Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

1. GENERAL INFORMATION 2

2. SYNTHESIS OF OSMIUM COMPLEXES 3

3. CATALYST SCREENING AND CONDITIONS OPTIMIZATION: REACTION OF 4-METHOXYBENZALDEHYDE WITH 4-METHOXYANILINE 10

4. MECHANISTIC INVESTIGATIONS 21

5. SYNTHESIS AND CHARACTERIZATION OF THE RA PRODUCTS 24

6. DETAILS OF DFT CALCULATIONS 33

7. X-RAY INVESTIGATIONS 38

8. ^{1}H AND ^{13}C NMR SPECTRA AND HRMS OF THE OBTAINED OSMIUM COMPLEXES 40

9. ^{1}H AND ^{13}C NMR SPECTRA OF THE RA PRODUCTS. 64

10. REFERENCES 80

1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification, THF was distilled over sodium/benzophenone.

Isolation of products was performed using column chromatography (Acros Organics, silica gel 0.06-0.200 mm) or using preparative flash chromatograph InterChim PuriFlash; DCM-MeOH binary system was used as an eluent. All details about particular chromatographic parameters are provided with the description of each compound.

^{1}H, ^{13}C, and ^{19}F spectra were recorded in $CDCl_3$ on Bruker Avance 300, Bruker Avance 400, or Varian Inova 400 spectrometers. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, dd = doublet of dublets, t = triplet, q = quartet, quint. = quintet, m = multiplet, br = broad, sept = septet; coupling constants are given in Hertz (Hz). NMR yields were determined with reference to an internal standard (dimethyl formamide).

High-resolution mass spectra (HRMS) were registered on a Bruker Daltonics micrOTOF-Q II hybrid quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI); measurements were done in a positive ion mode. The voltage on the capillary was 4500 V; range of scanned masses, *m/z* 50-3000; external calibration (Electrospray Calibrant Solution; Fluka, Germany); nebulizer pressure: 0.4 bar; flow rate: 3 μl/min; nitrogen as dry gas (6 l/min); interface temperature: 180 °C.

Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 gas chromatograph fitted with a flame ionization detector (He was used as the carrier gas, 37 mL/min) and a MS detector. Chromatec CR-5 and Chromatec CR-5MS (30 meters) capillary column were used.

GC settings for the yield determination using FID detector and CR5 column:

The injector temperature was 250 °C, split ratio of 50:1 at the moment of injection, the FID temperature was 250 °C. Column compartment temperature program: 100°C for 2 min, 100°C → 280°C at 30°C/min, 280°C for 3 min. Flow rate 2 mL/min, column CR-5. Retention time for 4-methoxy-N-(4-methoxybenzyl)aniline is 10.2 min; for N,1-bis(4-methoxyphenyl)methanimine 10.4 min; for 4-methoxyaniline 5.5 min.

GC settings for the qualitative analysis using MS detector and CR5-ms column:

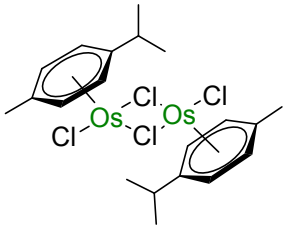
The injector temperature was 250 °C, split ratio of 75:1 at the moment of injection. Column compartment temperature program: 60°C for 4 min, 60°C → 250°C at 30°C/min, 250°C for 12 min. Flow rate 1 mL/min. MSD parameters: ion source temperature 200°C, transfer line temperature 230°C. Retention times (t_R) and integrated ratios were obtained using Chromatec Analytic Software.

Reactions with pressure were carried out in autoclaves made from either stainless steel or titanium. The autoclave material had no effect on the reactions.

2. Synthesis of osmium complexes

Complexes **Os1** $[(Cymene)OsCl_2]_2$[1], **Os7** (2,2'-bipyridine)$OsCl_2(CO)_2$[2], **Os9** (2,2'-bipyridine)$_2OsCl_2$[3], **Os10** $[(2,2'\text{-bipyridine})_2OsCl_2]Cl$[3] were prepared as described in the literature.

$[(\eta^6\text{-cymene})OsCl_2]_2$ (Os1)

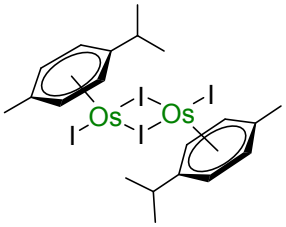


A mixture of Na_2OsCl_6 (300 mg, 0.67 mmol), 1.5 ml of γ-terpinene (9.2 mmol) in EtOH (4 ml) was heated in a sealed tube at 100 °C for 4 hours under argon atmosphere. The reaction mixture was cooled to room temperature and evaporated to dryness *in vacuo*. The orange product was crushed in hexane, filtered off, washed with water and dried. Yield:209 mg (79 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 6.4 Hz, 2H, Ar-H), 6.05 (d, *J* = 6.4 Hz, 2H, Ar-H), 2.80 (sept, *J* = 7.0 Hz, 1 H, C**H**$(Me)_2$), 2.22 (s, 3H, CH_3C), 1.31 (d, *J* = 7.0 Hz, 6H, CH(**C**$\mathbf{H_3}$)$_2$).

The obtained NMR data are in agreement with the literature report.[1]

$[(\eta^6\text{-cymene})OsI_2]_2$ (Os2)



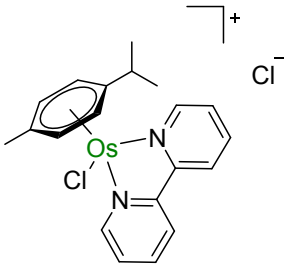
A mixture of $[(\eta^6\text{-cymene})OsCl_2]_2$ (100 mg, 0.126 mmol) and $NaI*2H_2O$ (300 mg, 1.61 mmol) was stirred in acetone (5 ml) at 100 °C in a sealed tube for 24 hours. The solvent was removed from the resulting dark-brown reaction mixture *in vacuo* and the residue was washed with water and dried. The product was extracted with CH_2Cl_2, precipitated by adding Et_2O, filtered off and air-dried to afford 128 mg (88%) of red-brown crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (d, *J* = 5.5 Hz, 2H, Ar-H), 5.95 (d, *J* = 5.5 Hz, 2H, Ar-H), 2.84 (sept, *J* = 6.8 Hz, 1H, C**H**$(Me)_2$), 2.32 (s, 3H, CH_3C), 1.25 (d, *J* = 6.9 Hz, 6H, CH(**C**$\mathbf{H_3}$)$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 96.1 (**C**$_{\mathbf{Ar}}$-C), 90.4 (**C**$_{\mathbf{Ar}}$-C), 75.3 (C_{Ar}-H), 75.2 (C_{Ar}-H), 31.7 (C**H**$(Me)_2$), 22.8 (CH(**C**$\mathbf{H_3}$)$_2$), 20.6 (CH_3Ar).

HRMS (ESI-MS): calcd. for $C_{12}H_{17}NOsI^+$, $[(\eta^6\text{-cymene})Os(CH_3CN)I]^+$ 494.0015, found 494.0013

[(η^6-cymene)Os(2,2'-bipyridine)Cl]Cl (Os3)



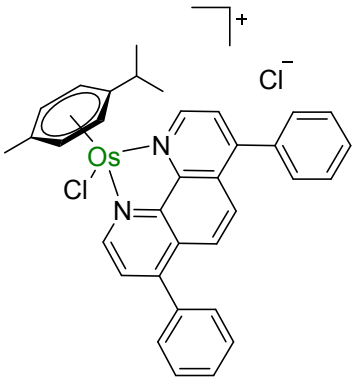
A solution of 2,2′-bipyridine (21 mg, 0.14 mmol) and [(η^6-cymene)$OsCl_2$]$_2$ (51 mg, 0.07 mmol) in methanol (3 ml) was stirred for 2 h at room temperature. The solvent volume was reduced *in vacuo* to ~0.5 ml and product crystallization was induced by the addition of Et_2O. A formed yellow precipitate was recovered by filtration, washed with Et_2O and air-dried. Yield 61 mg (86%).

^{1}H NMR (400 MHz, CD_3OD) δ 7.84 (d, *J* = 5.5 Hz, 2H, Ar-H (Bipy)), 7.03 (d, *J* = 8.1 Hz, 2H, Ar-H (Bipy)), 6.64 (t, *J* = 7.8 Hz, 2H, Ar-H (Bipy)), 6.14 (t, *J* = 6.6 Hz, 2H, Ar-H (Bipy)), 4.75 (d, *J* = 5.7 Hz, 2H, Ar-H (cymene)), 4.43 (d, *J* = 5.7 Hz, 2H, Ar-H (cymene)), 0.90 (sept, *J* = 6.9 Hz, 1H, C**H**$(Me)_2$), 0.75 (s, 3H, CH_3C), -0.61 (d, *J* = 6.9 Hz, 6H, CH(**CH_3**)$_2$).

^{13}C NMR (75 MHz, CD_3OD) δ 157.1 (C_{Ar} (Bipy)), 156.8 (C_{Ar} (Bipy)), 141.2 (C_{Ar} (Bipy)), 129.6 (C_{Ar} (Bipy)), 125.1 (C_{Ar} (Bipy)), 99.0 (C_{Ar}-C (cymene)), 96.8 (C_{Ar}-C (cymene)), 79.7 (C_{Ar}-H (cymene)), 75.4 (C_{Ar}-H (cymene)), 32.6 (C**H**$(Me)_2$), 22.6 (CH(**CH_3**)$_2$), 18.9 (CH_3Ar).

HRMS (ESI-MS): calcd. for $C_{20}H_{22}N_2OsCl^+$ $[M]^+$ 517.1071, found 517.1068.

[(η^6-cymene)Os(Bphen)Cl]Cl (Os4)



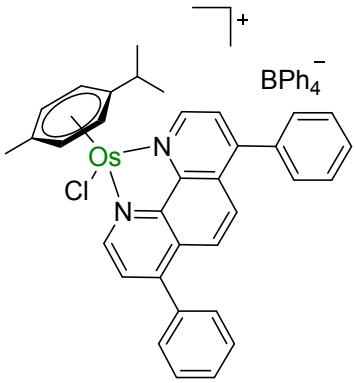
A mixture of [(η^6-cymene)$OsCl_2$]$_2$ (29 mg, 0.037 mmol) and bathophenanthroline (27 mg, 0.081 mmol) was stirred in acetone (3 ml) for 1 hour at room temperature. The reaction mixture was evaporated *in vacuo* to dryness and the product was recrystallized from CH_2Cl_2 – Et_2O. A formed yellow precipitate fwas recovered by filtration, washed with Et_2O and air-dried. Yield 61 mg (72%).

^{1}H NMR (400 MHz, CD_3OD) δ 8.25 (d, *J* = 5.6 Hz, 2H, CH=N), 6.59 (s, 2H, CH in the central ring), 6.43 (d, *J* = 5.6 Hz, 2H, C**H**CH=N), 6.17 – 5.97 (m, 10H, Ph-rings), 4.93 (d, *J* = 5.9 Hz, 2H, Ar-H (cymene)), 4.64 (d, *J* = 5.9 Hz, 2H, Ar-H (cymene)), 1.09 – 0.88 (m, 1H, C**H**$(Me)_2$), 0.76 (s, 3H, CH_3C), -0.58 (d, *J* = 6.9 Hz, 6H, CH(**CH_3**)$_2$).

^{13}C NMR (101 MHz, CD_3OD) δ 156.5, 152.8, 148.6, 136.5, 131.2, 131.1, 130.4, 130.1, 128.2, 127.1, 79.1 (C_{Ar}-H (cymene)), 76.1 (C_{Ar}-H (cymene)), 32.5 (C**H**$(Me)_2$), 22.7 (CH(**C**$\underline{\mathbf{H_3}}$)$_2$), 18.9 (CH_3Ar (cymene)).

HRMS (ESI-MS): calcd. for $C_{34}H_{30}N_2OsCl^+$ $[M]^+$ 693.1698, found 693.1701.

[(η^6-cymene)Os(Bphen)Cl]BPh$_4$ (Os5)



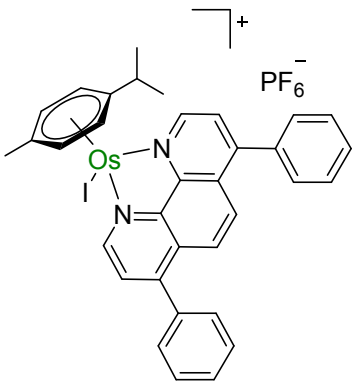
A mixture of [(η^6-cymene)$OsCl_2]_2$ (29 mg, 0.037 mmol) and bathophenanthroline (27 mg, 0.081 mmol) was stirred in acetone (3 ml) for 1 hour at room temperature. Solution of $NaBPh_4$ (40 mg, 0.117 mmol) in water (10 ml) was added and acetone was removed *in vacuo*. The yellow product was filtered off, washed with water and air-dried. Subsequent recrystallization from CH_2Cl_2-Et_2O gave 64 mg of the product (86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 5.1 Hz, 2H, CH=N), 8.04 (s, 2H, CH in the central ring), 7.62 – 7.57 (m, 6H), 7.52 – 7.44 (m, 14H), 6.96 (t, *J* = 7.3 Hz, 8H), 6.83 (t, *J* = 7.1 Hz, 4H), 5.59 (d, *J* = 5.1 Hz, 2H, Ar-H (cymene)), 5.31 (d, *J* = 5.1 Hz, 2H, Ar-H (cymene)), 2.38 – 2.31 (m, 1H, C**H**$(Me)_2$), 2.02 (s, 3H, CH_3C), 0.93 (d, *J* = 6.8 Hz, 6H, CH(**C**$\underline{\mathbf{H_3}}$)$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (m appears as 4 peaks with equel intensity – **C**(Ph)-B), 154.4, 151.3, 147.3, 136.5, 134.7, 130.3, 130.0, 129.4, 128.7, 127.4, 126.0, 125.9, 122.2, 96.4 (C_{Ar}-C (cymene)), 94.9 (C_{Ar}-C (cymene)), 77.4 (C_{Ar}-H (cymene)), 75.1 (C_{Ar}-H (cymene)), 31.3 (**C**H$(Me)_2$), 22.5 (CH(**C**$\underline{\mathbf{H_3}}$)$_2$), 18.7 (CH_3Ar (cymene)).

HRMS (ESI-MS): calcd. for $C_{34}H_{30}N_2OsCl^+$ $[M]^+$ 693.1698, found 693.1699.

[(η^6-cymene)Os(Bphen)I]PF$_6$ (Os6)



A mixture of [(η^6-cymene)$OsI_2]_2$ (31 mg, 0.027 mmol) and bathophenanthroline (19 mg, 0.057 mmol) was stirred in acetone (3 ml) for 1 hour at 50 °C. Then a solution on KPF_6 (25 mg, 0.136 mmol) in

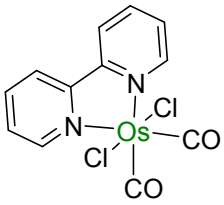
water (10 ml) was added and acetone was removed *in vacuo*. The red-orange product was filtered off, washed with water and air-dried. Subsequent recrystallization from CH_2Cl_2-Et_2O gave 46 mg of the iodide (92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 5.6 Hz, 2H, CH=N), 8.09 (s, 2H, CH in the central ring), 7.92 (d, *J* = 5.6 Hz, 2H, C**H**CH=N), 7.58 (m, appears as br s, 10H, Ph rings), 6.23 (d, *J* = 5.8 Hz, 2H, Ar-H(cymene)), 6.07 (d, *J* = 5.8 Hz, 2H, Ar-H(cymene)), 2.81 (sept, *J* = 6.8 Hz, 1H, C**H**$(Me)_2$), 2.40 (s, 3H, CH_3C), 1.08 (d, *J* = 6.8 Hz, 6H, CH(**CH_3**)$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 150.7, 147.0, 134.6, 129.8, 129.0, 128.5, 126.9, 125.7, 98.3 (C_{Ar}-C (cymene)), 93.66 (C_{Ar}-C (cymene)), 76.52 (C_{Ar}-H (cymene)), 76.48 (C_{Ar}-H (cymene)), 31.6 ((CH_3)$_2$**CH**Ar (Cymene)), 22.1 ((**CH_3**)$_2$CHAr (Cymene)), 19.7 (CH_3Ar (cymene)).

HRMS (ESI-MS): calcd. for $C_{34}H_{30}N_2OsI^+$ $[M]^+$ 785.1065, found 785.1064.

