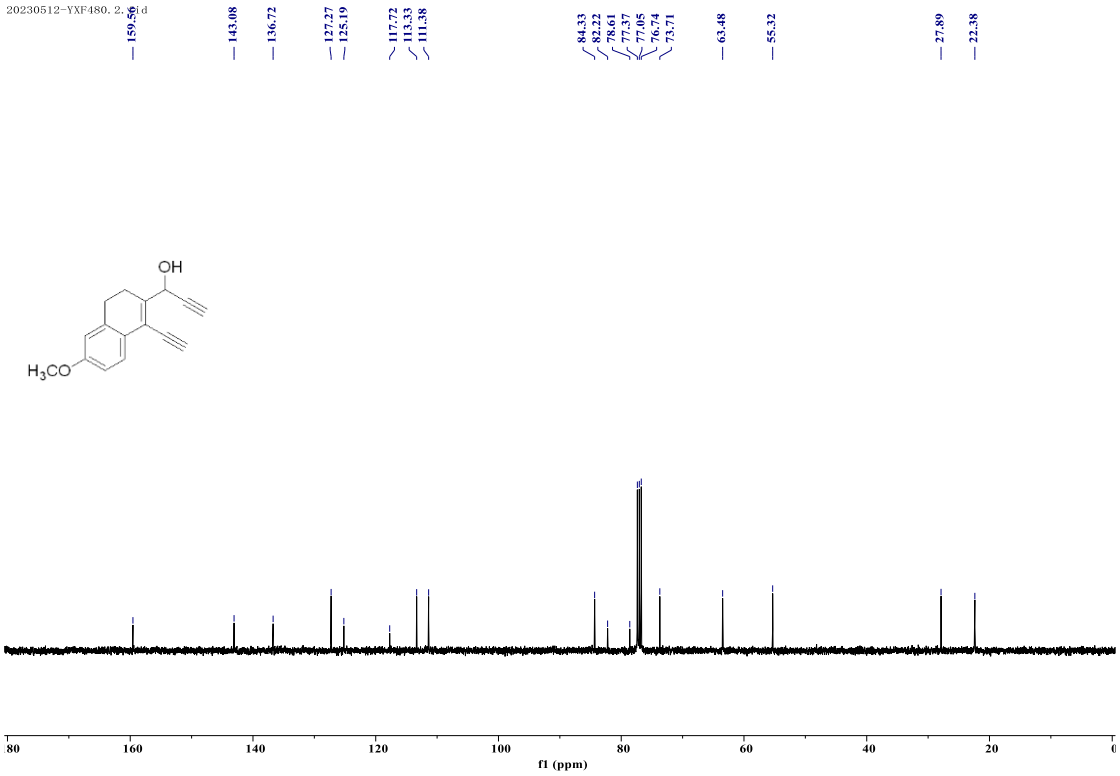
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5d**.



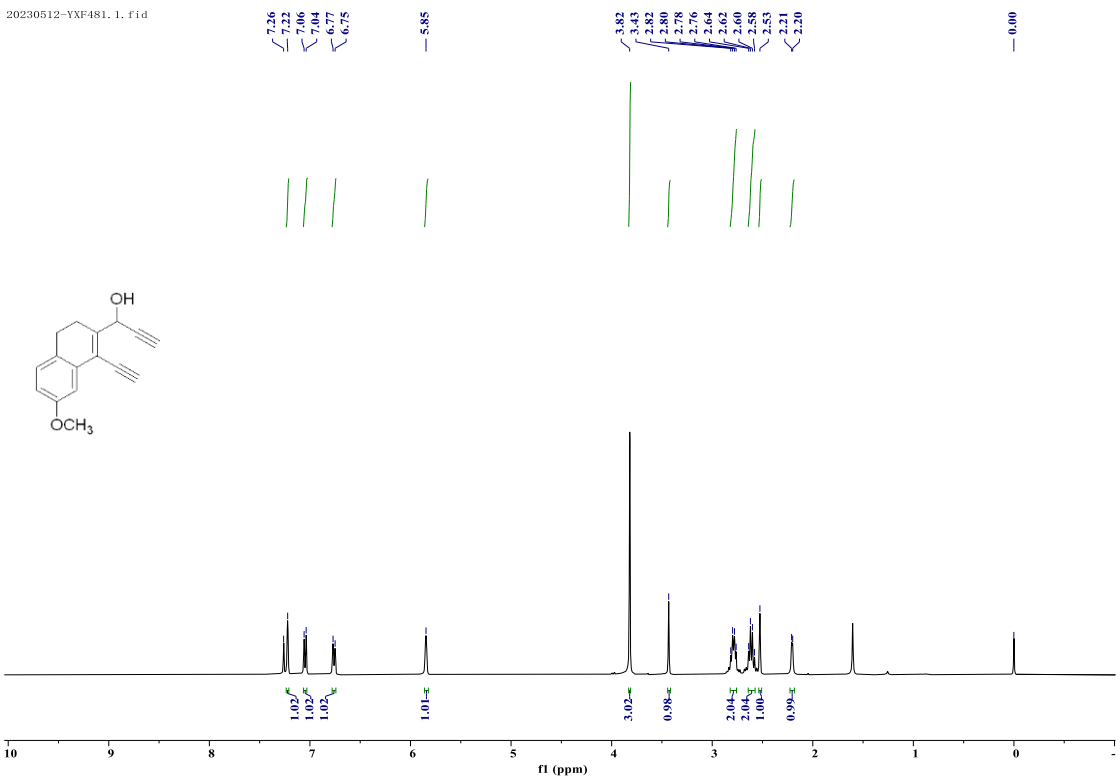
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5d**.



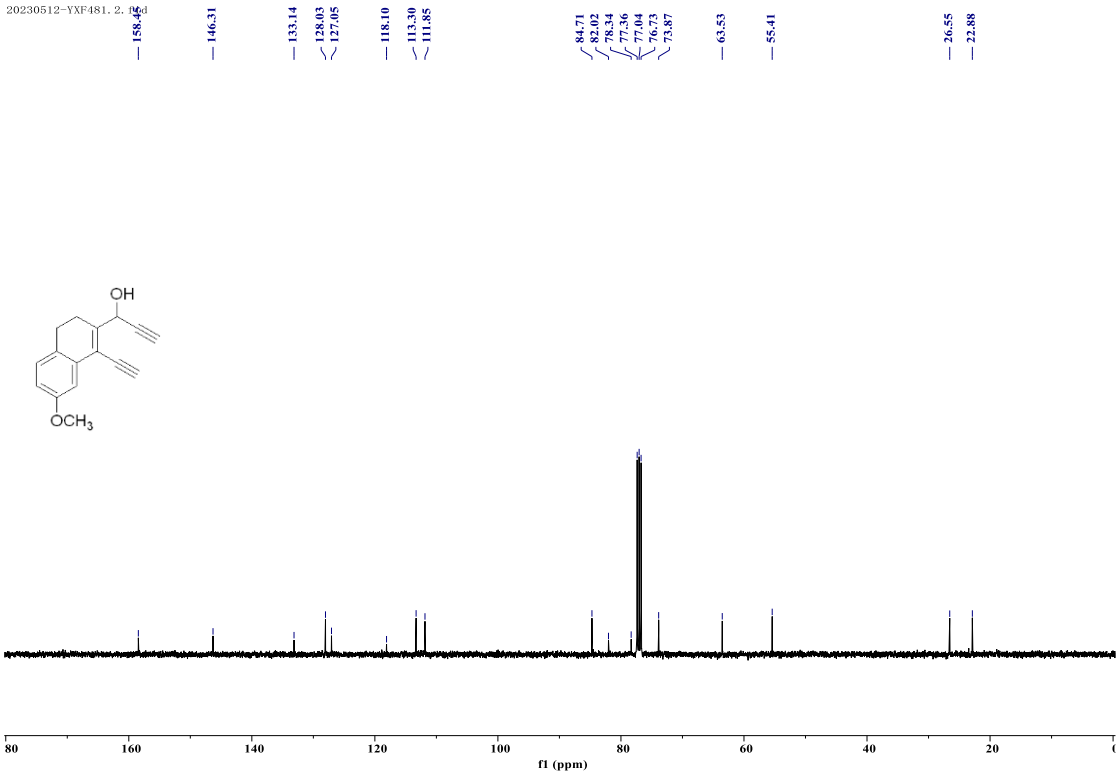
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5e**.



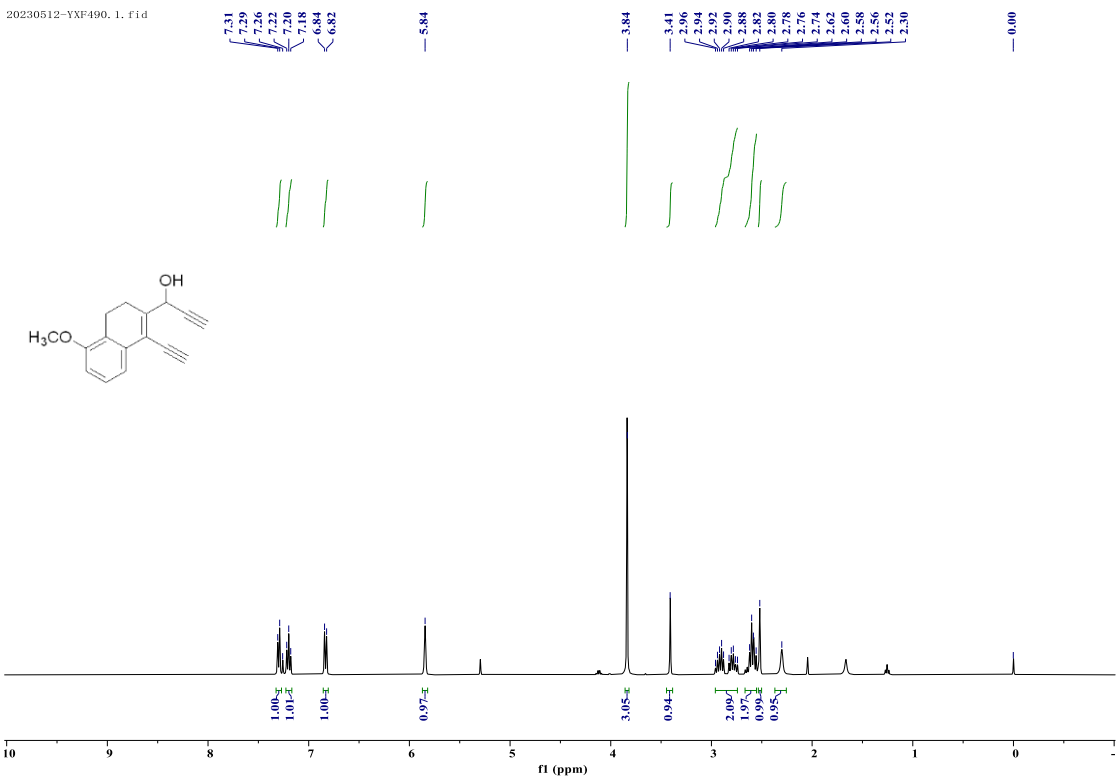
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5e**.