(2,2'-bipyridine)$OsCl_2(CO)_2$ (Os7)



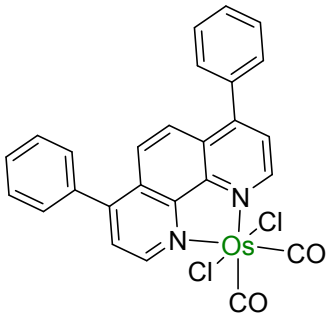
A 10 ml stainless steel autoclave was charged with Na_2OsCl_6 (61 mg, 0.136 mmol), 2,2'-bipyridine (22 mg, 0.138 mmol), formic acid (1.5 ml) and 37% formaldehyde in water (0.3 ml). The autoclave was sealed, flushed three times with 10 atm of CO, and then pressurized with 30 atm of CO. The reactor was placed into a preheated to 120°C oil bath. After 20h, the reactor was cooled to room temperature and depressurized. The solvent was removed from the reaction mixture *in vacuo* and the crude product was extracted by CH_2Cl_2. Organic extracts were concentrated and the residue was purified using column chromatography (Al_2O_3 was used as stationary phase), eluent: CH_2Cl_2. After concentrating the mixture *in vacuo* to ~1 ml, the complex was crystallized by addition of hexane. The formed yellow solid was filtered off and air-dried. Yield 14 mg (22%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 5.4 Hz, 2H), 8.25 (d, *J* = 8.1 Hz, 2H), 8.17 – 8.10 (m, 2H), 7.79 – 7.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 155.6, 153.1, 139.9, 128.1, 123.5.

HRMS (ESI-MS): calcd. for $C_{12}H_8N_2ClOsO_2^+$ $[M - Cl]^+$ 438.9873, found 438.9863.

(Bphen)$OsCl_2(CO)_2$ (Os8)



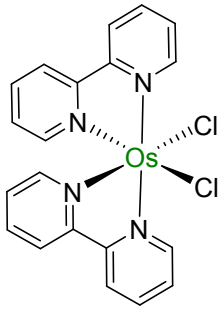
A 10 ml stainless steel autoclave was charged with Na_2OsCl_6 (61 mg, 0.136 mmol), bathophenanthroline (46 mg, 0.138 mmol), formic acid (1.5 ml) and 37% formaldehyde in water (0.3 ml). The autoclave was sealed, flushed three times with 10 atm of CO, and then pressurized with 30 atm of CO. The reactor was placed into a preheated to 120°C oil bath. After 20h, the reactor was cooled to room temperature and depressurized. The solvent was removed from the reaction mixture *in vacuo* and the crude product was extracted by CH_2Cl_2. Organic extracts were concentrated and the residue was purified using column chromatography (Al_2O_3 was used as stationary phase), eluent: CH_2Cl_2. After concentrating the mixture *in vacuo* to ~1 ml, the complex was crystallized by addition of hexane. The formed yellow solid was filtered off and air-dried. Yield 38 mg (43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 5.4 Hz, 2H, CH=N), 8.10 (s, 2H, CH in the central ring), 7.90 (d, *J* = 5.4 Hz, 2H, C**H**CH=N), 7.65 – 7.61 (m, 6H, Ph ring), 7.56 – 7.54 (m, 4H, Ph ring).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6 (C_q=N), 152.2 (CH=N), 147.4 (C_qPh), 135.2 (**C_q**C_qPh), 130.2, 129.7, 129.5, 129.4, 126.6, 126.1.

HRMS (ESI-MS): calcd. for $C_{26}H_{16}N_2OsCl_2O_2Na^+$ $[M+Na]^+$ 672.9964, found 672.9985.

(2,2'-bipyridine)$_2$OsCl$_2$ (Os9)

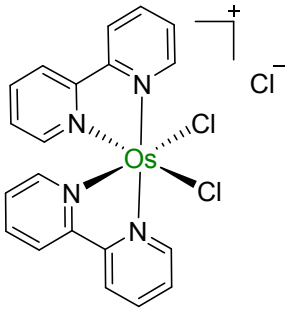


To a stirred solution of $[(bipy)_2OsCl_2]Cl$ (20 mg, 0.033 mmol) in methanol (4 ml) a solution of $Na_2S_2O_4$ (50 mg, 0.29 mmol) in water (1 ml) was added in one portion at room temperature. The color of a solution immediately changed from brown to mulberry-red. The mixture was stirred for 30 min. 3 ml of water was then added and the reaction mixture was stored at 6°C for an hour to complete crystallization of a product. Almost black solid precipitate of $(bipy)_2OsCl_2$ was filtered off, washed with water, methanol, dried and recrystallized from CH_2Cl_2 – hexane mixture. Yield 16 mg (85%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.71 (s, 2H), 8.26 (s, 2H), 8.16 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.45 (m, 2H), 7.11 (s, 2H), 6.88 (s, 2H), 6.78 (s, 2H), 6.12 (s, 2H).

HRMS (ESI-MS) of both $(bipy)_2OsCl_2$ and $[(bipy)_2OsCl_2]Cl$ exhibits the only peak cluster corresponding to $[(bipy)_2OsCl_2]^+$. This could be assigned to the oxidation of $(bipy)_2OsCl_2$ during the analysis: calcd. for $C_{20}H_{16}N_4Cl_2Os^+$ 574.0342, found 574.0364.

(2,2'-bipyridine)$_2$OsCl$_3$ (Os10)

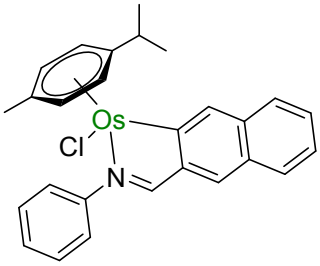


A mixture of Na_2OsCl_6 (147 mg, 0.33 mmol) and 2,2′-bipyridine (103 mg, 0.66 mmol) was refluxed in DMF (4 ml) under argon for 1 hour. The solution was cooled down and the formed NaCl was filtered off. The DMF was removed *in vacuo*, the product was extracted with methanol from the residue and diethyl ether was added to the extract. The crystallized brown $[(bipy)_2OsCl_2]Cl$ was filtered off and recrystallized from methanol – diethyl ether once again. After filtration, washing with diethyl ether and drying 134 mg (67%) of $[(bipy)_2OsCl_2]Cl$ was obtained.

^{1}H NMR (400 MHz, CD_3OD ***all signals appear as broad singlets***) δ 21.98, 17.97, 11.98, 7.72, -7.28, -11.39, -44.00, -51.67.

HRMS (ESI-MS) of both $(bipy)_2OsCl_2$ and $[(bipy)_2OsCl_2]Cl$ exhibits the only peak cluster corresponding to $[(bipy)_2OsCl_2]^+$. calcd. for $C_{20}H_{16}N_4Cl_2Os^+$ 574.0342, found 574.0364.

[(η^6-cymene)Os(N,C-napht)Cl] (Os11)



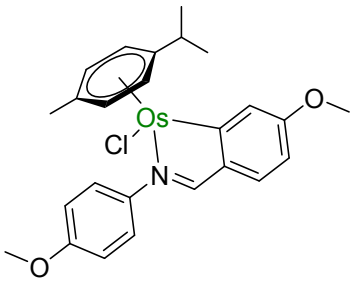
A mixture of $[(\eta^6\text{-cymene})OsCl_2]_2$ (31.7 mg, 0.040 mmol), TlOAc (21.1 mg, 0.080 mmol) and Schiff base (0.084 mmol) was stirred in methanol (2 ml) at 100 °C in a sealed tube and under argon atmosphere for 4 hours. The solvent was removed from the reaction mixture *in vacuo*, the residue was separated on SiO_2 with CH_2Cl_2 as eluent. After removing of the solvents *in vacuo* the product was obtained as orange-red crystals. Yield 21 mg (44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (br s, 1H, CH in *ortho*-position to Os), 8.35 (br s, 1H, CH in *ortho*-position to C=N group), 8.13 (br s, 1H, CH=N), 7.74 – 7.67 (m, 4H, Ar-H), 7.42 – 7.25 (m, 6H, Ar-H), 5.63 (br s, 1H, Ar-H(cymene)), 5.09 – 5.01 (m, 3H, Ar-H(cymene)), 2.23 (m, 1H, C**H**(Me)$_2$), 2.20 (s, 3H, CH_3Ar), 0.95 (br s, 3H, CH_3C), 0.75 (br s, 3H, CH_3C).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 163.9, 155.5, 147.4, 136.2, 130.8, 129.1, 127.9, 126.7, 123.8, 123.0, 96.6, 90.9, 83.9, 80.6, 72.9, 71.3, 31.2 ($(CH_3)_2$**CH**Ar (Cymene)), 23.6 (($\underline{\mathbf{CH_3}}$)$_2$CHAr (Cymene)), 21.7 (($\underline{\mathbf{CH_3}}$)$_2$CHAr (Cymene)), 18.8 ($CH_3$Ar (cymene)).

HRMS (ESI-MS): calcd. for $C_{27}H_{26}NOsCl^+$ $[M]^+$ 591.1353, found 591.1349.

[(η^6-cymene)Os(N,C-anis)Cl] (Os12)



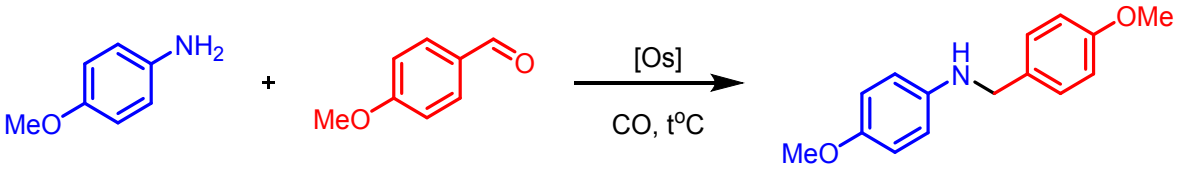
A mixture of [(η^6-cymene)$OsCl_2$]$_2$ (31.7 mg, 0.040 mmol), TlOAc (21.1 mg, 0.080 mmol) and Schiff base (0.084 mmol) was stirred in methanol (2 ml) at 100 °C in a sealed tube and under argon atmosphere for 4 hours. The solvent was removed from the reaction mixture *in vacuo*, the residue was separated on SiO_2 with CH_2Cl_2 as eluent. After removing of the solvents *in vacuo* the product was obtained as orange-red crystals. Yield 41 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, CH=N), 7.73 – 7.41 (m, 4H, Ar-H in *ortho*-position to N=C group + Ar-H in ortho position to OMe in the anisaldehyde moiety), 6.88 (d, J = 8.8 Hz, 2H, Ar-H in *ortho*-position to OMe group in anisidine moiety), 6.55 (dd, J = 8.4, 2.4 Hz, 1H, Ar-H in *ortho*-position to C=N group), 5.50 (d, J = 5.5 Hz, 1H, Ar-H(cymene)), 5.04 (dd, J = 8.4, 4.8 Hz, 3H, Ar-H(cymene)), 3.90 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 2.29 (sept, 6.9 Hz, 1H, C**H**$(Me)_2$), 2.17 (s, 3H, CH_3Ar), 0.97 (d, J = 6.9 Hz, 3H, CH_3C), 0.81 (d, J = 6.9 Hz, 3H, CH_3C).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 172.0, 161.7, 158.6, 149.1, 140.9, 131.1, 124.0, 122.9, 113.8, 109.2, 95.9, 90.7, 83.2, 79.9, 73.9, 71.9, 55.7 (CH_3O), 55.2 (CH_3O), 31.3 (($CH_3)_2$**CH**Ar (Cymene)), 23.5 ((**CH_3**)$_2$CHAr (Cymene)), 21.7 ((**CH_3**)$_2$CHAr (Cymene)), 18.7 (CH_3Ar (Cymene)).

HRMS (ESI-MS): calcd. for $C_{25}H_{28}NO_2OsCl^+$ $[M]^+$ 601.1415, found 601.1419.

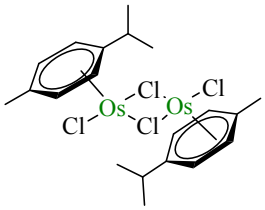
3. Catalyst Screening and Conditions Optimization: Reaction of 4-methoxybenzaldehyde with 4-methoxyaniline



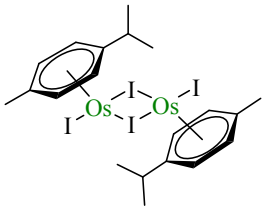
General procedure: A glass vial in a 10 mL stainless steel or titanium autoclave was charged with the prescribed quantity of the catalyst, co-catalyst, 4-methoxyaniline (24.7 – 98.8 mg, 50-200 mol %, 0.1 - 0.4 mmol), 4-methoxybenzaldehyde (48.8 µL, 100 mol%, 0.4 mmol) and 0.4 mL of the corresponding solvent if mentioned. The autoclave was sealed, flushed three times with 10 bar of CO, then charged with the indicated pressure of CO. The reactor was placed into a preheated oil bath. After the indicated time, the reactor was cooled down to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, and then a sample of the resulting solution was analyzed by GC. Unless otherwise mentioned, the yields were determined by GC.

All experiments were reproduced at least two times.

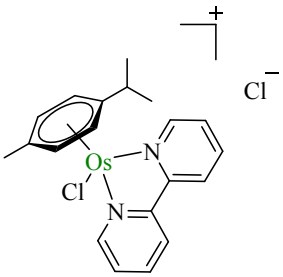
Table S1 Comparison of catalytic activity of different complexes.



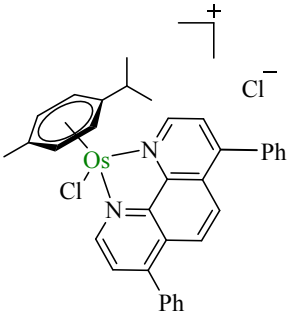
Os1



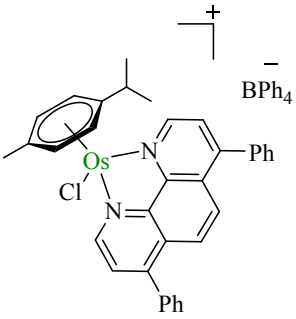
Os2



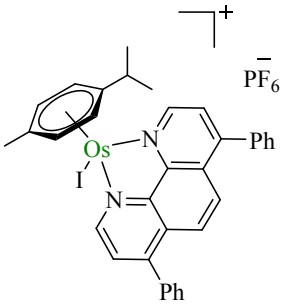
Os3



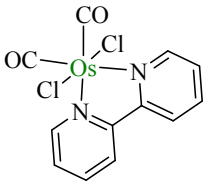
Os4



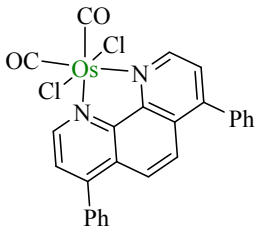
Os5



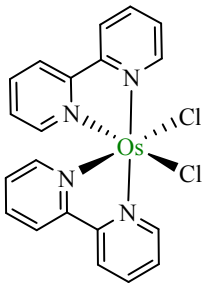
Os6



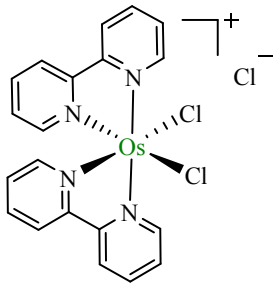
Os7



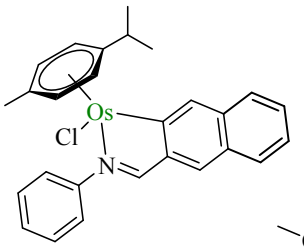
Os8



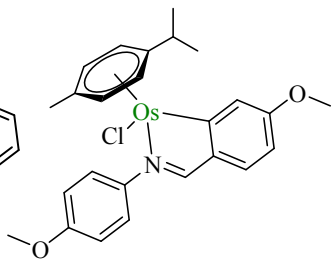
Os9



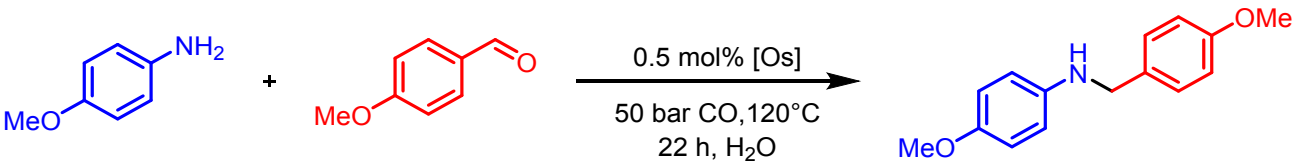
Os10



Os11



Os12

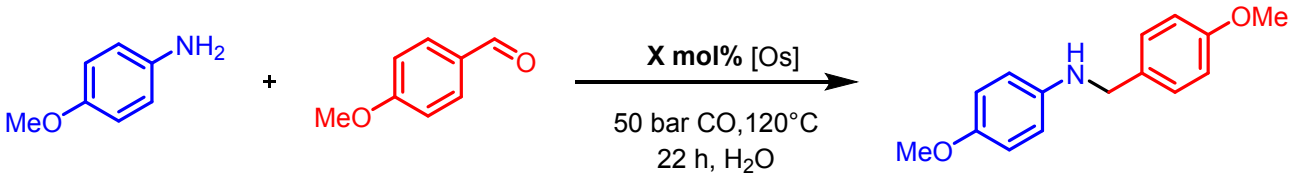


Entry [a]	Catalyst	Yield [b], %
1	Na_2OsCl_6	1
2	**Os1**	8
3	**Os2**	13

4	**Os3**	94
5	**Os4**	84
6	**Os5**	98
7	**Os6**	80
8	**Os7**	81
9	**Os8**	99
10	**Os9**	Traces
11	**Os10**	2
12	**Os11**	10
13	**Os12**	Traces

[a]Osmium catalyst (0.5 mol% [Os]), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL H_2O, 50 bar CO, 120 °C, 22 h.
[b] Yields of the experiments were determined by GC.