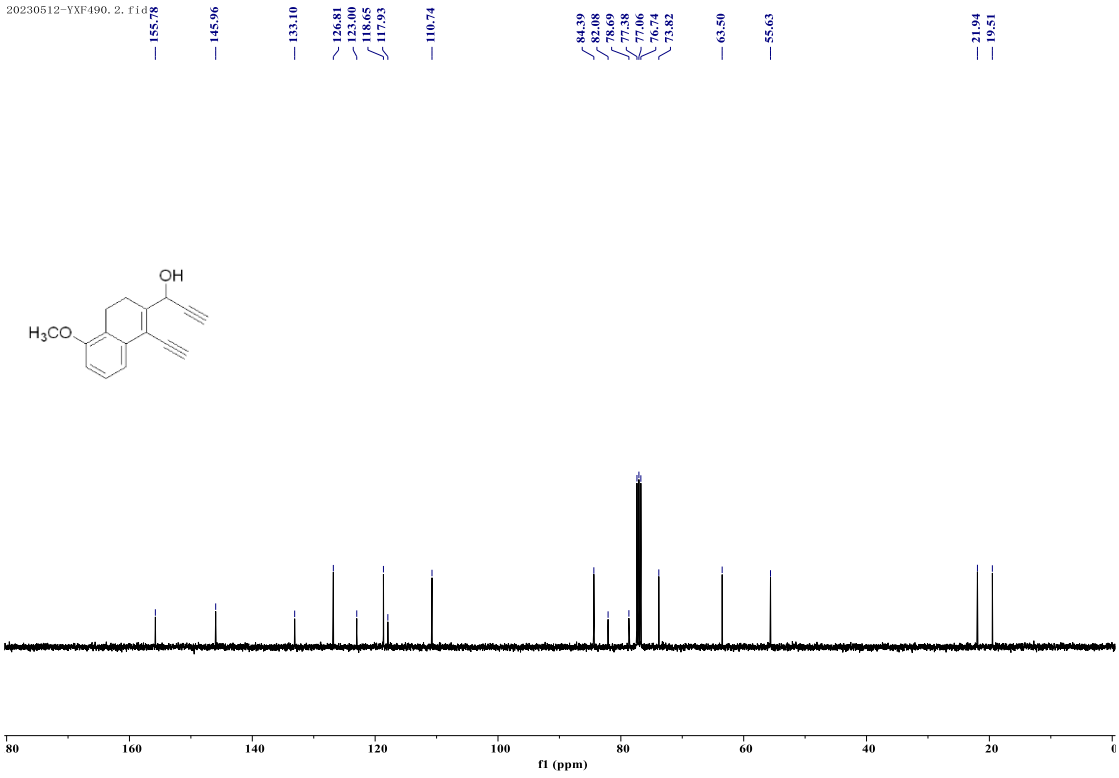
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5f**.



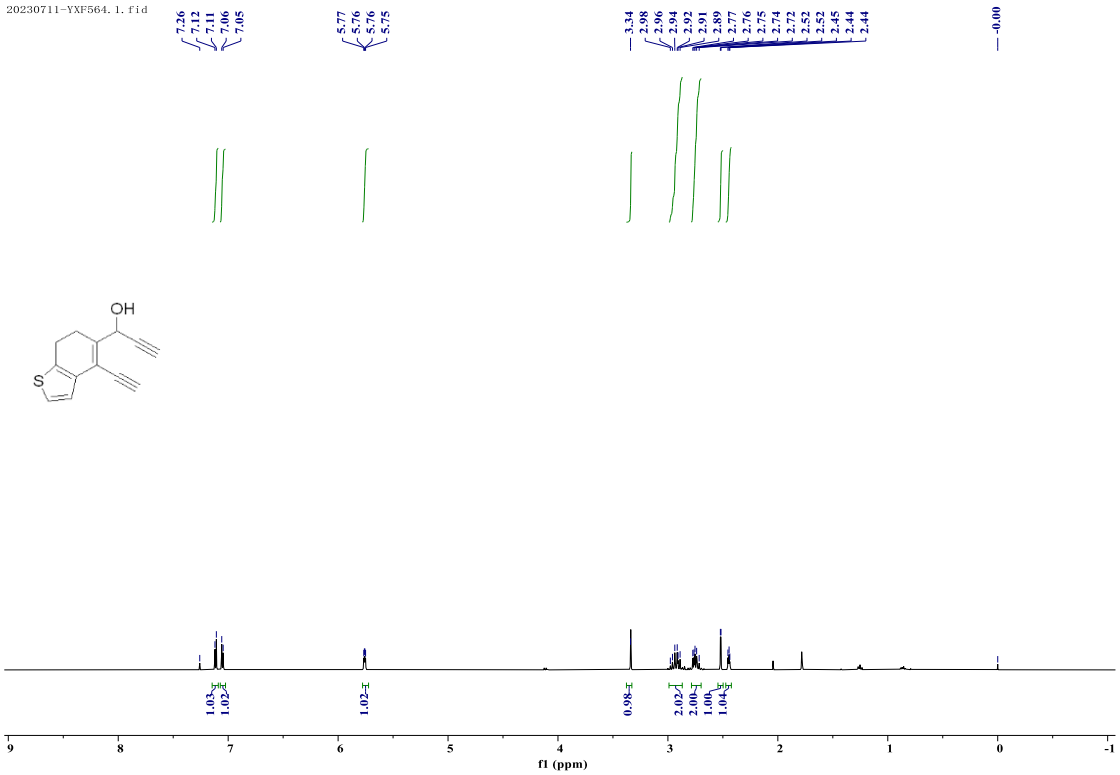
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5f**.



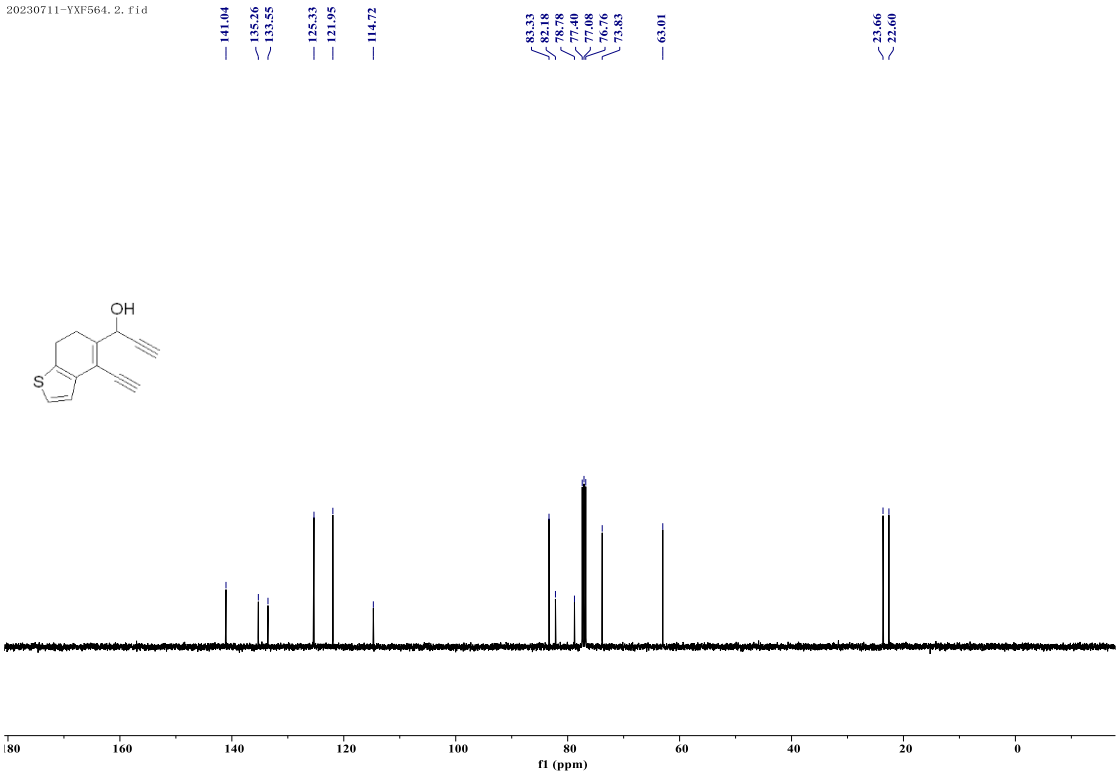
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5g**.



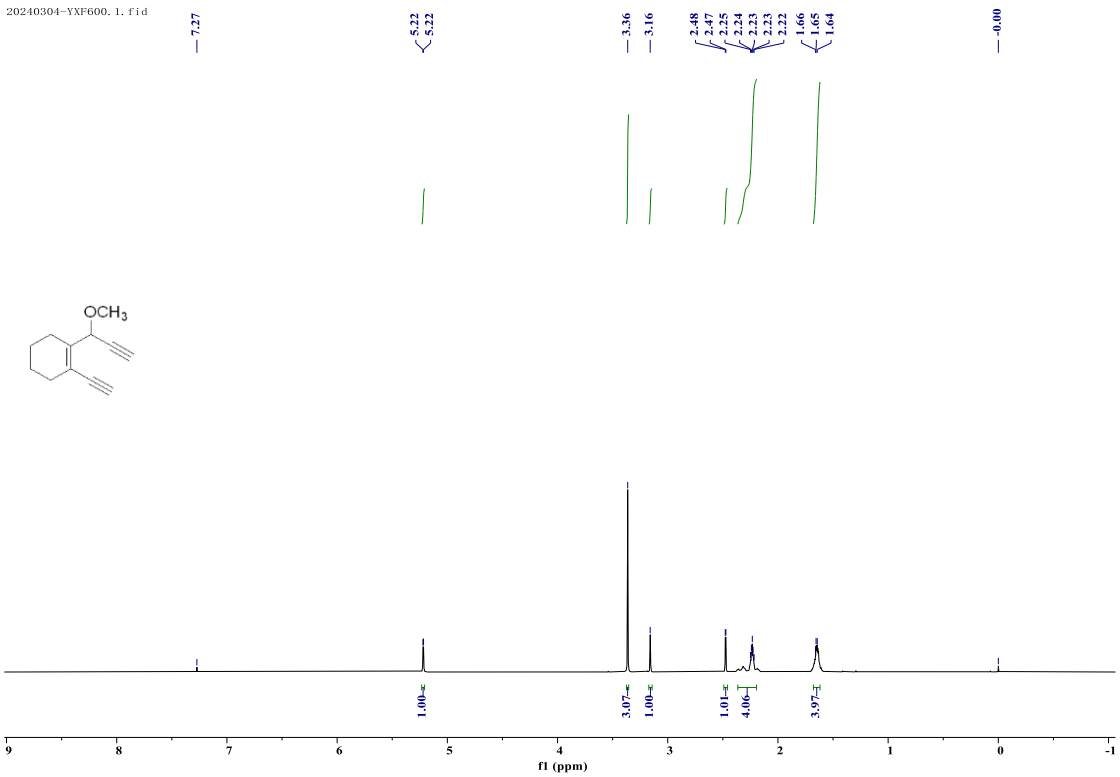
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5g**.