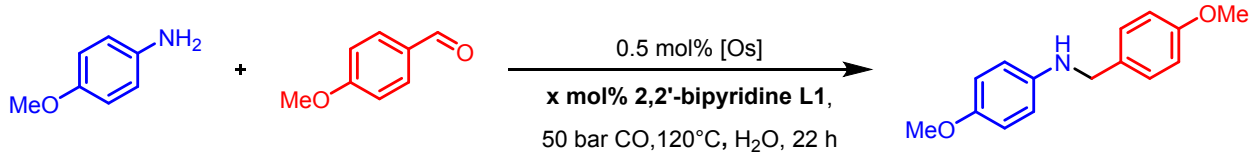
Table S2. Investigation of the effects of ancillary anions.



Entry	[Os] Loading, mol%	**Os1** + Bphen [a], %	**Os4** [b], %	**Os6** [b], %
Anions	-	Cl	Cl	I, PF_6
1	0.5	98	84	80
2	0.25	99	79	2
3	0.125	85	53	2

[a]98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 0.25-0.0625 mol% of catalyst, 1.5-0.375 mol% of bathophenanthroline **L3** 2-0,5 mg (6.0-1.5 µmol), 400 µL of H_2O, 50 bar CO, 120°C, 22 h. Yields of the experiments were determined by GC.
[b]98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 0.5-0.0625 mol% of catalyst, 400 µL of H_2O, 50 bar CO, 120°C, 22 h.Yields of the experiments were determined by GC

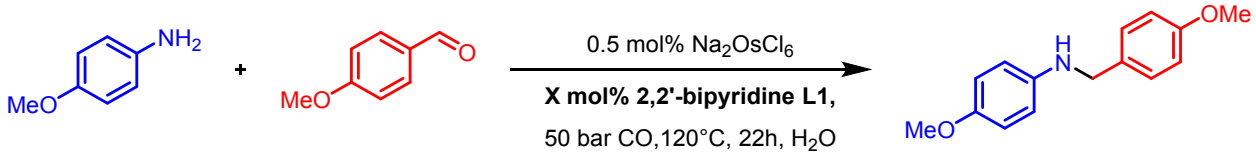
Table S3. Investigation of the effects of ancillary ligands.



Entry	Catalyst	2,2'-bipyridine **L1**, mol%	Yield [c], %
1[a]	Na_2OsCl_6	-	1
2[b]	Na_2OsCl_6	1.5	89
3[a]	**Os1**	-	8
4[b]	**Os1**	1.5	89
5[a]	**Os2**	-	13
6[b]	**Os2**	1.5	99
7[a]	**Os9**	-	Traces
8[b]	**Os9**	1.5	5
9[a]	**Os10**	-	2
10[b]	**Os10**	1.5	2
11[a]	**Os11**	-	10
12[b]	**Os11**	1.5	71
13[a]	**Os12**	-	Traces
14[b]	**Os12**	1.5	15

[a]Osmium catalyst (0.5 mol% [Os]), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL of H_2O, 50 bar CO, 120°C, 22 h.
[b]Osmium catalyst (0.5 mol% [Os]), **2,2'-bipyridine L1 0.96 mg (6.0 µmol)**, 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL of H_2O, 50 bar CO, 120°C, 22 h.
[c] Yields of the experiments were determined by GC.

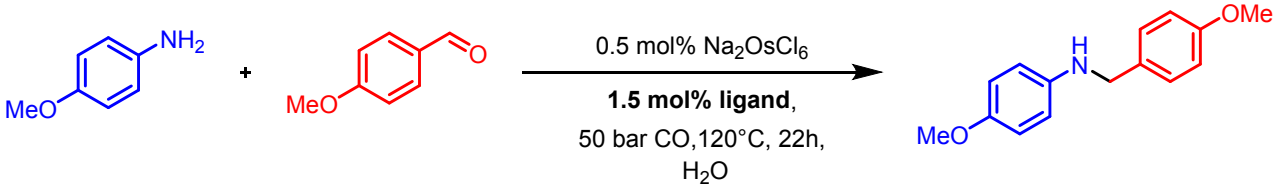
Table S4. Investigation of the effect of 2,2'-bipyridine amount



Entry [a]	2,2'-bipyridine, mol%	Yield [b], %
1	0.5	77
2	1.0	79
3	1.5	89
4	2.5	93
5	5	91

[a] Na_2OsCl_6 0.9 mg (2.0 µmol), 2,2'-bipyridine **L1** 0.32-3.2 mg (2.0–20 µmol), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL H_2O, 50 bar CO, 120°C, 22 h.
[b] Yields of the experiments were determined by GC.

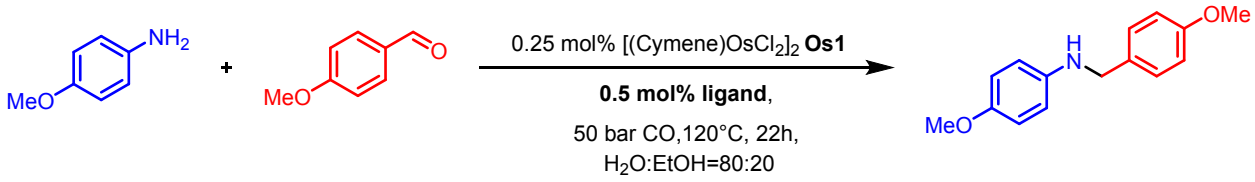
Table S5. Screening of ancillary ligands (Na_2OsCl_6).



Entry [a]	Ligand	Yield [b], %
1	2,2'-bipyridine **L1**	89
2	7,8-benzoquinoline **L2**	4
3	Bathophenanthroline **L3**	99
4	2,2'-biquinoline **L4**	5
5	Neocuproine **L5**	4
6	2,3-Bis(2-pyridyl)-pyrazine **L6**	11
7	1,10-phenanthroline **L7**	99

[a] Na_2OsCl_6 0.9 mg (2.0 µmol), 1.5 mol% of ligand, 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL H_2O, 50 bar CO, 120°C, 22 h.
[b] Yields of the experiments were determined by GC.

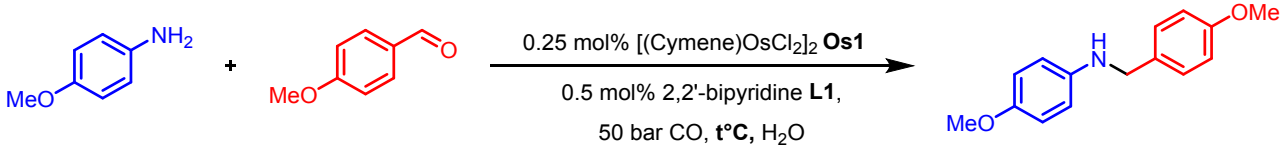
Table S6. Screening of ancillary ligands ([(p-cymene)$OsCl_2]_2$, Os1).



Entry [a]	Ligand	Yield [b], %
1	2,2'-bipyridine **L1**	96
2	7,8-benzoquinoline **L2**	7
3	Bathophenanthroline **L3**	74
4	2,2'-biquinoline **L4**	3
5	Neocuproine **L5**	8
6	2,3-Bis(2-pyridyl)-pyrazine **L6**	41
7	1,10-phenanthroline **L7**	71

[a]Osmium catalyst **Os1** 0.8 mg (1.0 µmol), 0.5 mol% of ligand, 98.8 mg (0.8 mmol), 4-methoxyaniline, 48.8 µL (0.4 mmol) 4-methoxybenzaldehyde, 320 µL H_2O + 80 µL EtOH, 50 bar CO, 120°C, 22 h.
[b] Yields of the experiments were determined by GC.

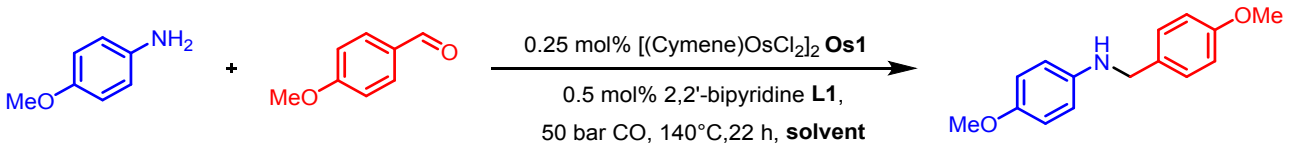
Table S7. Investigation of the temperature effect.



Entry [a]	temperature, °C	Yield [b], %
1	60	Traces
2	80	Traces
3	100	27
4	120	81
5	140	88
6	160	74
7	180	41
8	200	15

[a]Osmium catalyst **Os1** 0.8 mg (1.0 µmol),2,2'-bipyridine **L1** 0.32 mg (2.0 µmol), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL of H_2O, 50 bar CO, corresponding temperature, 22 h.
[b] Yields of the experiments were determined by GC.

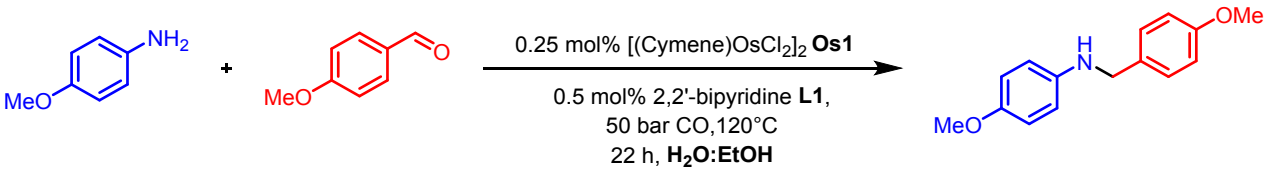
Table S8. Screening of solvents.



Entry[a]	Solvent	Yield [c], %
1	THF (20 ppm H_2O)	12
2	Et_2O (20 ppm H_2O)	11
3	MeCN (20 ppm H_2O)	10
4	Dioxane (20 ppm H_2O)	7
5	EtOAc (0.1% H_2O)	25
6	t-BuOMe (0.5% H_2O)	10
7	H_2O	88
8	$PhCH_3$ (0.03% H_2O)	15
9[b]	MeOH (0.0096% H_2O)	65
10[b]	MeOH (0.014% H_2O)	62
11[b]	EtOH (1.4% H_2O)	67
12[b]	EtOH (4.86% H_2O)	62
13[b]	i-PrOH (0.0092% H_2O)	41
14[b]	i-PrOH (0.1% H_2O)	31
15	t-BuOH (0.1% H_2O)	16

[a]Osmium catalyst **Os1** 0.8 mg (1.0 μmol), 2,2'-bipyridine **L1** 0.32 mg (2.0 μmol), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 μL (0.4 mmol) 4-methoxybenzaldehyde, 400 μL of corresponding solvent, 50 bar CO, 140°C, 22 h.
[b]The proportion of water was measured by Fischer titration.
[c] Yields of the experiments were determined by GC.

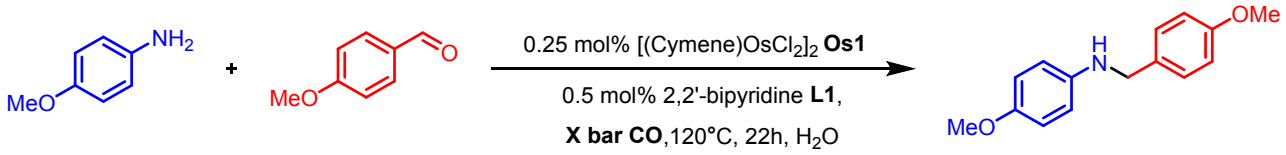
Table S9. Assessment of ethanol as a cosolvent



Entry [a]	H_2O:EtOH	Yield[b], %
1	80:20	96
2	20:80	94
3	50:50	86
4	100:0	81

[a]Osmium catalyst **Os1** 0.8 mg (1.0 μmol), 2,2'-bipyridine **L1** 0.32 mg (2.0 μmol), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 μL (0.4 mmol) 4-methoxybenzaldehyde, 400 μL of H_2O-EtOH mixtures, 50 bar CO, 140°C, 22 h.
[b] Yields of the experiments were determined by GC.

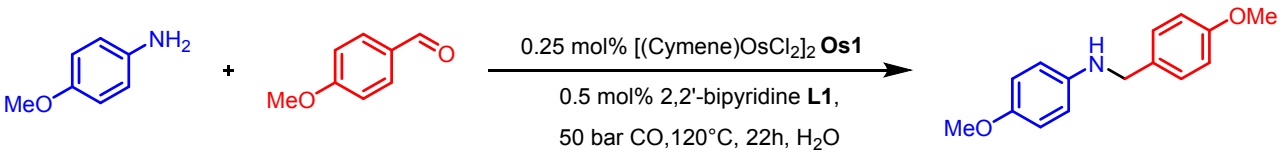
Table S10. Investigation of pressure influence on the Os-catalyzed alkylation.



Entry[a]	Pressure , bar	Yield [b], %
1	5	Traces
2	10	13
3	30	36
4	50	81

[a]Osmium catalyst **Os1** 0.8 mg (1.0 μmol),2,2'-bipyridine **L1** 0.32 mg (2.0 μmol), 98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8 μL (0.4 mmol) 4-methoxybenzaldehyde, 400 μL of H_2O, corresponding preassure, 120°C, 22 h.
[b] Yields of the experiments were determined by GC.

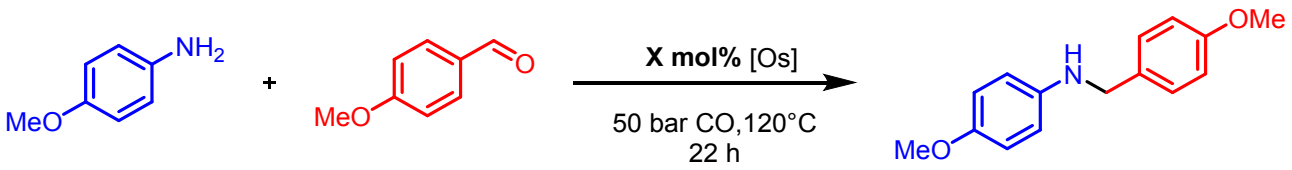
Table S11. Effect of the stoichiometric ratio of reagents.



Entry[a]	4-methoxyaniline,eq.	Yield [c], %
1[b]	0.5	66
2	1	78
3	2	81

[a]Osmium catalyst **Os1** 0.8 mg (1.0 μmol), 2,2'-bipyridine **L1** 0.32 mg (2.0 μmol), 24.7-98.8 mg (0.2-0.8 mmol) 4-methoxyaniline, 48.8 μL (0.4 mmol) 4-methoxybenzaldehyde, 400 μL of H_2O, 50 bar CO, 120°C, 22 h.
[b]The yield was calculated relative to 4-methoxyaniline.
[c]Yields of the experiments were determined by GC.