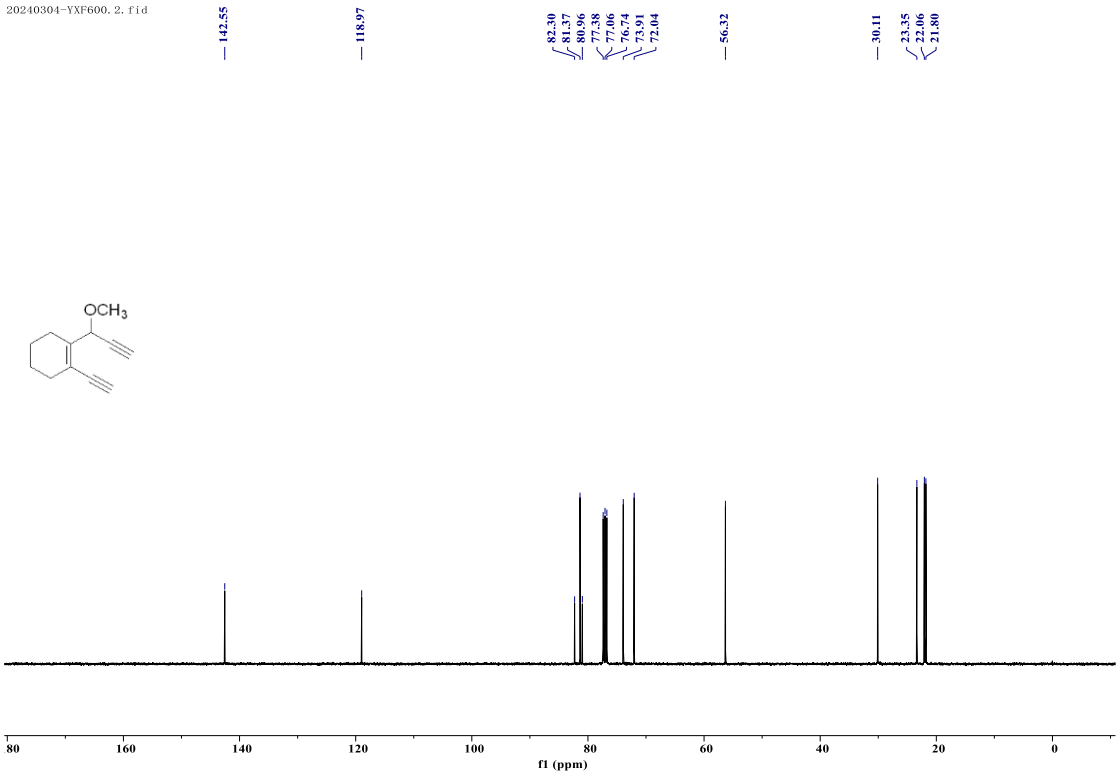
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5h**.



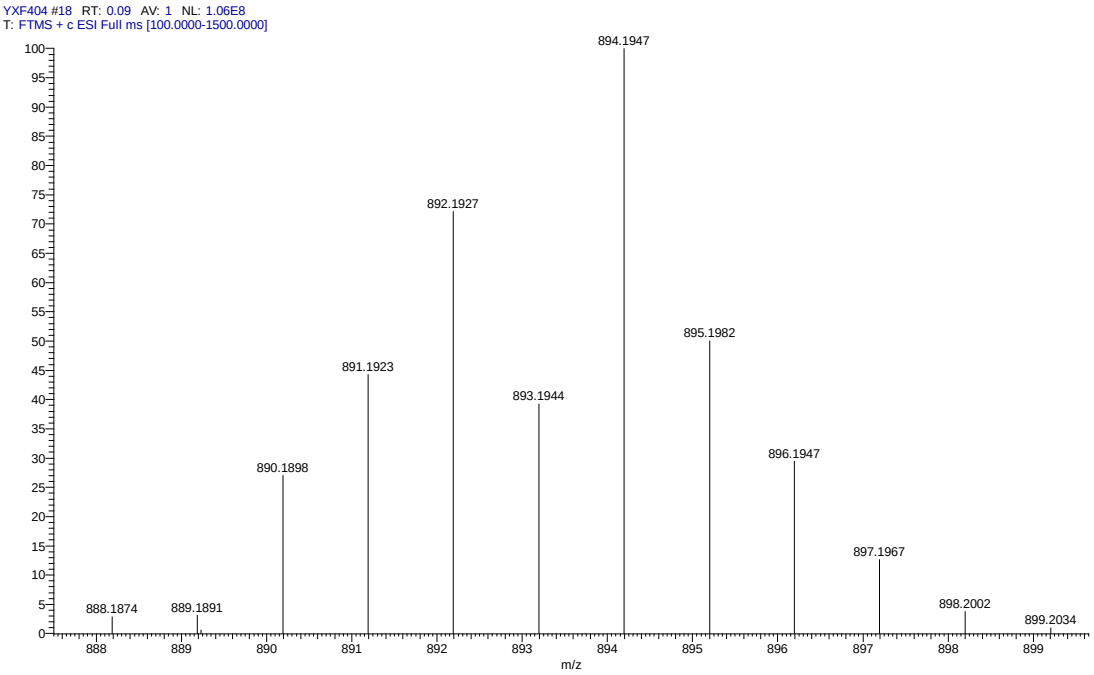
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **5h**.



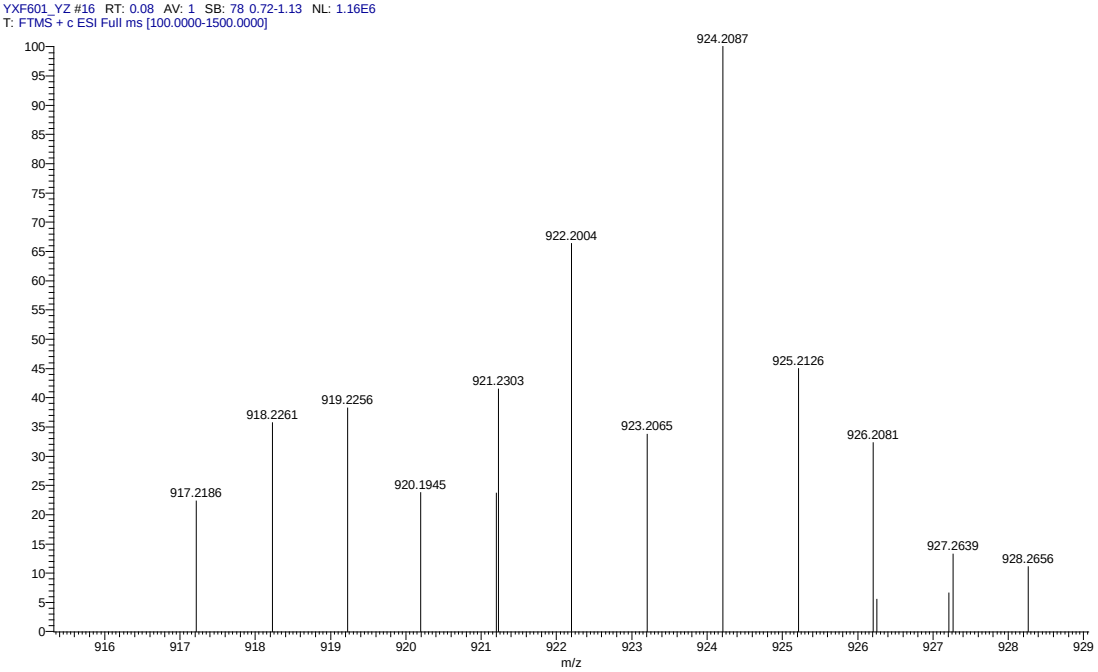
The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**.



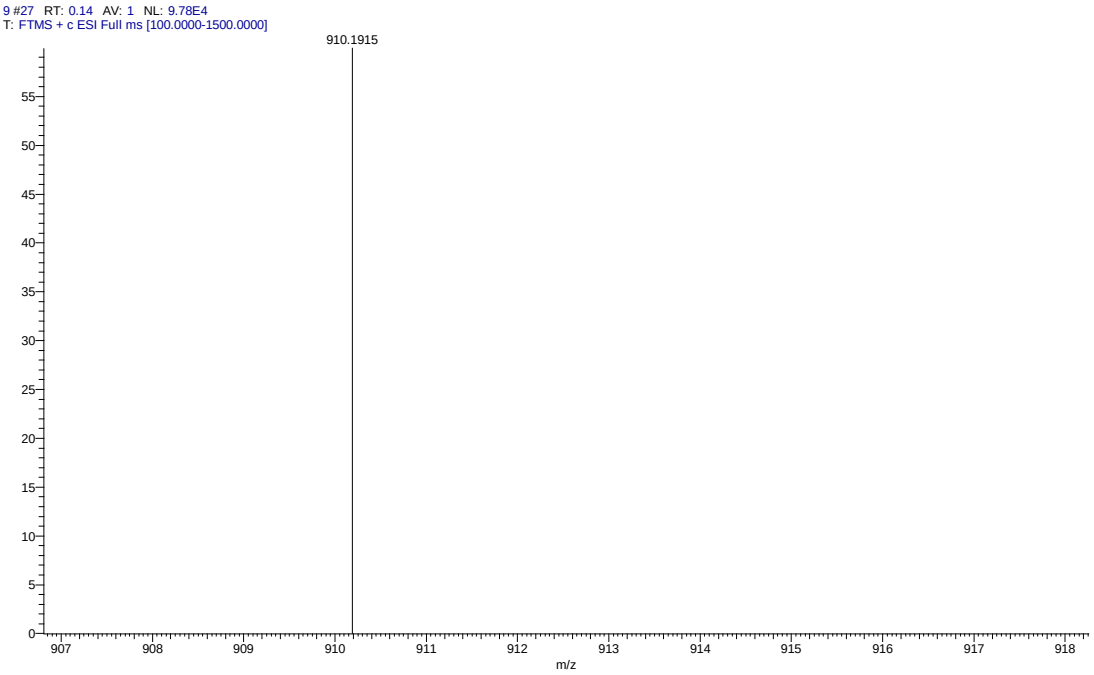
The ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **6**.



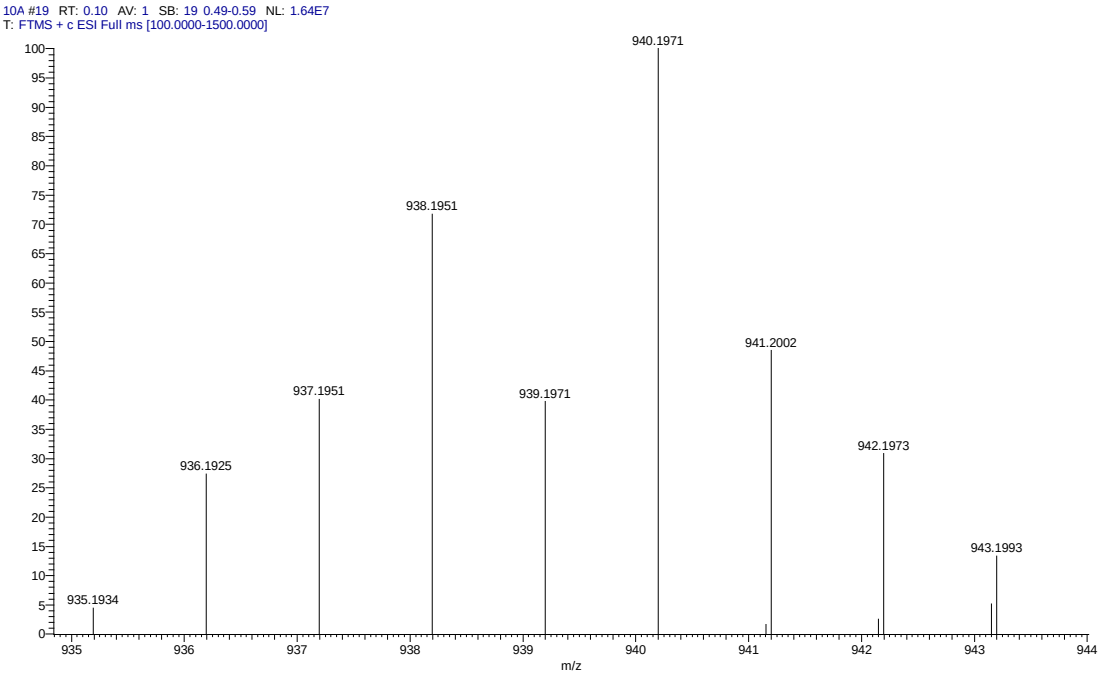
Positive-ion ESI-MS spectrum of [**7a**-Cl^-]$^+$ measured in MeOH.



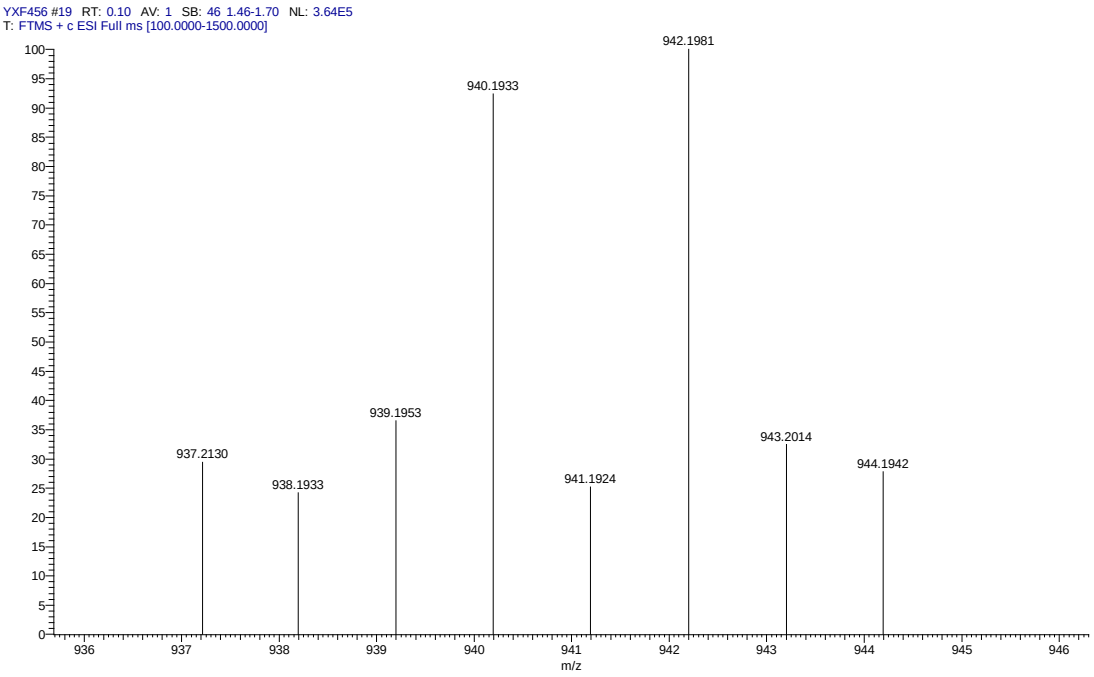
Positive-ion ESI-MS spectrum of [**8**-Cl^-]$^+$ measured in MeOH.



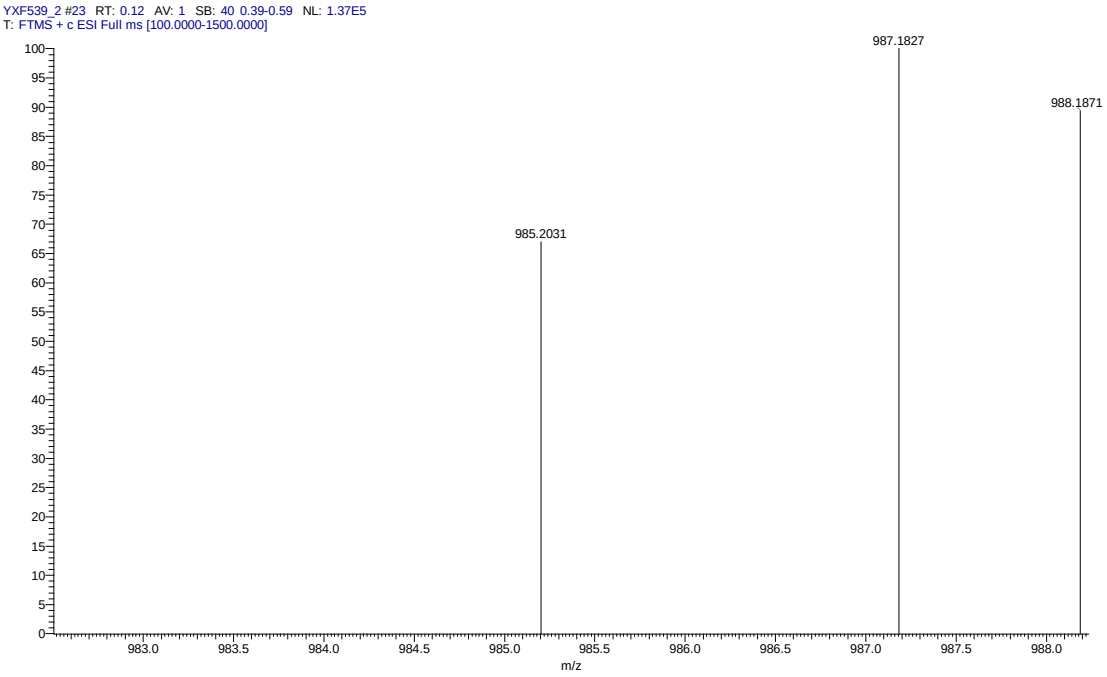
Positive-ion ESI-MS spectrum of [**9**-Cl^-]$^+$ measured in MeOH.



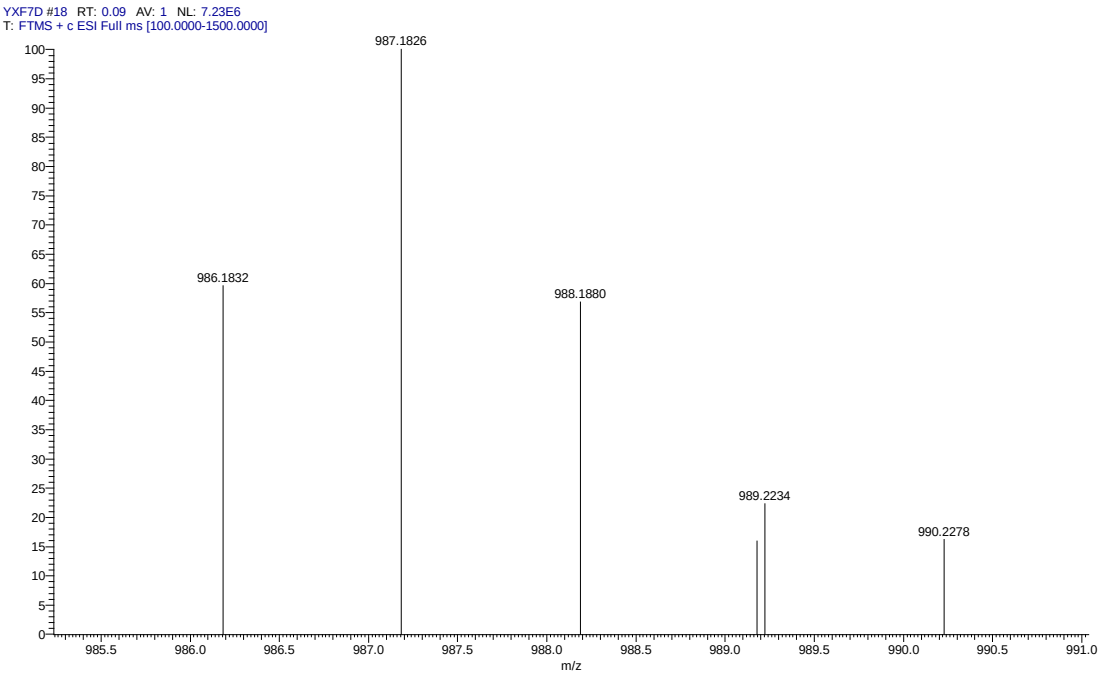
Positive-ion ESI-MS spectrum of [**10a**-Cl^-]$^+$ measured in MeOH.



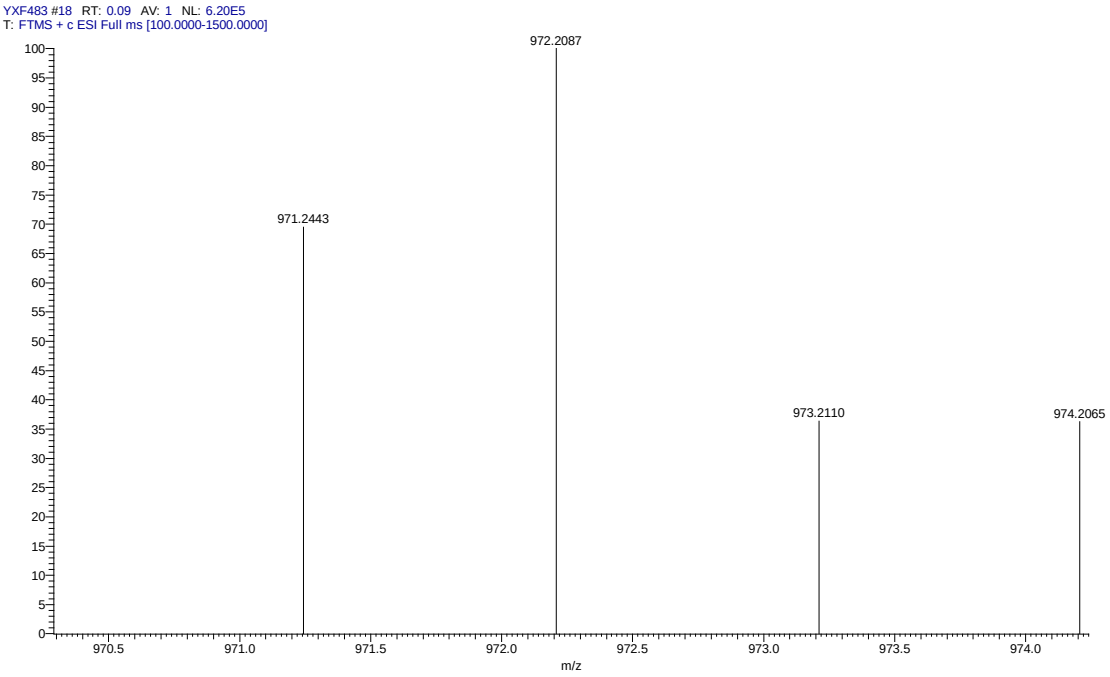
Positive-ion ESI-MS spectrum of [**7b**-Cl^-]$^+$ measured in MeOH.