Table S12. Investigation of the catalysts' loading



Entry	[Os] Loading, mol%	Na_2OsCl_6 + BiPy **L1** [a], %	**Os1**+ BiPy **L1** [b], %	**Os2**+Bipy **L1**[a], %	**Os3** [c], %	**Os3** + BiPy **L1**[a], %	**Os3** 140°C[d], %	**Os4** [c], %	**Os7** [c], %	**Os8** [c], %	**Os9**[c], %	**Os9**+ BiPy **L1** [a], %
1	0,5	89	88	99	94	-	-	84	81	99	0	5
2	0,25	76	44	97	86	-	-	79	72	98	0	-
3	0,125	64	34	78	23	52	58	61	6	6	0	-
4	0,0625	30	26	54	12	-	-	18	25	6	0	-

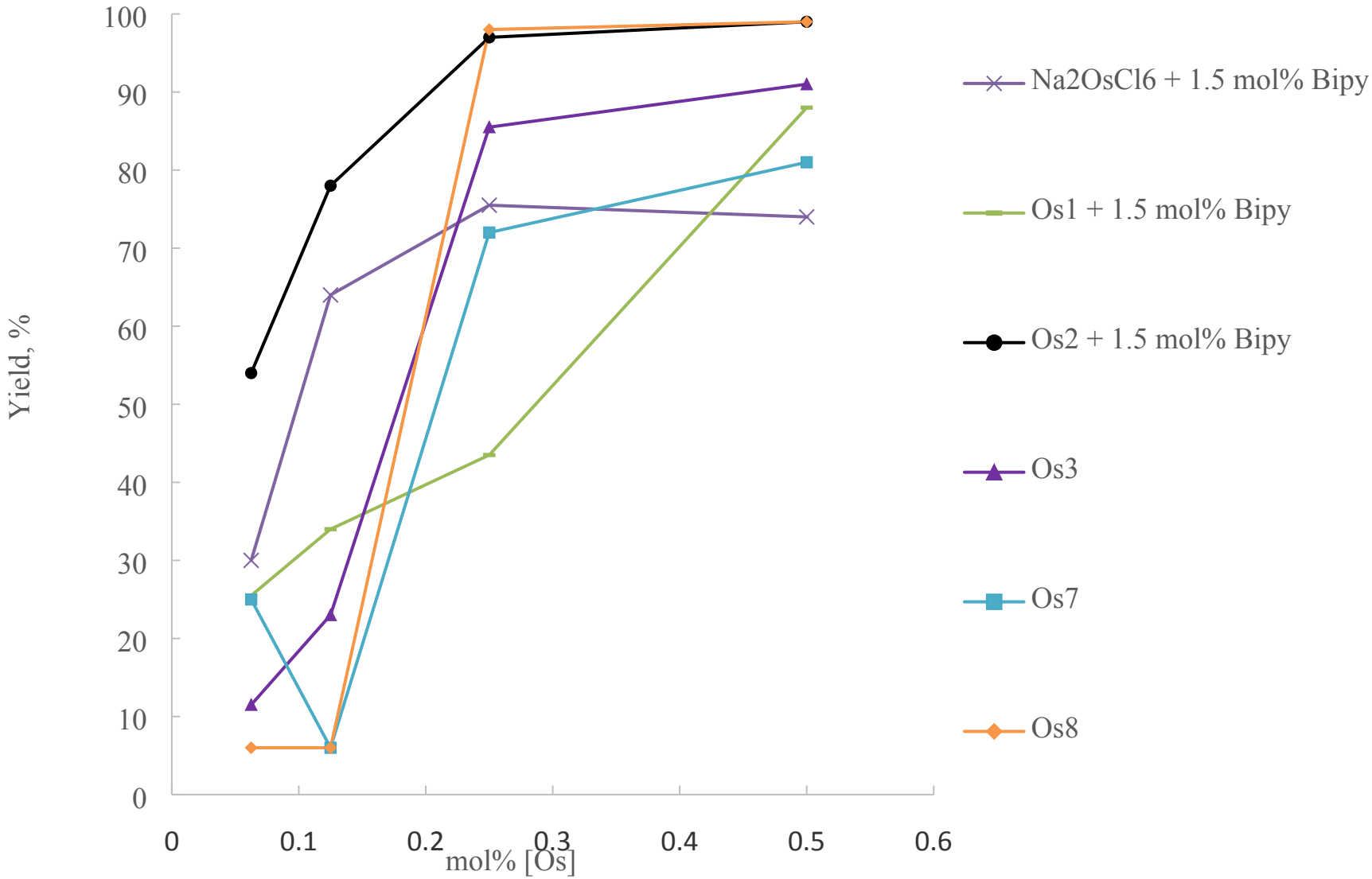
[a]98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 0.5-0.0625 mol% of catalyst, 1.5 mol% of 2,2'-bipyridine 0.96 mg (6.0 µmol), 400 µL of H_2O, 50 bar CO, 120°C, 22 h . Yields of the experiments were determined by GC.

[b]98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, **320 µL H_2O 80 µLEtOH**, 0.25-0.03125mol% % of catalyst, **1.5 mol% of 2,2'-bipyridine L1**,. Yields of the experiments were determined by GC.

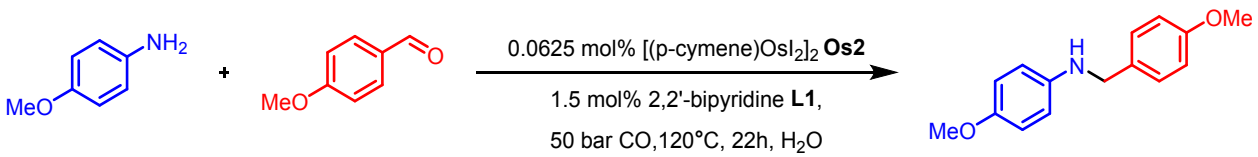
[c]98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 0.5-0.0625 mol% of catalyst, 400 µL of H_2O, 50 bar CO, 120°C, 22 h.Yields of the experiments were determined by GC.

[d]98.8 mg (0.8 mmol) 4-methoxyaniline, 48.8µL (0.4 mmol) 4-methoxybenzaldehyde, 400 µL H_2O, 0.5-0.0625 mol% of catalyst, **140°C**, Yields of the experiments were determined by GC.

«-» - Experiment was not conducted.


Yield, %
100
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
mol% [Os]
Na2OsCl6 + 1.5 mol% Bipy
Os1 + 1.5 mol% Bipy
Os2 + 1.5 mol% Bipy
Os3
Os7
Os8

Finally, optimal conditions are:

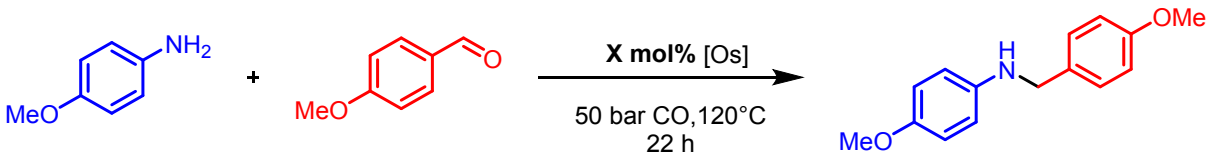


Os2 (0.0625 – 0.25 mol%), 1.5 mol% 2,2'-bipyridine **L1**, 2 equiv. of amine, H_2O, 50 bar CO, 120°C, 22 h.

Os2 was selected as the benchmark catalyst due to its low cost and relative simplicity. Moreover, the reaction requires minimal loading of this catalyst. Thus, this catalyst represents the optimal combination of catalytic activity and cost.

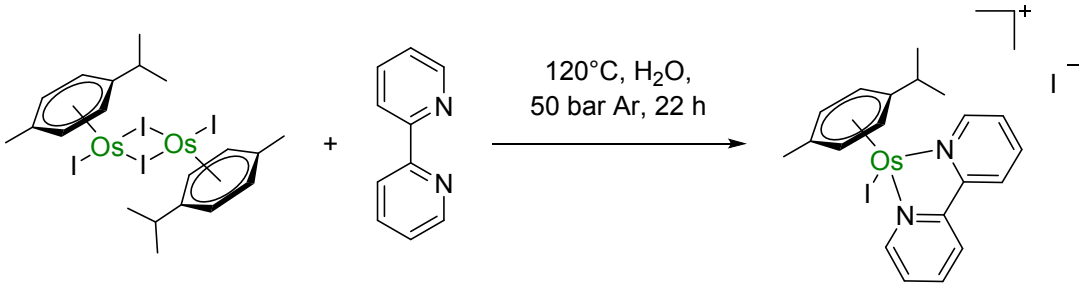
Other active catalytic systems are listed in the table below along with their price and optimal conditions for catalysis. The prices were calculated on the basis of Sigma Aldrich catalogue.

Table S13. Comparison of the working catalytic systems.



Entry	Osmium source	Additive	Minimal [Os] loading required for preparative yield	Number of steps for the osmium precursor preparation	Additive/Ligand cost, EUR for 1 g	Yield at the standard conditions using the mentioned catalytic osmium loading, %
1	Na_2OsCl_6	Bipy **L1** 1.5 mol%	0.125 mol%	0	11 EUR/g	64
2	Na_2OsCl_6	BPhen **L3** 1.5 mol%	0.5 mol%	0	549 EUR/g	99
3	**Os1**	Bipy **L1** 1.5 mol%	0.5 mol% (H_2O:EtOH 4:1)	1	11 EUR/g	88
4	**Os1**	BPhen **L3** 1.5 mol%	0.125 mol% with 0.3725 mol% Bphen	1	549 EUR/g	85
5	**Os2**	Bipy **L1** 1.5 mol%	0.0625 mol%	2	11 EUR/g	54
6	**Os7**	-	0.25 mol%	1	11 EUR/g	72
7	**Os8**	-	0.25 mol%	1	549 EUR/g	98
8	**Os3**	1.5 mol% Bipy **L1**	0.125 mol%	2	11 EUR/g	52
9	**Os3**	-	0.125 mol%, 140°C	2	11 EUR/g	58
10	**Os4**	-	0.125	2	549 EUR/g	61
11	**Os6**	-	0.5	2	549 EUR/g	80

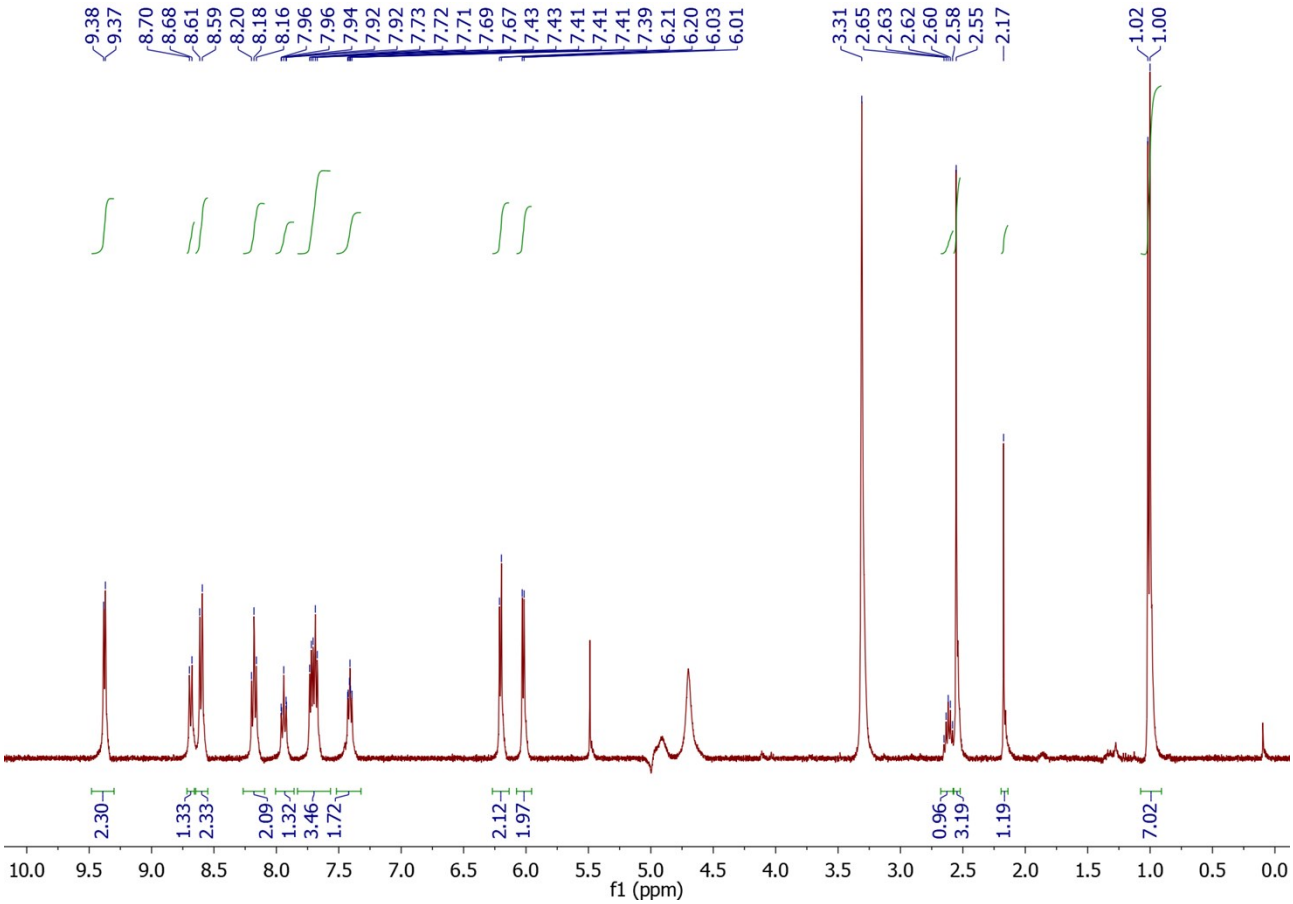
4. Mechanistic investigations

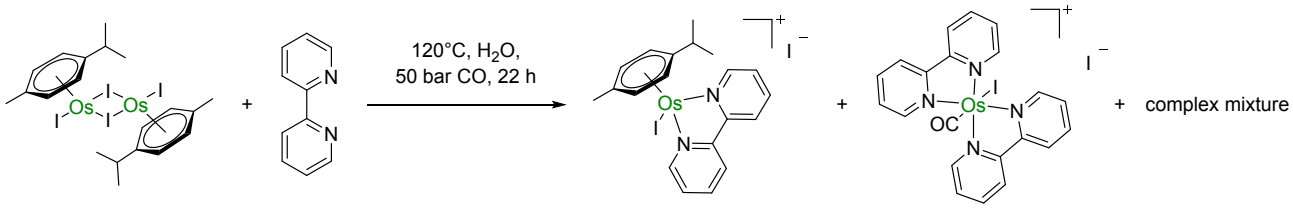


Os2 **L1**

A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (5.2 mg, 4.5 µmol, 50 mol%), 2,2'-bipyridine (1.4 mg, 9.0 µmol, 100 mol%) and water (100 µL). The autoclave was sealed, flushed three times with 10 bar of Ar, and then charged with Ar (50 bar). The reactor was placed into a preheated to 120°C oil bath for 18 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was analyzed by NMR and LCMS. The main component is CymeneOsBiPyI$_2$.

Reaction mixture ^{1}H NMR (400 MHz, CD_3OD, signal of water was supressed)