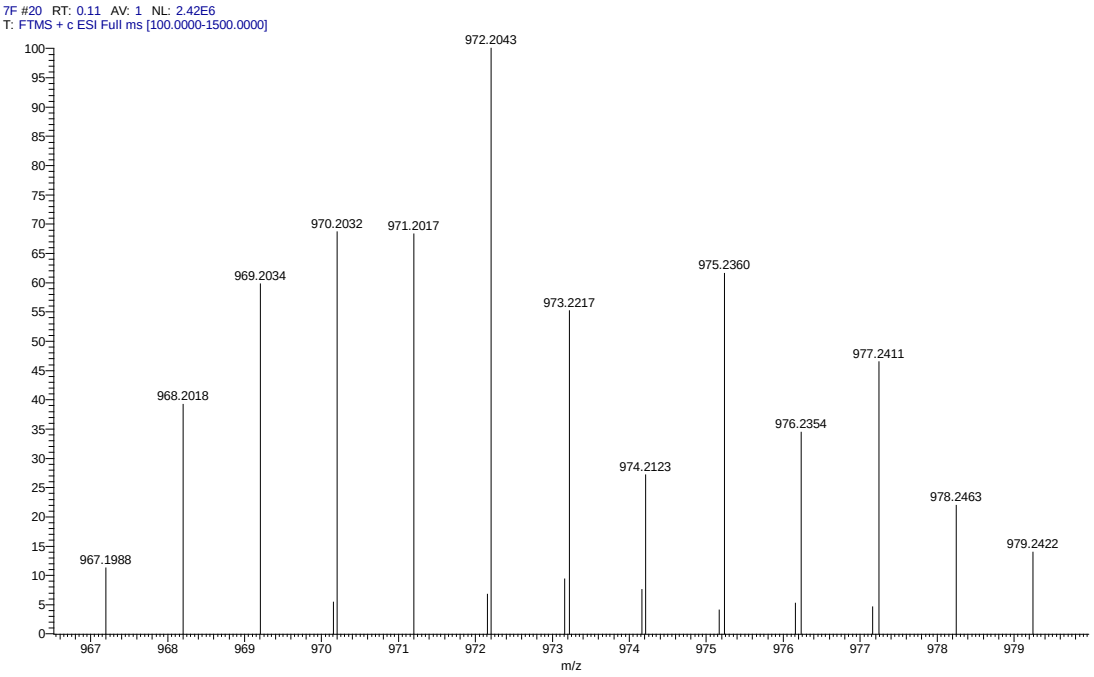
Positive-ion ESI-MS spectrum of [**7c**-Cl^-]$^+$ measured in MeOH.



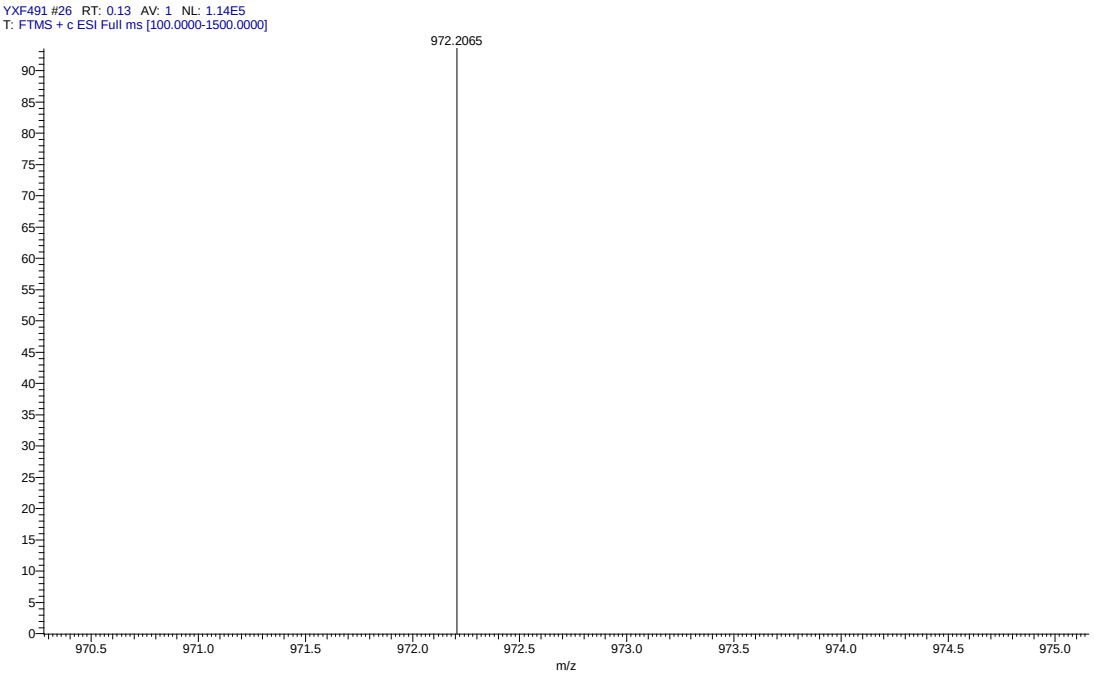
Positive-ion ESI-MS spectrum of [**7d**-Cl^-]$^+$ measured in MeOH.



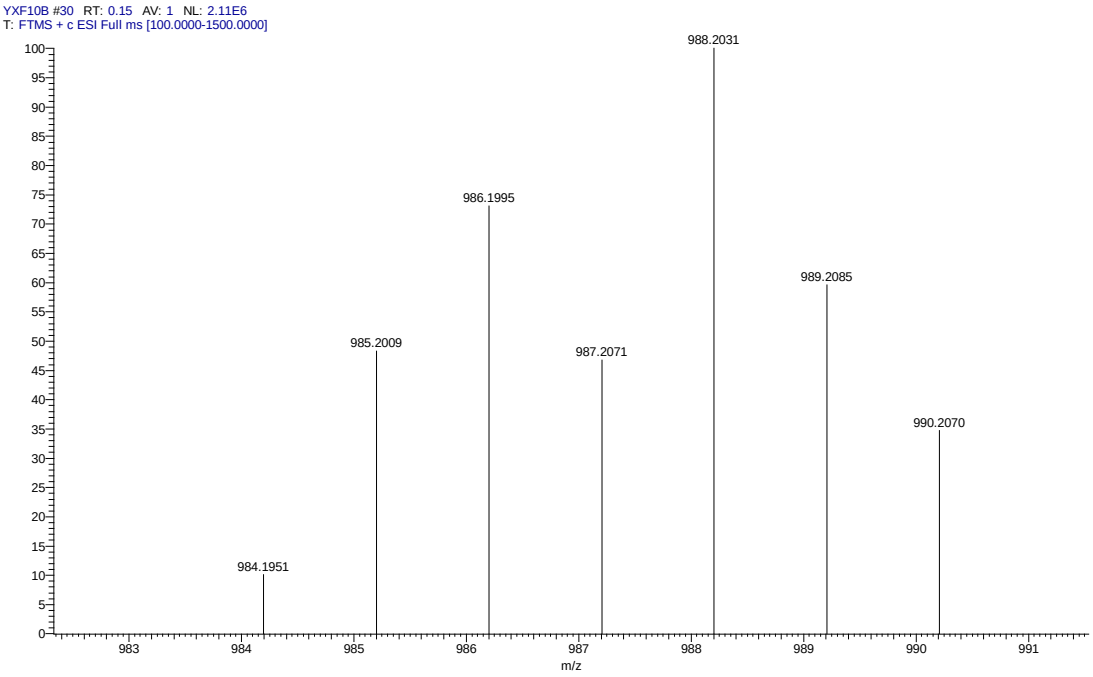
Positive-ion ESI-MS spectrum of [**7e**-Cl^-]$^+$ measured in MeOH.



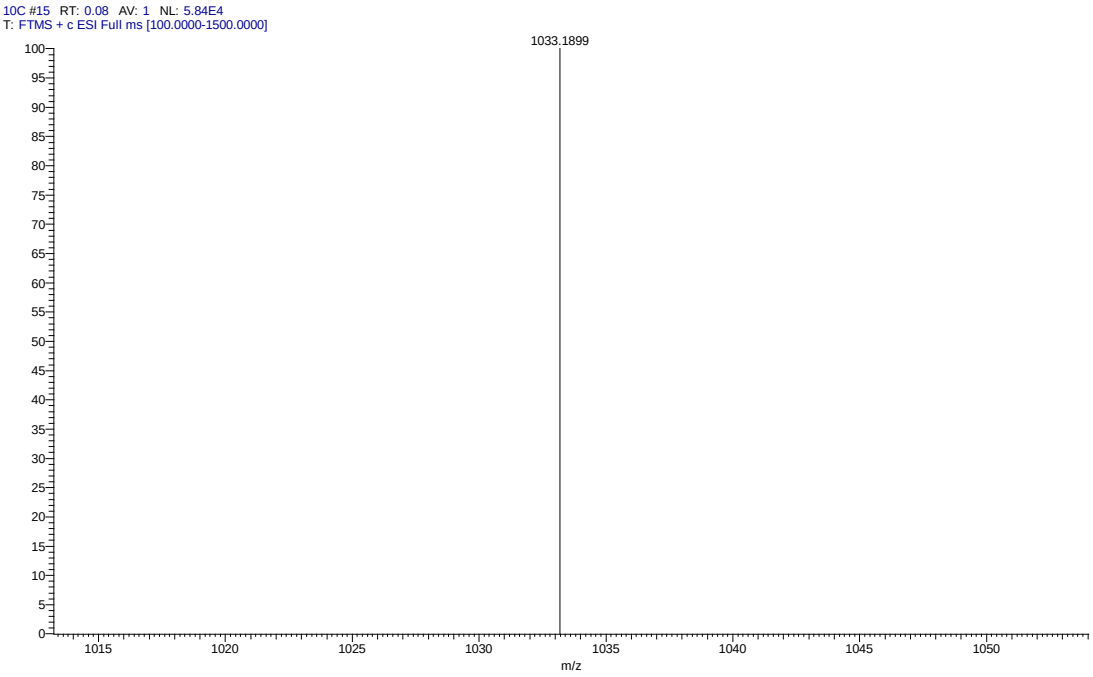
Positive-ion ESI-MS spectrum of [**7f**-Cl^-]$^+$ measured in MeOH.