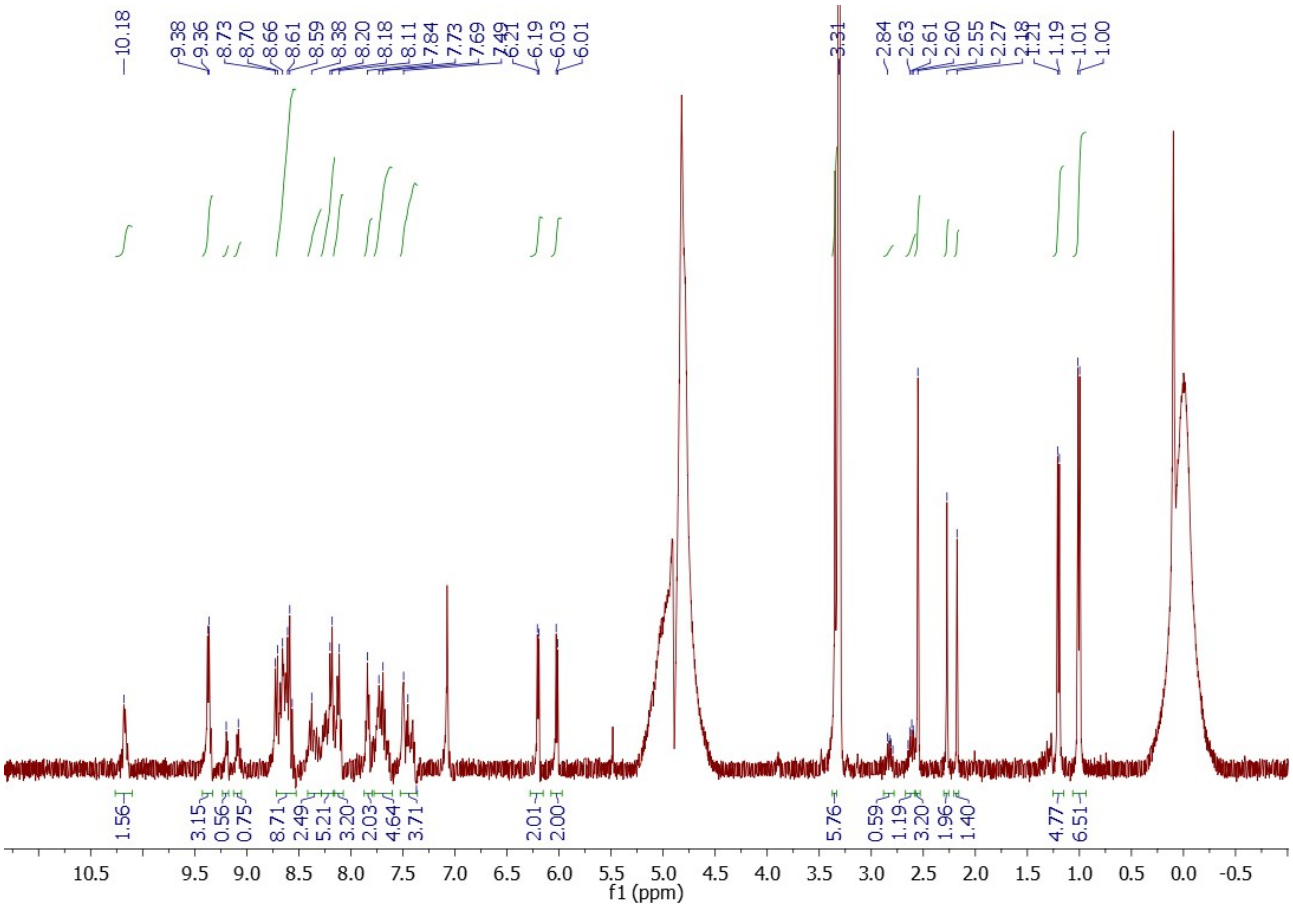


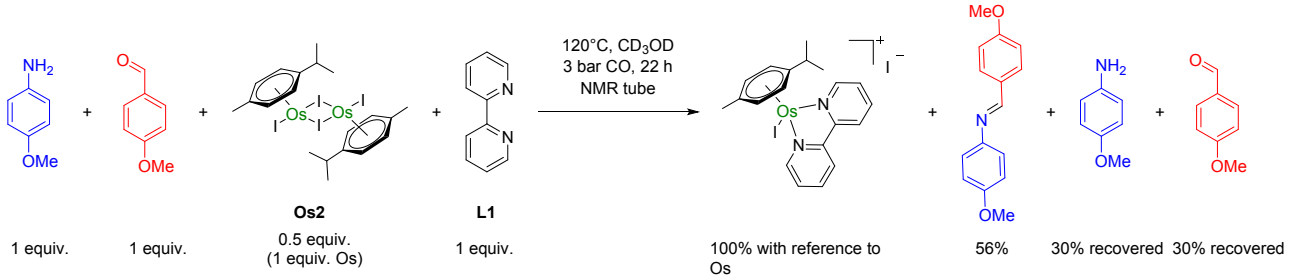


Os2 **L1**

A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (5.2 mg, 4.5 µmol, 50 mol%), 2,2'-bipyridine (1.4 mg, 9.0 µmol, 100 mol%) and water (100 µL). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 18 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was analyzed by NMR and LCMS. The main component is CymeneOsBiPyI$_2$, and (BiPy)$_2$OsCOI$_2$ was identified by MS.

Reaction mixture ^{1}H NMR (400 MHz, CD_3OD, signal of water was supressed)

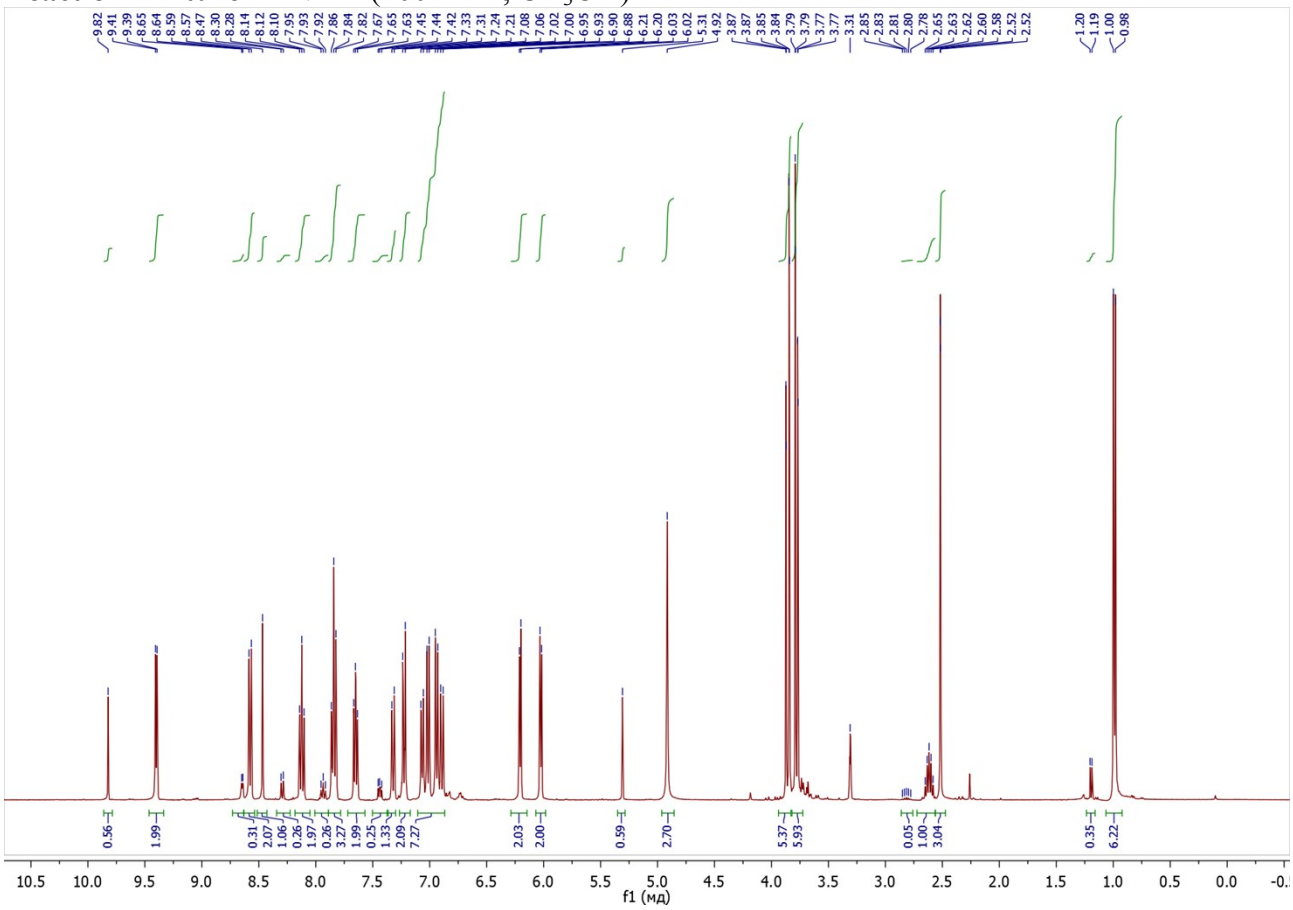




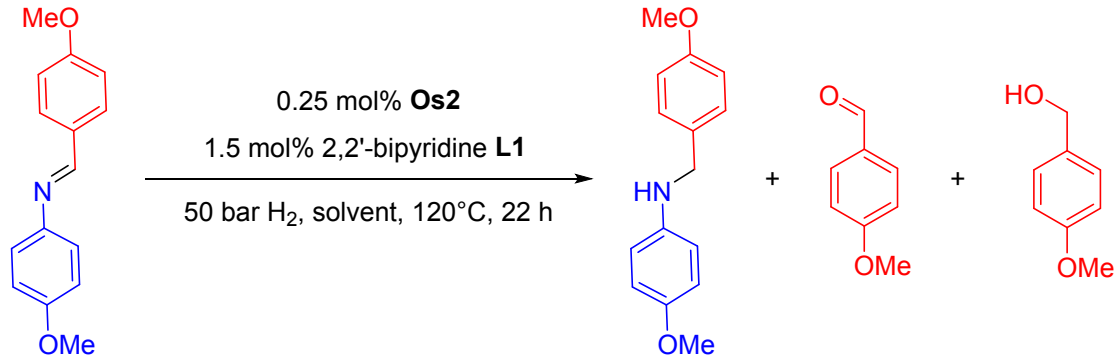
A high pressure NMR tube was charged with catalyst **Os2** (10 mg, 8.7 µmol, 50 mol%), 2,2'-bipyridine (2.7 mg, 17 µmol, 100 mol%), 4-methoxyaniline (2.1 mg, 100 mol %, 17 µmol), 4-methoxybenzaldehyde (2.1 µL, 100 mol%, 17 µmol) and CD_3OD (400 µL). The tube was sealed,

flushed three times with 3 bar of CO, and then charged with CO (3 bar). The tube was placed into a preheated to 120°C oil bath for 16 h. After the indicated time, the tube was cooled to room temperature and the reaction mixture was analyzed by NMR.

Reaction mixture ^{1}H NMR (400 MHz, CD_3OD)



Hydrogenation under the developed reaction conditions

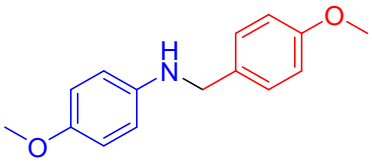


THF: 56% conversion	42%	2%	not detected
H_2O: 36% conversion	10%	9%	1%

A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), N,1-bis(4-methoxyphenyl)methanimine (96.8 mg, 100 mol %, 0.4 mmol), water or THF (400 µL). The autoclave was sealed, flushed three times with 10 bar of H_2, and then charged with H_2 (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR.

5. Synthesis and characterization of the RA products

4-methoxy-N-(4-methoxybenzyl)aniline (1)



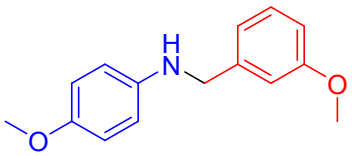
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol), water (400 µL) and 4-methoxybenzaldehyde (48.8 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 93% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography using InterChim PuriFlash chromatograph in hexane-ethyl acetate gradient system (Rf=0.5 hexane/ethyl acetate/trimethylamine = 4/1/0.05). Isolated as a white solid - 93% (90.9 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H, ArH), 6.88 (d, *J* = 8.7 Hz, 2H, ArH), 6.79 (d, *J* = 8.9 Hz, 2H, ArH), 6.61 (d, *J* = 8.9 Hz, 2H, ArH), 4.21 (s, 2H, NCH_2), 3.81 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (C_{Ar}-O), 152.2 (C_{Ar}-O), 142.6 (C_{Ar}-N), 131.8 ($\underline{C_{Ar}}$-CH_2), 128.9 (C_{Ar}), 115.0 (C_{Ar}), 114.2 (C_{Ar}), 114.06 (C_{Ar}), 55.9 (OCH_3), 55.4 (OCH_3), 48.8 (NCH_2).

The obtained NMR data are in agreement with the literature report.[4]

4-methoxy-N-(3-methoxybenzyl)aniline (2)



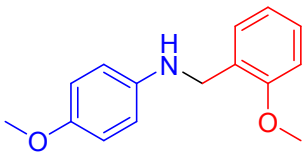
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol), water (400 µL) and 3-methoxybenzaldehyde (49 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 86% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography, eluent hexane/ethyl acetate/triethylamine 10/1/0.1 (Rf = 0.11). Isolated as a yellow oil - 71% (69.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 1H, ArH), 7.05 – 6.90 (m, 2H, ArH), 6.89 – 6.71 (m, 3H, ArH), 6.62 (d, *J* = 8.9 Hz, 2H, ArH), 4.27 (s, 2H, NCH_2), 3.81 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0 (C_{Ar}-O), 152.3 (C_{Ar}-O), 142.5 (C_{Ar}-N), 141.5 ($\underline{C_{Ar}}$-C), 129.7 (C_{Ar}), 119.9 (C_{Ar}), 115.0 (C_{Ar}), 114.2 (C_{Ar}), 113.1 (C_{Ar}), 112.7 (C_{Ar}), 55.9 (OCH_3), 55.3 (OCH_3), 49.3 (NCH_2).

The obtained NMR data are in agreement with the literature report.[4]

4-methoxy-N-(2-methoxybenzyl)aniline (3)



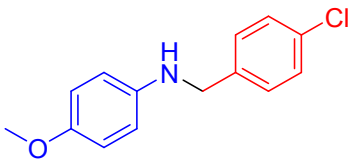
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol) water (400 µL) and 2-methoxybenzaldehyde (48.6 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 140°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 86% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography, eluent hexane/ethyl acetate/triethylamine 10/1/0.1 (Rf = 0.11). Isolated as a yellow oil - 80% (77.7 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.4 Hz, 1H, ArH), 7.26 (t, J = 7.7 Hz, 1H, ArH), 6.98 – 6.95 (m, 2H, ArH), 6.79 (d, *J* = 8.9 Hz, 2H, ArH), 6.64 (d, *J* = 8.9 Hz, 2H, ArH), 4.30 (s, 2H, NCH_2), 3.87 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (C_{Ar}-O), 152.2 (C_{Ar}-O), 142.8 (C_{Ar}-N), 129.1 (C_{Ar}), 128.4 (C_{Ar}), 127.7 ($\underline{C_{Ar}}$-CH_2), 120.6 (C_{Ar}), 114.9 (C_{Ar}), 114.54 (C_{Ar}), 110.3 (C_{Ar}), 55.9 (OCH_3), 55.4 (OCH_3), 44.6 (NCH_2).

The obtained NMR data are in an agreement with literature data.[4]

N-(4-chlorobenzyl)-4-methoxyaniline (4)



A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol) 4-chlorobenzaldehyde (56.4 mg, 100 mol%, 0.4 mmol) and water (400 µL). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 160°C oil bath for 22 h. After the indicated time, the reactor was cooled

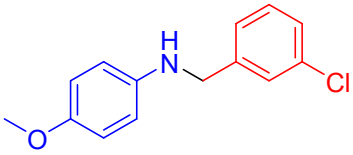
to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 80% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography, eluent: hexane/ethyl acetate/triethylamine 20/1/0.1 (Rf = 0.11) to hexane/ethyl acetate/triethylamine 10/1/0.1 (Rf = 0.2). Isolated as a yellow oil. Isolated as a yellow oil - 70% (69 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 4H, Cl-Ar**H**), 6.79 (d, *J* = 8.9 Hz, 2H, ArH), 6.59 (d, *J* = 8.9 Hz, 2H, ArH), 4.27 (s, 2H, NCH_2), 3.75 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4 (C_{Ar}-O), 142.1 (C_{Ar}-N), 138.4 (**C**$_{Ar}$-C), 132.8 (C_{Ar}-Cl), 128.83 (C_{Ar}), 128.78 (C_{Ar}), 115.0 (C_{Ar}), 114.2 (C_{Ar}), 55.9 (OCH_3), 48.6 (NCH_2).

The obtained NMR data are in agreement with the literature report.[5]

N-(3-chlorobenzyl)-4-methoxyaniline (5)



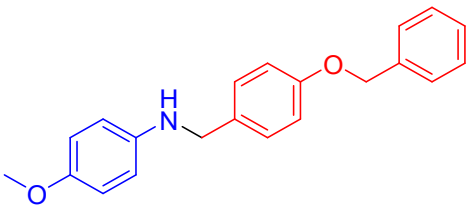
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol), water (400 µL) and 3-chlorobenzaldehyde (45.2 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 160°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 78% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography, eluent hexane/ethyl acetate/triethylamine 10/1/0.1 (Rf = 0.2). Isolated as a yellow oil - 73% (72.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H, Cl-Ar**H**) , 7.26 (s, 3H, Cl-Ar**H**), 6.79 (d, *J* = 7.0 Hz, 2H, ArH), 6.59 (d, *J* = 7.0 Hz, 2H, ArH), 4.28 (s, 2H, NCH_2), 3.75 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4 (C_{Ar}-O), 142.1 (C_{Ar}-N), 134.6 (**C**$_{Ar}$-C), 130.0 (C_{Ar}), 127.6 (C_{Ar}), 127.4 (C_{Ar}), 125.6 (C_{Ar}), 115.0 (C_{Ar}), 114.2 (C_{Ar}), 55.9 (OCH_3), 48.7 (NCH_2).

The obtained NMR data are in agreement with the literature report.[6]

N-(4-(benzyloxy)benzyl)-4-methoxyaniline (6)



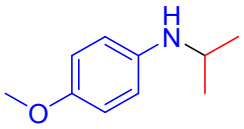
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol), 4-(benzyloxy)benzaldehyde (84.9 mg, 100 mol%, 0.4 mmol) and water (400 µL). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 160°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 68% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography using InterChim PuriFlash chromatograph in hexane-DCM gradient system (Rf=0.16 DCM). Isolated as a yellowish solid - 56% (71.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.21 (m, 7H, ArH), 6.97 (d, *J* = 8.5 Hz, 2H, ArH), 6.80 (d, *J* = 8.9 Hz, 2H, ArH), 6.62 (d, *J* = 8.9 Hz, 2H , ArH), 5.07 (s, 2H, OCH_2), 4.22 (s, 2H, NCH_2), 3.76 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (C_{Ar}-O), 152.3 (C_{Ar}-O), 142.6 (C_{Ar}-N), 137.1 (**C_{Ar}**-C), 132.1 (**C_{Ar}**-C), 129.0 (C_{Ar}), 128.7 (C_{Ar}), 128.1 (C_{Ar}), 127.6 (C_{Ar}), 115.0 (C_{Ar}), 115.0 (C_{Ar}), 114.2 (C_{Ar}), 70.1 (OCH_2), 55.9 (OCH_3), 48.8 (NCH_2).

The obtained NMR data are in agreement with the literature report.[4]

N-isopropyl-4-methoxyaniline (7)



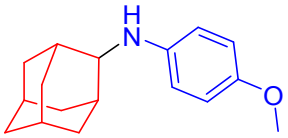
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (2.32 mg, 2.0 µmol, 0.25 mol%), 2,2'-bipyridine (1.92 mg, 12.0 µmol, 1.5 mol%), 4-methoxyaniline (98.8 mg, 100 mol %, 0.8 mmol) water (800 µL), and acetone (1164 µL, 2000 mol%, 16 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 160°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 87% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography, eluent hexane/ethyl acetate/triethylamine 10/1/0.1 (Rf = 0.22). Isolated as a yellow oil - 67% (88 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.9 Hz, 2H, ArH), 6.58 (d, *J* = 8.9 Hz, 2H, ArH), 3.75 (s, 3H, OCH_3), 3.55 (sept, *J* = 6.3 Hz, 1H, **CH**$(CH_3)_2$), 1.20 (d, *J* = 6.3 Hz, 6H, C(**CH_3**)**$_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0 (C_{Ar}-O), 141.9 (C_{Ar}-N), 115.0 (2C, C_{Ar}), 55.9 (OCH_3), 45.3 (NCH), 23.2 (CH_3).

The obtained NMR data are in agreement with the literature report[7]

N-(4-methoxyphenyl)adamantan-2-amine (8)



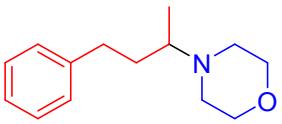
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), 4-methoxyaniline (98.8 mg, 200 mol %, 0.8 mmol) and 2-adamantanoe (60.5 mg, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 180°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 82% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography using InterChim PuriFlash chromatograph in DCM-MeOH gradient system (Rf=0.3 DCM). Isolated as a brown solid - 70% (72.5 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, J = 8.9 Hz, 2H, ArH), 6.59 (d, J = 8.9 Hz, 2H, ArH), 3.75 (s, 3H, OCH_3), 3.48 (s, 1H, NCH), 2.10 – 1.69 (m, 12H, Adamantyl), 1.59 (m appears as d, J = 12.9 Hz, 2H, Adamantyl).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8 (C_{Ar}-O), 141.7 (C_{Ar}-N), 115.1 (C_{Ar}), 114.7 (C_{Ar}), 57.9 (NCH), 56.0 (OCH_3), 37.9 (Adamantyl), 37.6 (Adamantyl), 31.7 (Adamantyl), 31.6 (Adamantyl), 27.6 (Adamantyl), 27.5 (Adamantyl).

The obtained NMR data are in agreement with the literature report.[4]

4-(4-phenylbutan-2-yl)-morpholine (9)



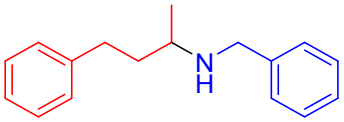
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), morpholine (70 µL, 200 mol %, 0.8 mmol) and 4-phenylbutan-2-one (60.1 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 83% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent/hexane/ethyl acetate/triethylamine = 4/1/0.1, Rf = 0.19) to afford 62 mg (71 %) of the product as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.07 (m, 5H, ArH), 3.79 – 3.53 (m, 4H, CH_2O), 2.81 – 2.24 (m, 7H, Ph**$\underline{CH_2}$**, CH_3**$\underline{CH}$**N, CH_2N), 1.90 – 1.78 (m, 1H, CC**$\underline{H}$**HC), 1.65 – 1.42 (m, 1H, CCH**$\underline{H}$**C), 1.02 (d, J = 6.6 Hz, 3H, CH**$\underline{CH_3}$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (C_{Ar}-C), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 125.8 (C_{Ar}), 67.4 (CH_2O), 58.5 (CHN), 48.7 (CH_2N), 35.2 (C**CH_2**C), 32.9 (Ph**CH_2**), 13.9 (CH_3).

The obtained NMR data are in agreement with the literature report.[10]

N-benzyl-4-phenylbutan-2-amine (10)



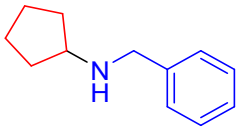
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), phenylmethanamine (87.6 µL, 200 mol %, 0.8 mmol) and 4-phenylbutan-2-one (60.1 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 140°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 84% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent/hexane/ethyl acetate/triethylamine = 4/1/0.1, Rf = 0.17) to afford 79.7 mg (83 %) of the product as a yellowish oil.

^{1}H NMR (400 MHz, CDC_3) δ 7.47 – 7.00 (m, 10H, ArH), 3.79 (m, 2H, NCH_2), 2.80 – 2.58 (m, 3H, Ph**CH_2**C, N**C**HCH_3), 2.51 (s, 1H, NH), 1.88 – 1.77 (m, 1H, CCH**H**C), 1.74 – 1.60 (m, 1H, CC**H**HC), 1.16 (d, J = 6.3 Hz, 3H, CH**CH_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (C_{Ar}-C), 140.9 (C_{Ar}-C), 128.5 (C_{Ar}), 128.46 (C_{Ar}), 128.45 (C_{Ar}), 128.3 (C_{Ar}), 127.0 (C_{Ar}), 125.8 (C_{Ar}), 52.1 (C-N), 51.4 (C-N), 38.8 (C**CH_2**C), 32.4 (Ph**CH_2**C), 20.5 (CH**CH_3**).

The obtained NMR data are in agreement with the literature report.[8]

N-benzylcyclopentanamine (11)



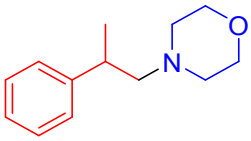
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), cyclopentanone (35.4 µL, 100 mol%, 0.4 mmol) and phenylmethanamine (87.6 µL, 200 mol %, 0.8 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 140°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 72% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent/hexane/ethyl acetate/triethylamine = 20/1/1, Rf = 0.33) to afford 49.5 mg (65%) of the product as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H, ArH), 7.30 – 7.23 (m, 1H, ArH), 3.79 (s, 2H, Ph**CH$_2$**N), 3.14 (quint., *J* = 6.7 Hz, 1H, NCH), 1.93 – 1.81 (m, 2H, Cyclopentyl), 1.78 – 1.65 (m, 2H, Cyclopentyl), 1.62 – 1.48 (m, 2H, Cyclopentyl), 1.46 – 1.34 (m, 3H, NH, Cyclopentyl).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (C_{Ar}-C), 128.5 (C_{Ar}), 128.3 (C_{Ar}), 126.9 (C_{Ar}), 59.2 (NCH), 52.9 (Ph**CH$_2$**N), 33.3 (Cyclopentyl), 24.2 (Cyclopentyl).

The obtained NMR data are in agreement with the literature report.[9]

4-(2-phenylpropyl)morpholine (12)



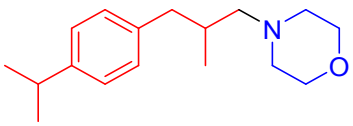
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), morpholine (70 µL, 200 mol %, 0.8 mmol) and 2-phenylpropanal (48.9 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 71% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent/hexane/ethyl acetate/triethylamine = 10/1/0.1, Rf = 0.13) to afford 50.9 mg (63 %) of the product as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 5H, ArH), 3.74 – 3.63 (m, 4H, O**CH$_2$**CH_2N), 3.03 – 2.87 (m, 1H, **CH**CH_3), 2.59 – 2.44 (m, 4H, OCH_2**CH$_2$**N), 2.44 – 2.32 (m, 2H, N**CH$_2$**CH), 1.29 (d, *J* = 6.6 Hz, 3H, CH**CH$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1 (C_{Ar}-C), 128.4 (C_{Ar}), 127.3 (C_{Ar}), 126.2 (C_{Ar}), 67.2 (O**CH$_2$**CH_2N), 66.7 (N**CH$_2$**CH), 54.1 (OCH_2**CH$_2$**N), 37.2 (**CH**CH_3), 20.0 (CH**CH$_3$**).

The obtained NMR data are in agreement with the literature report.[10]

4-(3-(4-isopropylphenyl)-2-methylpropyl)morpholine (13)



A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), morpholine (70 µL, 200 mol %, 0.8 mmol) and 3-(4-isopropylphenyl)-2-methylpropanal (80.1 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 71% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under

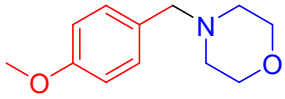
reduced pressure and the residue was purified by column chromatography (eluent: hexane/ethyl acetate/triethylamine = 4/1/0.1, Rf = 0.27), dissolved in diluted HCl and washed with diethyl ether (2 x 3 ml). The water solution was basified with KOH, the product extracted with diethyl ether (3 x 3 ml) and dried with Na_2SO_4. After removal of the solvent *in vacuo* 69 mg (66 %) of the product was obtained as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.7 Hz, 2H, ArH), 7.08 (d, *J* = 7.7 Hz, 2H, ArH), 3.73 (t, *J* = 4.3 Hz, 4H, O**CH$_2$**CH_2N), 2.95 – 2.83 (m, 1H, **CH**$(CH_3)_2$), 2.82 - 2.74 (m, 1H, CH**CH$_2$**), 2.43 (br. s, 4H, OCH_2**CH$_2$**N), 2.35 – 2.19 (m, 2H, CH**CH$_2$**), 2.18 – 2.10 (m, 1H, CH**CH$_2$**), 2.05 – 1.88 (m, 1H, **CH**CH_3), 1.25 (d, *J* = 6.9 Hz, 6H, CH**(CH$_3$)$_2$**), 0.87 (d, *J* = 6.5 Hz, 3H, CH**CH$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3 (**C$_{Ar}$**-$CH(CH_3)_2$), 138.3 (**C$_{Ar}$**-CH_2), 129.3 (C_{Ar}), 126.2 (C_{Ar}), 67.2 (O**CH$_2$**CH_2N), 65.5 (N**CH$_2$**CH), 54.1 (OCH_2**CH$_2$**N), 40.9 (Ph**CH$_2$**), 33.8 (CH), 32.1 (CH), 24.2 (CH**(CH$_3$)$_2$**), 18.2 (CH**CH$_3$**).

HRMS (TOF ESI+): for $C_{17}H_{28}NO^+$ $[M+H]^+$ calculated m/z 262.2165, found m/z 262.2165.

4-(4-methoxybenzyl)morpholine (14)



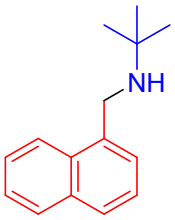
A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (0.29 mg, 0.25 µmol, 0.0625 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), morpholine (70 µL, 200 mol %, 0.8 mmol) and 4-methoxybenzaldehyde (48.8 µL, 100 mol%, 0.4 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 120°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 80% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified using column chromatography, eluent hexane/ethyl acetate/triethylamine 4/1/0.05 (Rf = 0.13). Isolated as a yellow oil - 75% (65.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H, ArH), 6.85 (d, *J* = 8.6 Hz, 2H, ArH), 3.79 (s, 3H, OCH_3), 3.70 (t, *J* = 4.7 Hz, 4H, O**CH$_2$**CH_2N), 3.43 (s, 2H, Ph**CH$_2$**N), 2.45 – 2.39 (m, 4H, OCH_2**CH$_2$**N).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (C_{Ar}-O), 130.5 (C_{Ar}-C), 129.8 (C_{Ar}), 113.7 (C_{Ar}), 67.1 (O**CH$_2$**CH_2N), 63.0 (Ph**CH$_2$**N), 55.3 (OCH_3), 53.6 (OCH_2**CH$_2$**N).

The obtained NMR data are in agreement with the literature report.[11]

2-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine (15)



A glass vial in a 10 mL titanium autoclave was charged with catalyst **Os2** (1.16 mg, 1.0 µmol, 0.25 mol%), 2,2'-bipyridine (0.96 mg, 6.0 µmol, 1.5 mol%), water (400 µL), 1-naphthaldehyde (54 µL, 100 mol%, 0.4 mmol) and tert-butylamine (421.6 µL, 500 mol %, 2 mmol). The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with CO (50 bar). The reactor was placed into a preheated to 160°C oil bath for 22 h. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, 1 ml aliquot was analyzed by NMR. 63% NMR yield. Purification: DCM fraction was washed with water, after that solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent/hexane/ethyl acetate/triethylamine = 20/1/1, Rf = 0.41) to afford 43.8 mg (51 %) of the product as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H, ArH), 7.87 (d, *J* = 8.1 Hz, 1H, ArH), 7.78 (d, *J* = 8.2 Hz, 1H, ArH), 7.62 – 7.37 (m, 4H, ArH), 4.20 (s, 2H, CH_2N), 1.30 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (C_{Ar}-CH_2), 134.0 (C_{Ar}-C), 132.0 (C_{Ar}-C), 128.8 (C_{Ar}), 127.7 (C_{Ar}), 126.4 (C_{Ar}), 126.1 (C_{Ar}), 125.7 (C_{Ar}), 125.6 (C_{Ar}), 123.9 (C_{Ar}), 51.0 (**C**$(CH_3)_3$), 44.9 (CH_2N), 29.3 ($C(\mathbf{CH_3})_3$).

The obtained NMR data are in agreement with the literature report.[12]

6. Details of DFT calculations

Geometry optimizations and frequency calculations for the decarboxylation stage of the WGSR catalyzed by osmium complexes were carried out using Gaussian 09 software (revision D.01)[13] applying the M06-L functional[14] with SDD basis set. Water solvation was included using SMD model.[15] The optimized geometries were verified to have no negative frequencies for all intermediates and only one negative frequency for the transition states.