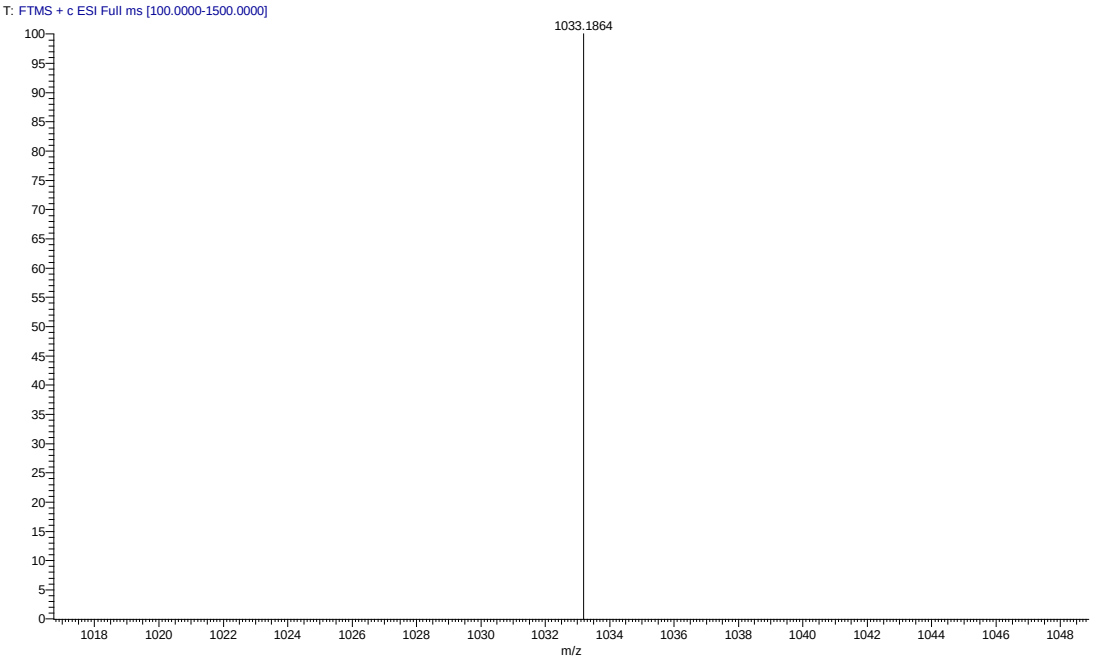
Positive-ion ESI-MS spectrum of [**7g**-Cl^-]$^+$ measured in MeOH.



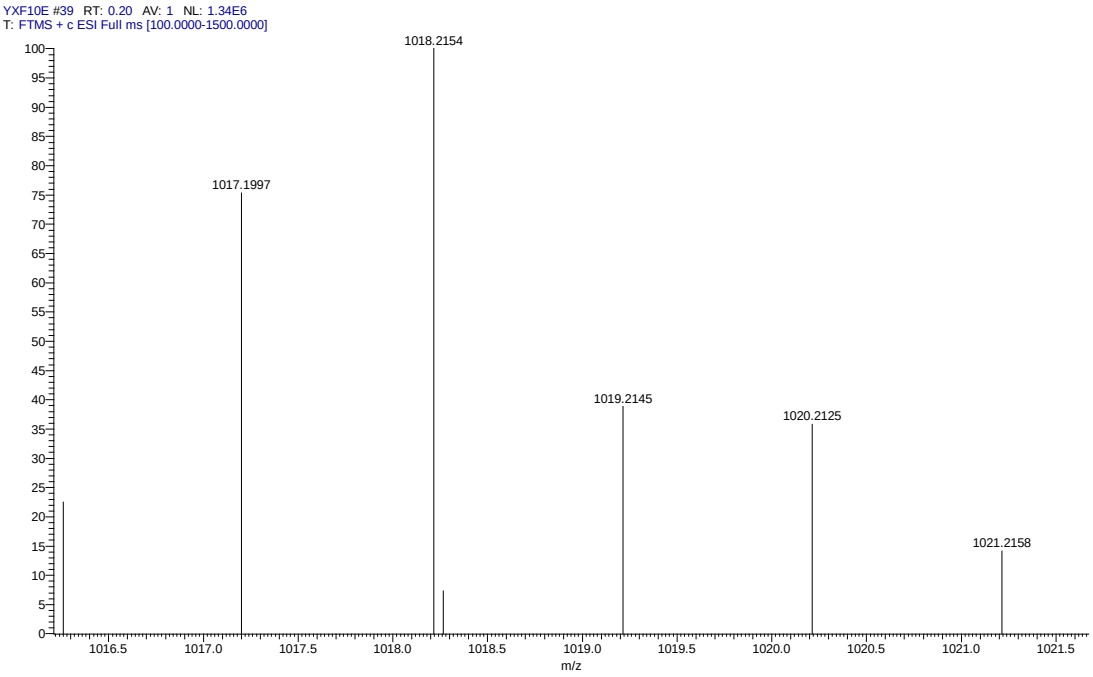
Positive-ion ESI-MS spectrum of [**10b**-Cl^-]$^+$ measured in MeOH.



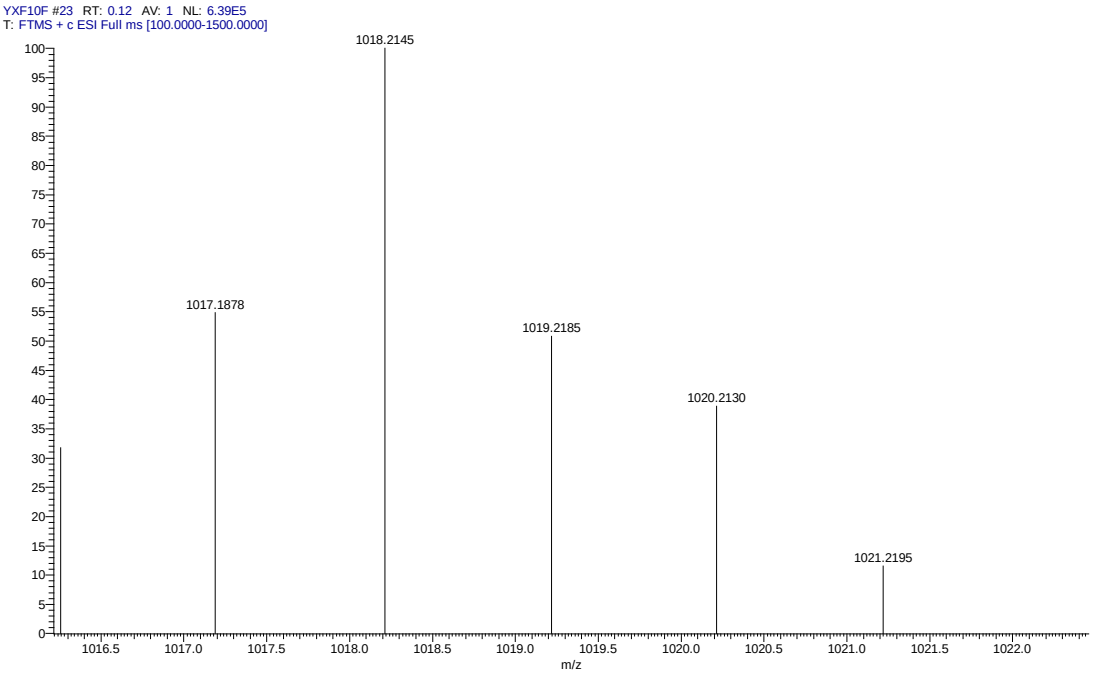
Positive-ion ESI-MS spectrum of [**10c**-Cl^-]$^+$ measured in MeOH.



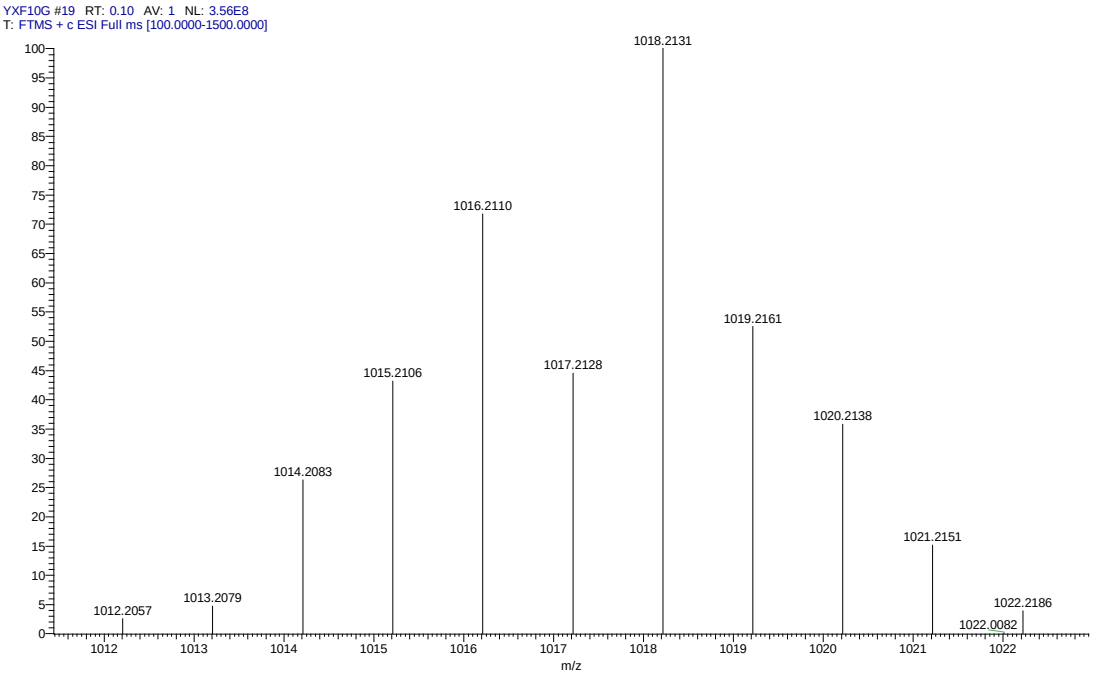
Positive-ion ESI-MS spectrum of [**10d**-Cl^-]$^+$ measured in MeOH.



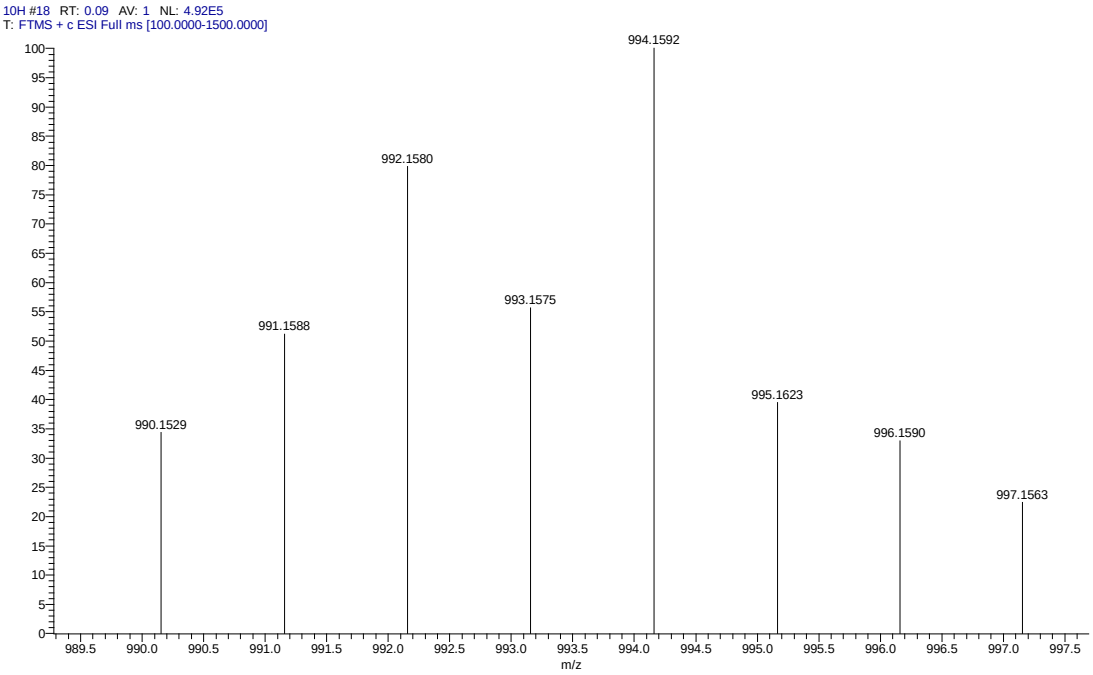
Positive-ion ESI-MS spectrum of [**10e**-Cl^-]$^+$ measured in MeOH.



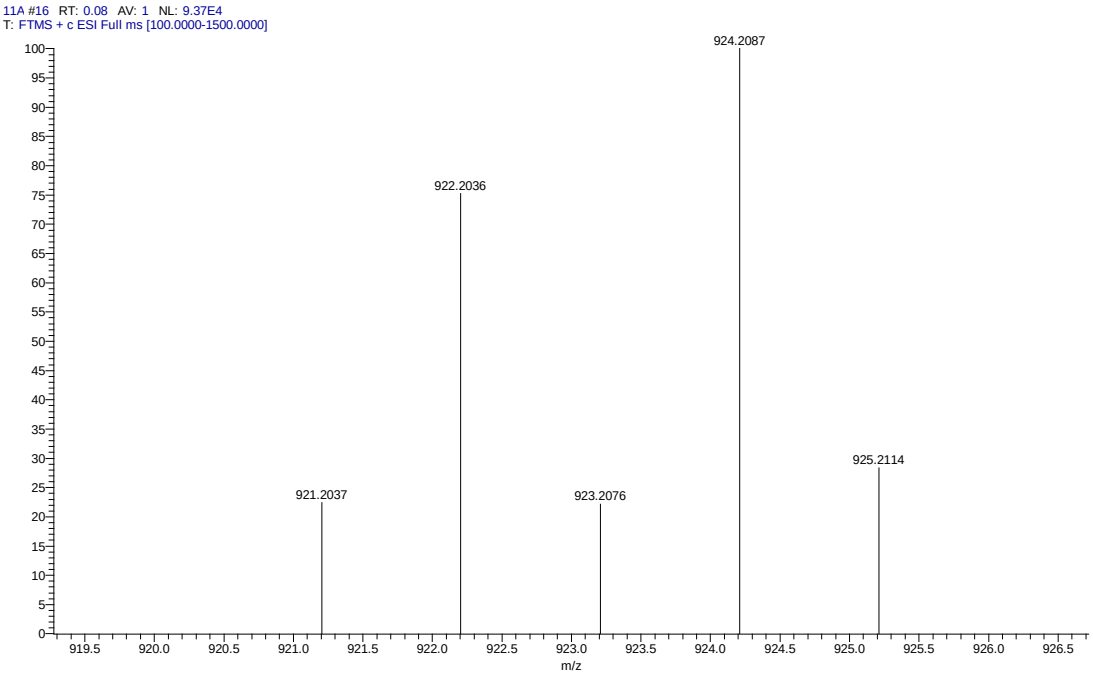
Positive-ion ESI-MS spectrum of [**10f**-Cl^-]$^+$ measured in MeOH.



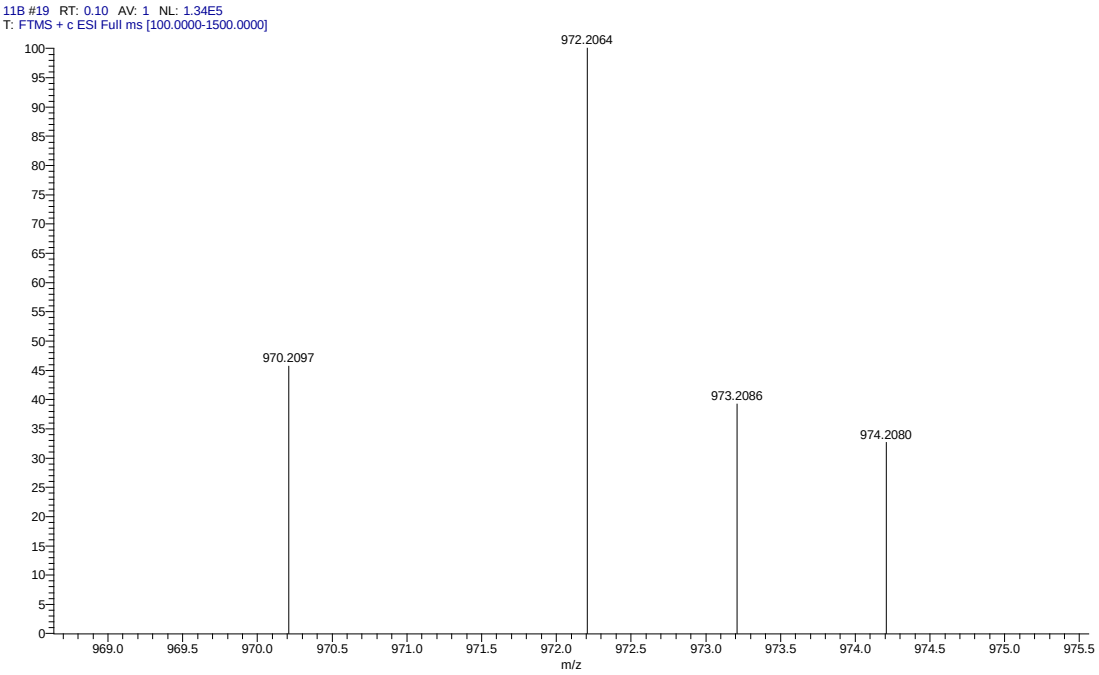
Positive-ion ESI-MS spectrum of [**10g**-Cl^-]$^+$ measured in MeOH.



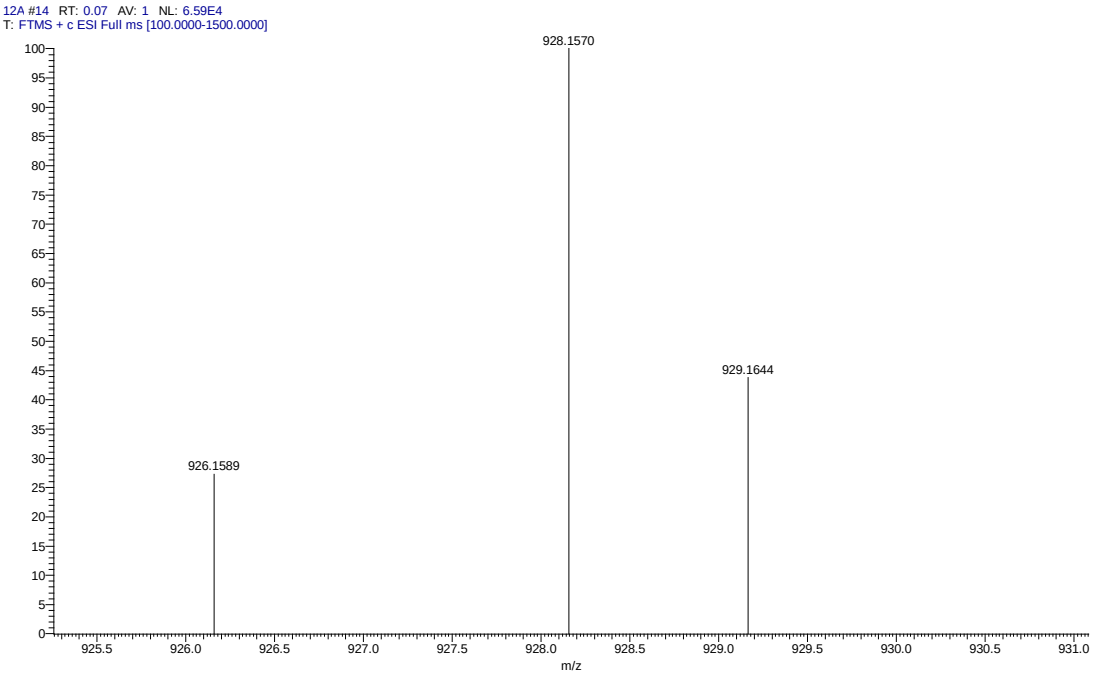
Positive-ion ESI-MS spectrum of [**10h**-Cl^-]$^+$ measured in MeOH.



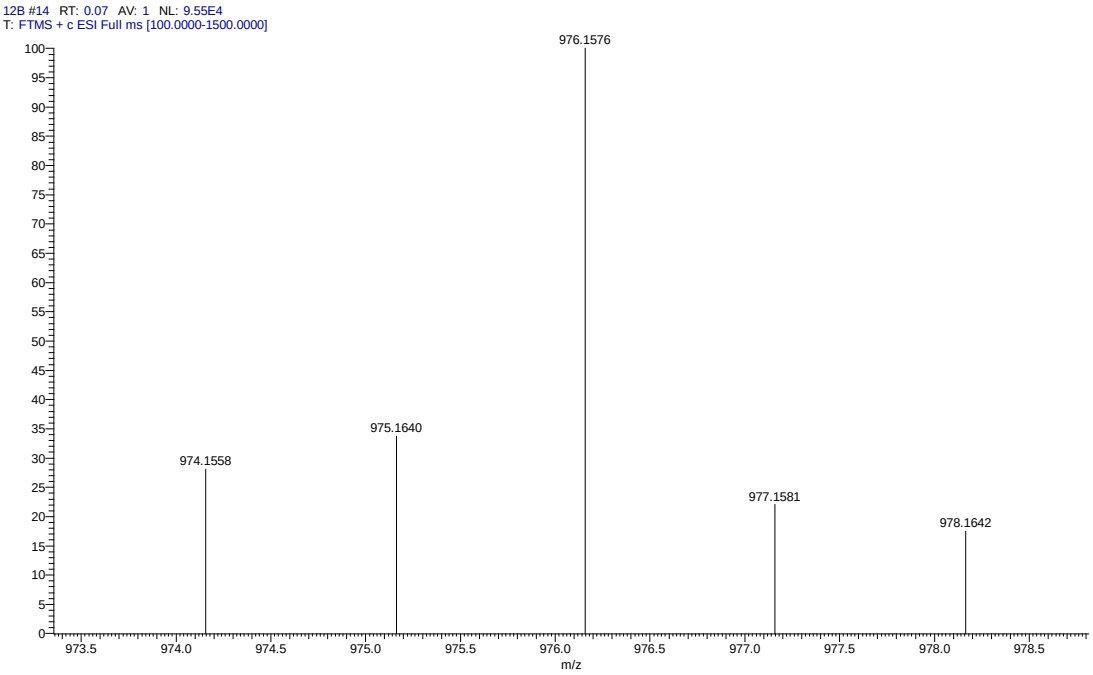
Positive-ion ESI-MS spectrum of [**11a**-Cl^-]$^+$ measured in MeOH.