Cartesian coordinates optimized at the M06-L/SDD level

$[Os(CO)_3Cl_2(COOH)]^-$ (the COOH group is opposite to the CO ligand)

76	-0.039379000	0.483018000	0.509308000
17	-1.961343000	1.528528000	1.853353000
17	-0.230623000	-1.607191000	1.938434000
6	0.138747000	2.121886000	-0.412878000
6	1.384612000	-0.328525000	-0.416960000
8	0.248253000	3.157063000	-0.970186000
8	2.277853000	-0.853790000	-0.980577000
6	1.348368000	1.141693000	1.998951000
8	2.582833000	0.905886000	2.016470000
6	-1.438457000	-0.249070000	-0.698049000
8	-2.294741000	-0.670181000	-1.378457000
8	0.870267000	1.869436000	3.098687000
1	-0.109252000	2.004692000	3.027172000

TS for decarboxylation of $[Os(CO)_3Cl_2(COOH)]^-$ (the COOH group is opposite to the CO ligand)

76	-0.153717000	0.468903000	0.512197000
17	-2.097293000	1.445752000	1.853487000
17	-0.357340000	-1.655231000	1.858846000
6	-0.009043000	2.131270000	-0.386945000
6	1.363605000	-0.256690000	-0.361020000
8	0.068853000	3.172354000	-0.932286000
8	2.309766000	-0.717526000	-0.883603000
6	1.428155000	1.146112000	2.118479000
8	2.461396000	0.441430000	2.190531000
6	-1.399091000	-0.290494000	-0.786483000
8	-2.167942000	-0.738916000	-1.547307000
8	1.152050000	2.250196000	2.850317000
1	0.121531000	1.553019000	2.146242000

$[Os(CO)_3Cl_2(COOH)]^-$ (the COOH group is opposite to Cl^-)

76	-0.059202000	0.502054000	0.545961000
17	-1.966647000	1.560066000	1.967406000
17	-0.337246000	-1.645307000	1.932046000
6	0.126090000	2.071888000	-0.448696000
6	1.480763000	-0.394373000	-0.551938000
8	0.234292000	3.074236000	-1.071118000
8	1.996423000	0.044332000	-1.607465000
6	1.257481000	1.079777000	1.895659000
8	2.035092000	1.396380000	2.711199000
6	-1.416797000	-0.203391000	-0.687981000
8	2.029197000	-1.591387000	-0.068146000
1	1.530910000	-1.906869000	0.729315000
8	-2.249517000	-0.637496000	-1.387397000

TS for decarboxylation of $[Os(CO)_3Cl_2(COOH)]^-$ (the COOH group is opposite to Cl^-)

76	0.015794000	0.431533000	0.642004000
17	-2.008767000	1.609772000	1.775251000
17	-0.578471000	-1.688431000	1.914368000
6	0.439670000	2.005238000	-0.319322000
6	1.356583000	-0.513658000	-0.881732000
8	0.699204000	2.987180000	-0.916845000
8	1.204633000	-0.298324000	-2.104912000
6	1.129450000	1.062656000	2.124872000
8	1.735257000	1.436677000	3.052848000
6	-1.359261000	-0.282160000	-0.639704000
8	2.265112000	-1.278307000	-0.288900000
1	1.456027000	-0.565249000	0.782505000
8	-2.196147000	-0.713044000	-1.323907000

$[Os(bipy)(CO)Cl_2(COOH)]^-$

76	1.286658000	5.599103000	13.014583000
17	2.631154000	6.185324000	15.065689000
17	0.043374000	5.229799000	10.831790000
8	3.811447000	3.990614000	12.660532000
8	-0.562230000	3.718585000	14.537181000
7	2.416905000	7.129628000	11.948940000
7	0.201301000	7.436694000	13.378228000
6	1.958013000	8.419924000	12.064845000
6	3.508294000	6.878289000	11.180471000
1	3.822375000	5.845229000	11.113258000
6	4.196262000	7.893257000	10.513476000
1	5.059098000	7.647104000	9.911732000
6	3.746358000	9.214563000	10.640844000
6	2.616914000	9.477033000	11.420138000
6	0.149001000	9.842027000	13.112614000
6	-1.014749000	9.915569000	13.882716000
6	-1.564441000	8.732291000	14.396789000
1	-2.463613000	8.743040000	14.996064000
6	-0.933306000	7.518137000	14.126427000
1	-1.329061000	6.585587000	14.504989000
6	0.745043000	8.595177000	12.871358000
6	2.552405000	4.072208000	12.529238000
6	0.187524000	4.451746000	13.931413000
1	2.250145000	10.488706000	11.519165000
1	4.259979000	10.022782000	10.137858000
1	0.588095000	10.743228000	12.707258000
1	-1.480585000	10.872513000	14.075105000
8	2.001820000	2.898330000	11.910165000
1	1.050282000	3.061176000	11.712958000

TS for decarboxylation of $[Os(bipy)(CO)Cl_2(COOH)]^-$

76	1.230096000	5.544666000	12.980380000
17	2.491333000	6.157784000	15.053170000
17	-0.322130000	5.599919000	10.943510000
8	3.928798000	4.014807000	13.155565000
8	-0.502927000	3.587535000	14.545831000
7	2.376846000	7.061737000	11.922031000
7	0.161942000	7.423061000	13.377487000
6	1.936144000	8.358907000	12.042429000
6	3.465674000	6.797532000	11.153831000
1	3.765916000	5.761996000	11.074344000
6	4.167320000	7.803627000	10.489027000
1	5.027515000	7.546065000	9.888286000

6	3.735229000	9.129425000	10.618599000
6	2.608907000	9.406366000	11.398291000
6	0.167990000	9.818046000	13.110240000
6	-0.986325000	9.914228000	13.893326000
6	-1.560713000	8.747225000	14.413864000
1	-2.452545000	8.779557000	15.022948000
6	-0.958053000	7.518867000	14.135920000
1	-1.363911000	6.592846000	14.519867000
6	0.730791000	8.558548000	12.859447000
6	2.764384000	4.085506000	12.655133000
6	0.186900000	4.349916000	13.923566000
1	2.257387000	10.423356000	11.497881000
1	4.260731000	9.931744000	10.118805000
1	0.622508000	10.711968000	12.707032000
1	-1.425977000	10.881633000	14.094032000
8	2.365337000	3.201428000	11.682641000
1	1.293192000	4.231265000	11.837567000

$[Os(bipy)(CO)Cl_2(COOH\ldots OH_2)]^-$

76	1.529749000	5.654959000	12.852308000
17	2.758381000	6.218530000	14.981326000
17	0.424258000	5.457471000	10.565649000
8	4.170258000	4.330343000	12.390433000
8	-0.280679000	3.696604000	14.313919000
7	2.614992000	7.322007000	11.938665000
7	0.314477000	7.405751000	13.261149000
6	2.053040000	8.568967000	12.081248000
6	3.769301000	7.191397000	11.235968000
1	4.166066000	6.188109000	11.156268000
6	4.417979000	8.285549000	10.660370000
1	5.336396000	8.132971000	10.111691000
6	3.857769000	9.561215000	10.809341000
6	2.664600000	9.701063000	11.522866000
6	0.093156000	9.808438000	13.092776000
6	-1.104884000	9.761411000	13.810633000
6	-1.584808000	8.519740000	14.251652000
1	-2.506659000	8.437572000	14.809746000
6	-0.851733000	7.369320000	13.961582000
1	-1.190772000	6.393626000	14.282991000
6	0.790887000	8.620275000	12.827636000
6	2.899150000	4.209094000	12.371941000
6	0.453725000	4.441462000	13.698628000
1	2.213467000	10.676429000	11.639633000
1	4.336129000	10.428757000	10.375130000
1	0.480952000	10.756736000	12.747137000
1	-1.649513000	10.671492000	14.022007000
8	2.499848000	2.918603000	11.952487000
1	1.503227000	2.807594000	11.861834000
8	-0.108966000	2.487594000	11.432287000
1	-0.699339000	2.306523000	12.187812000
1	-0.328506000	3.376276000	11.065088000

TS for decarboxylation of $[Os(bipy)(CO)Cl_2(COOH\ldots OH_2)]^-$

76	1.375686000	5.645407000	12.863627000
17	2.392848000	6.214699000	15.116608000
17	0.154519000	5.678658000	10.624772000
8	4.198645000	4.698062000	12.722669000
8	-0.569773000	3.673134000	14.107010000
7	2.501763000	7.270903000	11.906166000
7	0.229945000	7.470971000	13.280845000
6	2.006094000	8.541280000	12.068872000

6	3.546105000	7.072044000	11.062518000
1	3.879917000	6.048714000	10.965526000
6	4.165804000	8.125061000	10.385370000
1	4.994846000	7.919025000	9.723480000
6	3.693917000	9.429534000	10.580740000
6	2.598827000	9.636316000	11.424639000
6	0.233433000	9.884221000	13.278795000
6	-0.929508000	9.894706000	14.054329000
6	-1.512408000	8.676019000	14.428786000
1	-2.413218000	8.641183000	15.024532000
6	-0.904774000	7.485936000	14.024855000
1	-1.317289000	6.523499000	14.297977000
6	0.799664000	8.658168000	12.899124000
6	3.002184000	4.244186000	12.954701000
6	0.225909000	4.442485000	13.619934000
1	2.198698000	10.630536000	11.565332000
1	4.155503000	10.266162000	10.073628000
1	0.698489000	10.814165000	12.981412000
1	-1.368817000	10.834055000	14.361368000
8	2.819249000	3.008372000	13.391499000
1	1.774566000	2.374166000	11.842079000
8	1.564809000	3.004176000	11.105505000
1	0.672224000	2.870206000	10.729065000
1	1.674245000	4.099295000	11.698284000

$[Os(bipy)(CO)I_2(COOH)]^-$

76	1.269484000	5.589536000	12.952008000
53	2.693304000	6.188665000	15.329637000
53	-0.171936000	5.158142000	10.532890000
8	3.841891000	4.099654000	12.518353000
8	-0.639859000	3.732276000	14.424517000
7	2.411002000	7.143786000	11.909080000
7	0.182853000	7.440397000	13.326066000
6	1.962322000	8.436222000	12.052444000
6	3.496040000	6.902623000	11.126297000
1	3.800184000	5.868435000	11.039509000
6	4.190336000	7.926216000	10.480334000
1	5.047458000	7.685277000	9.868031000
6	3.756175000	9.248594000	10.643822000
6	2.630795000	9.502130000	11.432087000
6	0.181344000	9.853800000	13.151623000
6	-0.979341000	9.922493000	13.925863000
6	-1.557359000	8.732336000	14.391737000
1	-2.456306000	8.739396000	14.991591000
6	-0.953295000	7.516512000	14.073268000
1	-1.367260000	6.577742000	14.415466000
6	0.750225000	8.604384000	12.860831000
6	2.570717000	4.074082000	12.520128000
6	0.139793000	4.450430000	13.838393000
1	2.273023000	10.514610000	11.555551000
1	4.277763000	10.064319000	10.162134000
1	0.640899000	10.760486000	12.783297000
1	-1.421085000	10.881229000	14.160798000
8	2.072154000	2.779739000	12.153771000
1	1.093140000	2.814154000	12.076292000

TS for decarboxylation of $[Os(bipy)(CO)I_2(COOH)]^-$

76	-0.178519000	-0.656415000	-0.136874000
53	-2.841577000	0.386862000	-0.041999000
53	2.631437000	-1.011151000	-0.535045000
8	-1.775000000	-2.154449000	2.047498000

8	-1.001225000	-2.252960000	-2.600542000
7	0.404554000	0.650008000	1.512657000
7	0.267771000	1.285971000	-1.076882000
6	0.714789000	1.951168000	1.193776000
6	0.548599000	0.229527000	2.797417000
1	0.311593000	-0.806105000	2.998923000
6	0.989997000	1.078767000	3.812216000
1	1.094436000	0.696998000	4.817484000
6	1.291941000	2.410643000	3.498501000
6	1.153840000	2.846941000	2.178500000
6	0.798852000	3.611109000	-0.709248000
6	0.677783000	3.863511000	-2.078456000
6	0.354217000	2.808194000	-2.942396000
1	0.252562000	2.961668000	-4.007088000
6	0.154710000	1.534778000	-2.407110000
1	-0.105543000	0.693917000	-3.035999000
6	0.592576000	2.311854000	-0.223882000
6	-0.813498000	-2.173732000	1.212771000
6	-0.675473000	-1.637973000	-1.619243000
1	1.397040000	3.866693000	1.916429000
1	1.638150000	3.092673000	4.262825000
1	1.047056000	4.413914000	-0.029392000
1	0.831291000	4.862824000	-2.462130000
8	0.050498000	-3.240066000	1.168286000
1	0.607797000	-2.188460000	0.275288000

7. X-ray investigations

Crystals of complexes **Os8** and **Os12** were obtained by slow interdiffusion of a two-phase system comprising hexane and a solution of the complex in dichloromethane (for **Os8**) and acetone (for **Os12**). X-ray diffraction data were collected at 120 K with APEX2 DUO CCD diffractometer using graphite monochromic Mo-Kα radiation (lλ = 0.71073 Å, ω-scans). Using Olex2,[16] the structures were solved with the ShelXT structure solution program [17] using Intrinsic Phasing and refined with the XL refinement package[18] using Least Squares minimization. Positions of hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model. Crystallographic data and structure refinement parameters are listed in Table S14. CCDC 2075332 and 2075331 contain the supplementary crystallographic data for **Os8** and **Os12**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

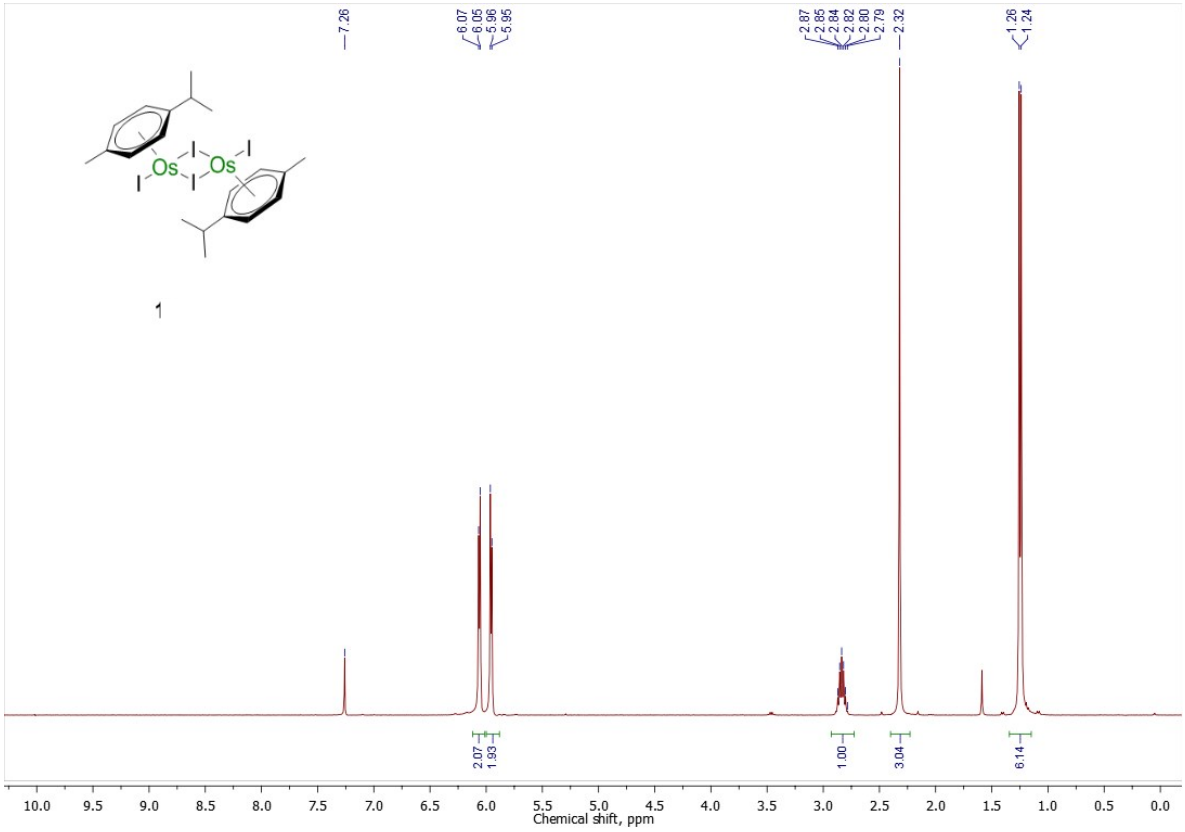
Table S14. Crystallographic data and structure refinement parameters for Os8 and Os12.

Compound	**Os8**	**Os12**
Empirical formula	$C_{26}H_{16}Cl_2N_2O_2Os$	$C_{25}H_{28}ClNO_2Os$
Molecular weight	649.51	600.13
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	6.961(3)	9.4652(9)
b (Å)	19.454(7)	9.6082(9)
c (Å)	16.217(6)	24.647(3)
β(deg)	95.607(8)	90.999(3)
V (Å^3)	2185.4(14)	2241.1(4)
Z	4	4
D_{calcd} (g cm^{-3})	1.974	1.779
$2\theta_{max}$(deg)	58	54
μ(Mo-*K*α) (cm^{-3})	61.08	58.31
Collected reflections	5808	12741

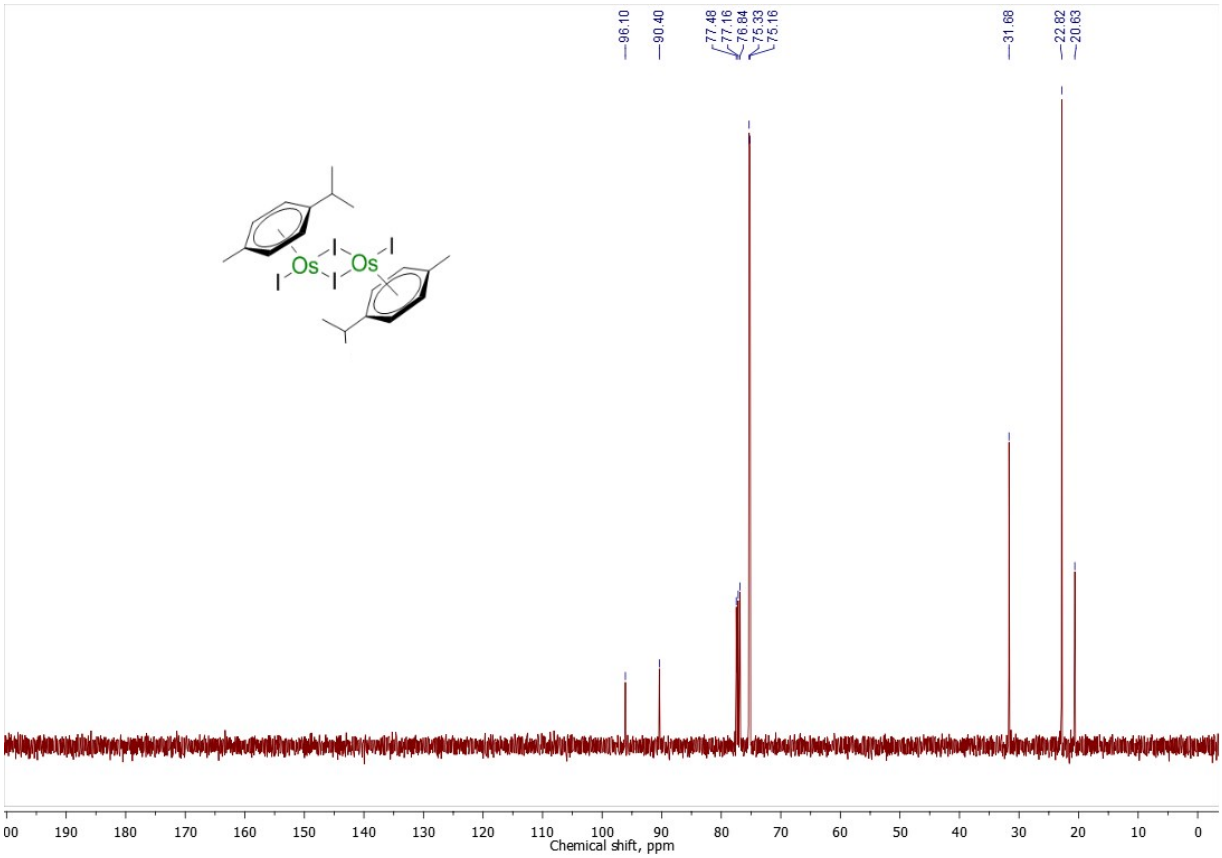
Independent reflections	5808 (R_{int} = 0.0597)	4884 (R_{int} = 0.0670)
Observed reflections (I> 2σ(I))	3768	3625
Parameters	299	276
R_1 (on F for obs. refls)	0.0765	0.0404
wR_2 (on F^2 for all refls)	0.1486	0.0798
F(000)	1248	1176
GOF	1.072	0.969
Largest diff. peak and hole (e Å^{-3})	1.939 and −1.029	1.296 and −1.148

8. ^{1}H and ^{13}C NMR spectra and HRMS of the obtained osmium complexes.