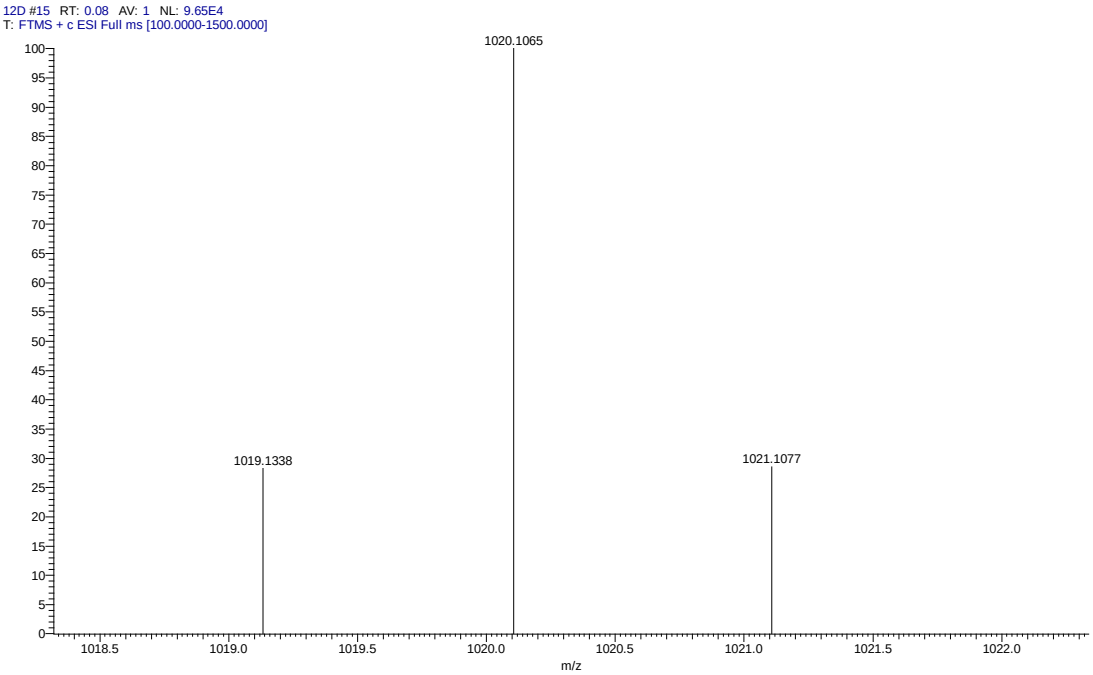
Positive-ion ESI-MS spectrum of [**11b**-Cl^-]$^+$ measured in MeOH.



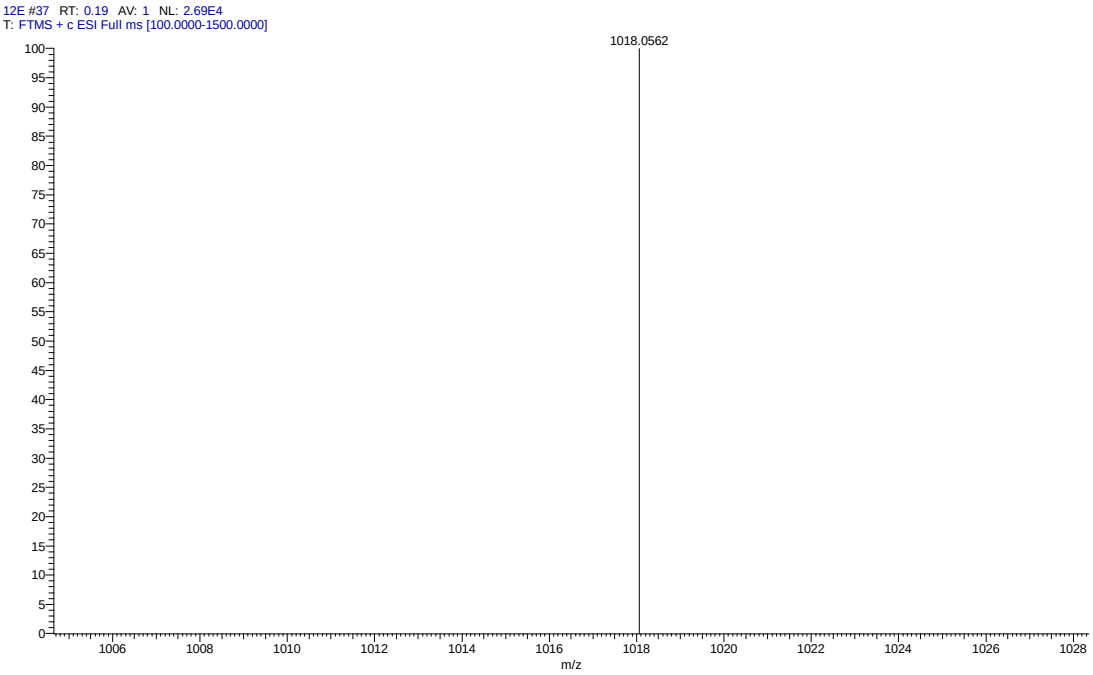
Positive-ion ESI-MS spectrum of [**12a**-Cl^-]$^+$ measured in MeOH.



Positive-ion ESI-MS spectrum of [**12b**-Cl^-]$^+$ measured in MeOH.



Positive-ion ESI-MS spectrum of [**12d**-Cl^-]$^+$ measured in MeOH.



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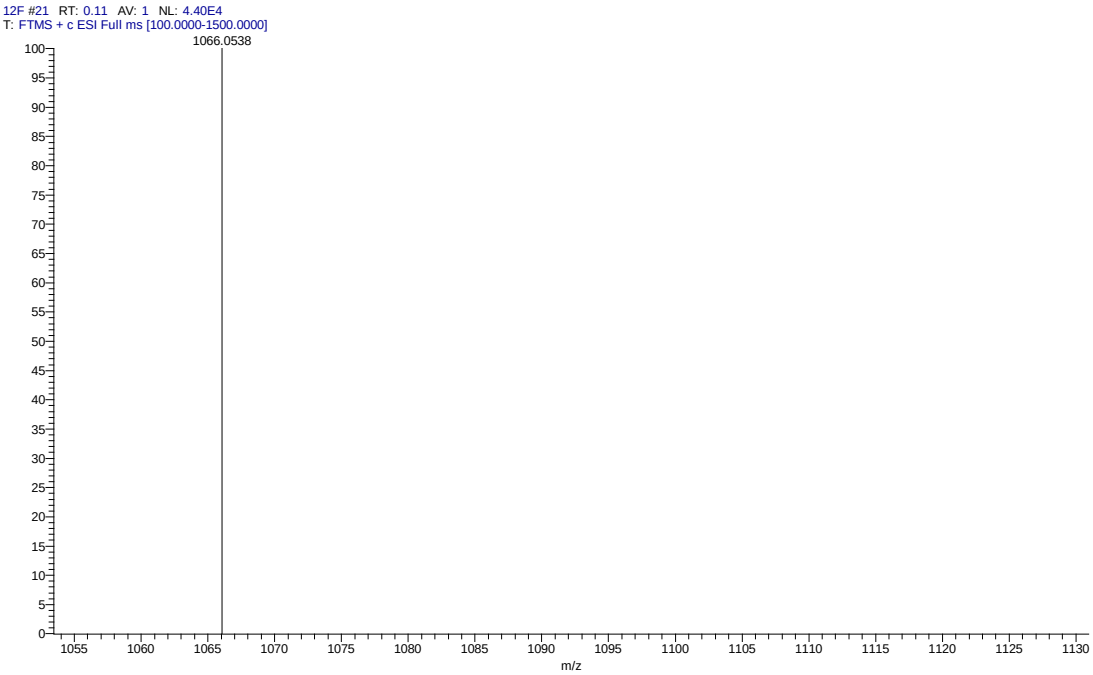
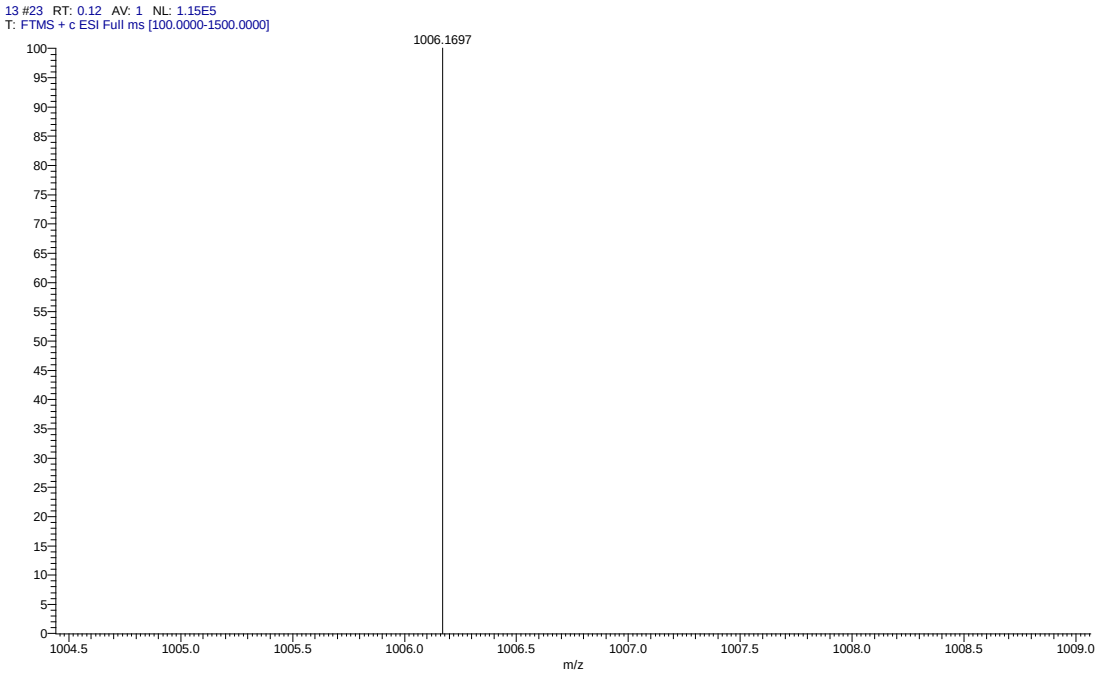


Positive-ion ESI-MS spectrum of [**12f**-Br$^-$]$^+$ measured in MeOH.



Positive-ion ESI-MS spectrum of [**13**-Cl^-]$^+$ measured in MeOH.

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