[(η^{6}-cymene)OsI$_2$]$_2$ Os2 ^{1}H NMR (400 MHz, $CDCl_3$)



[(η^{6}-cymene)OsI$_2$]$_2$ Os2 ^{13}C NMR (101 MHz, $CDCl_3$)



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Analysis Info

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Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-32	Instrument / Ser#	micrOTOF 10248
Comment	C20H28I4Os2 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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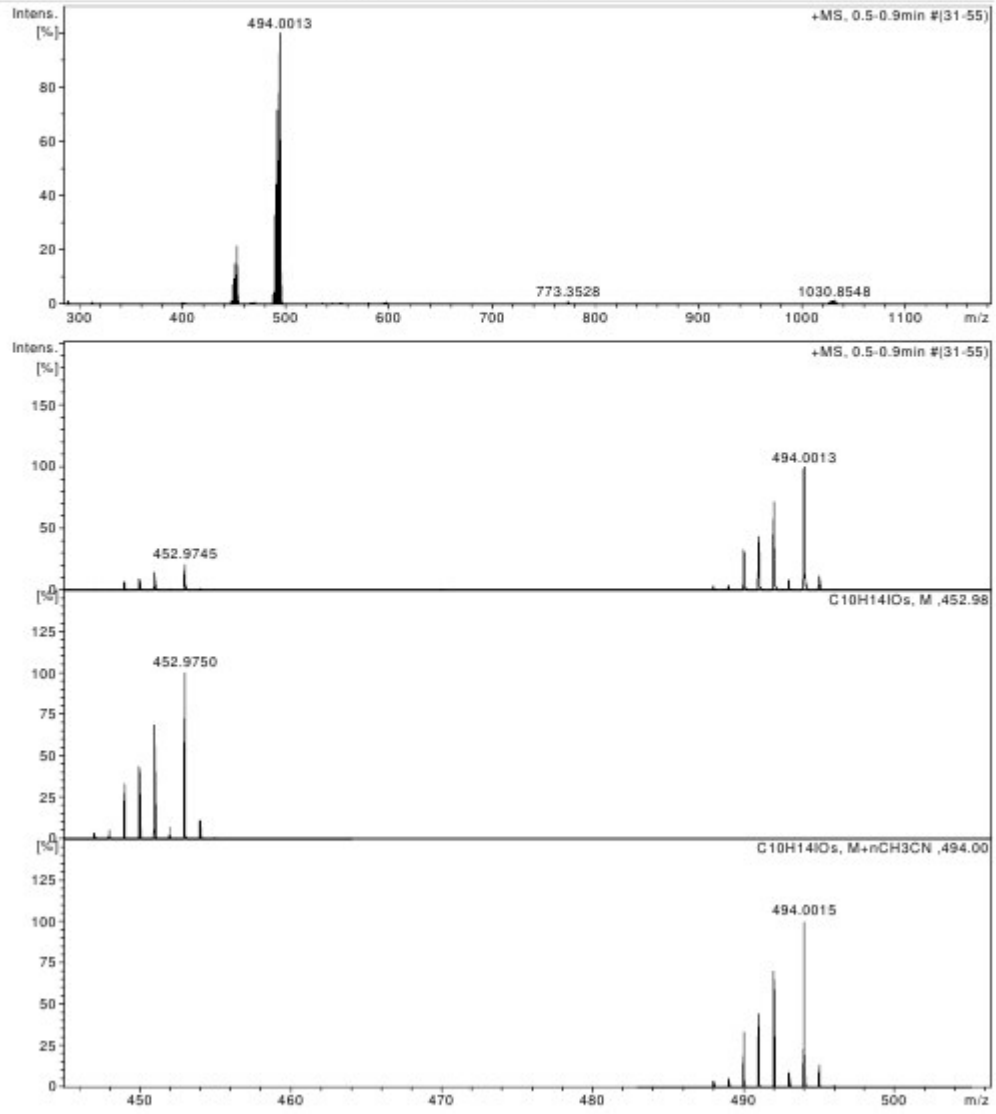
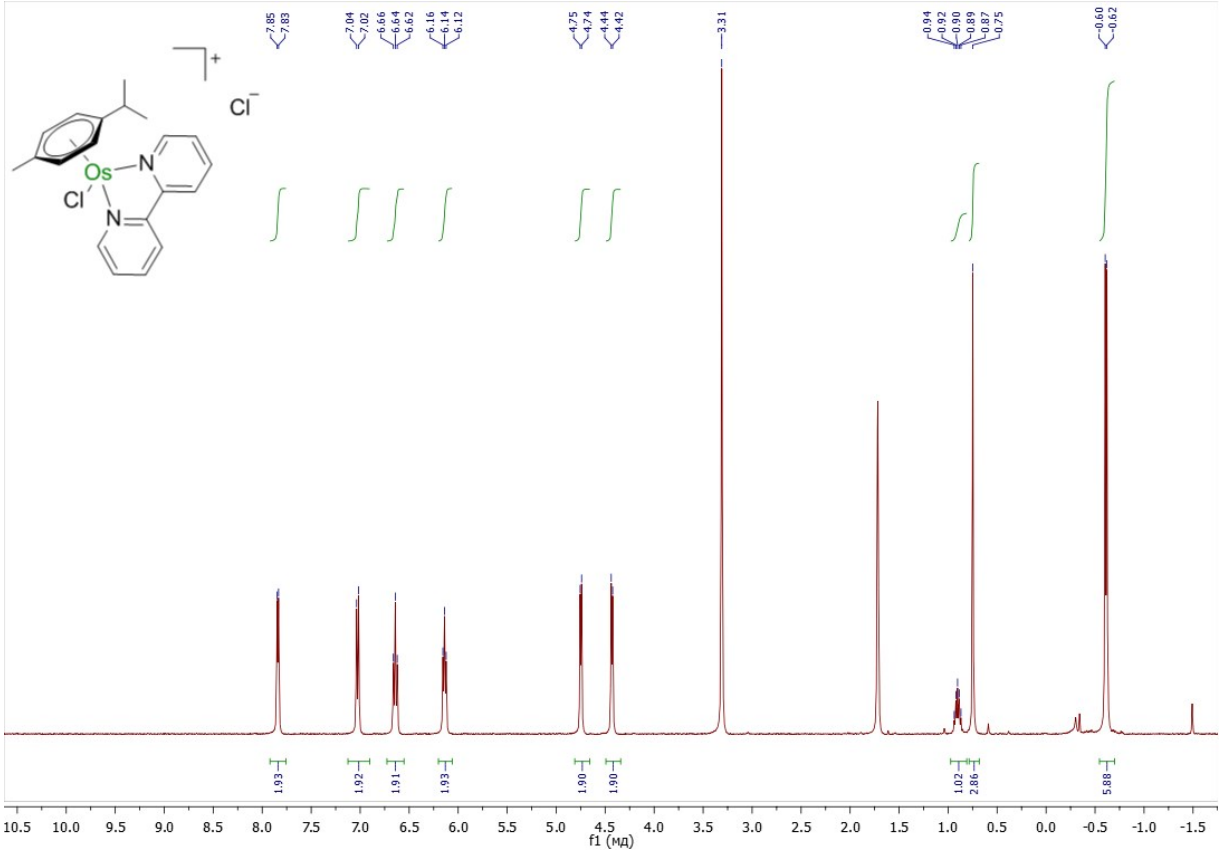
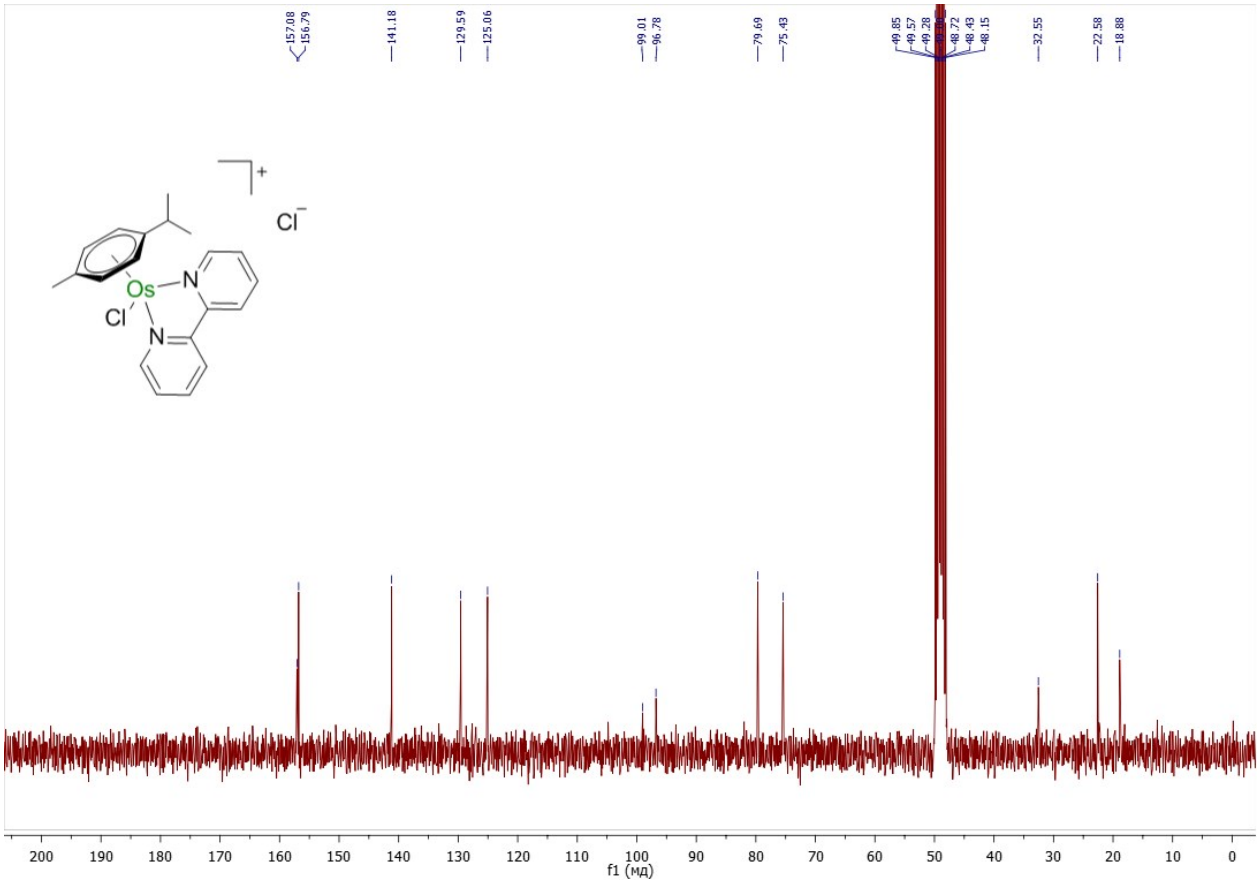
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



[(η^6-cymene)Os(2,2'-bipyridine)Cl]Cl Os3 ^{1}H NMR (400 MHz, CD_3OD)



[(η^6-cymene)Os(2,2'-bipyridine)Cl]Cl Os3 ^{13}C NMR (75 MHz, CD_3OD)



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Sample Name	/NGKO LD-28	Instrument / Ser#	micrOTOF 10248
Comment	C20H22N2OsCl calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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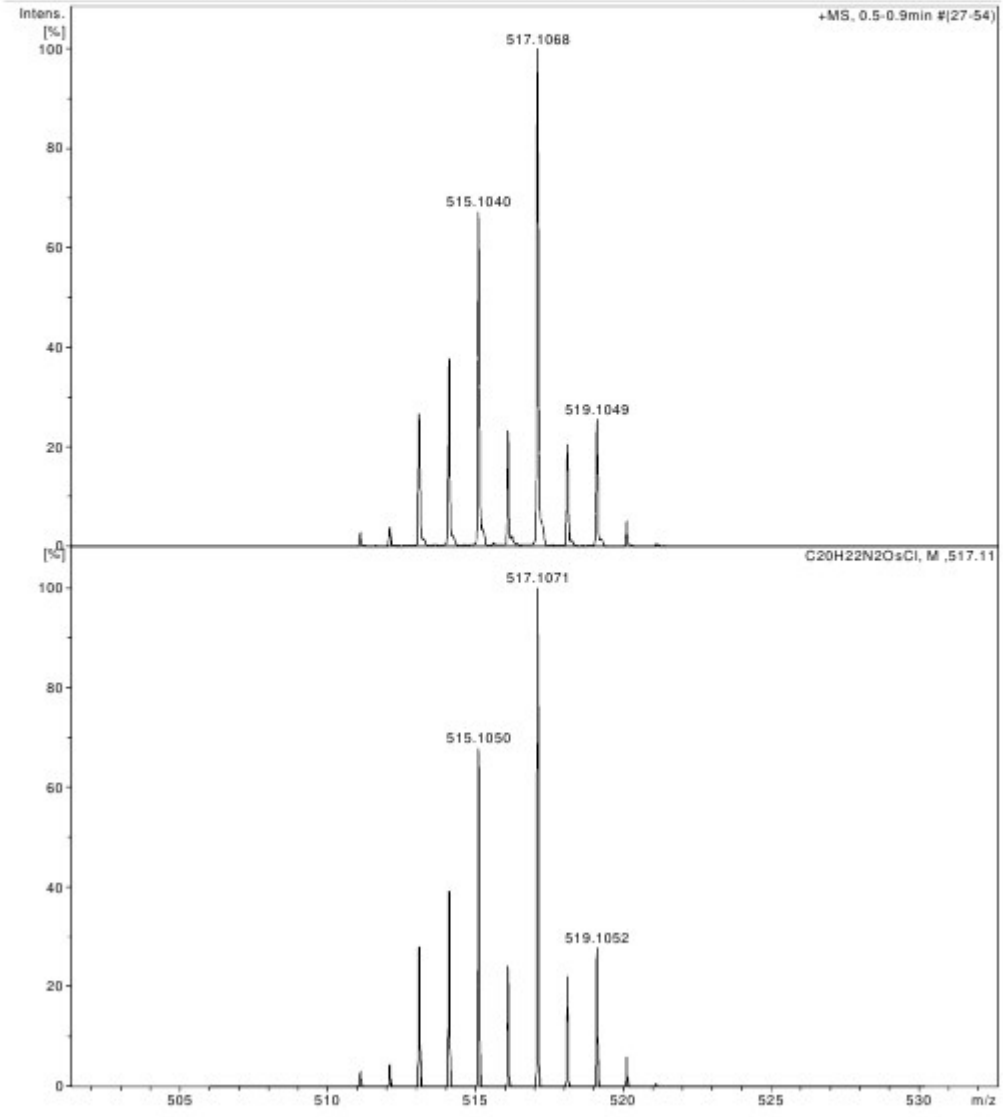
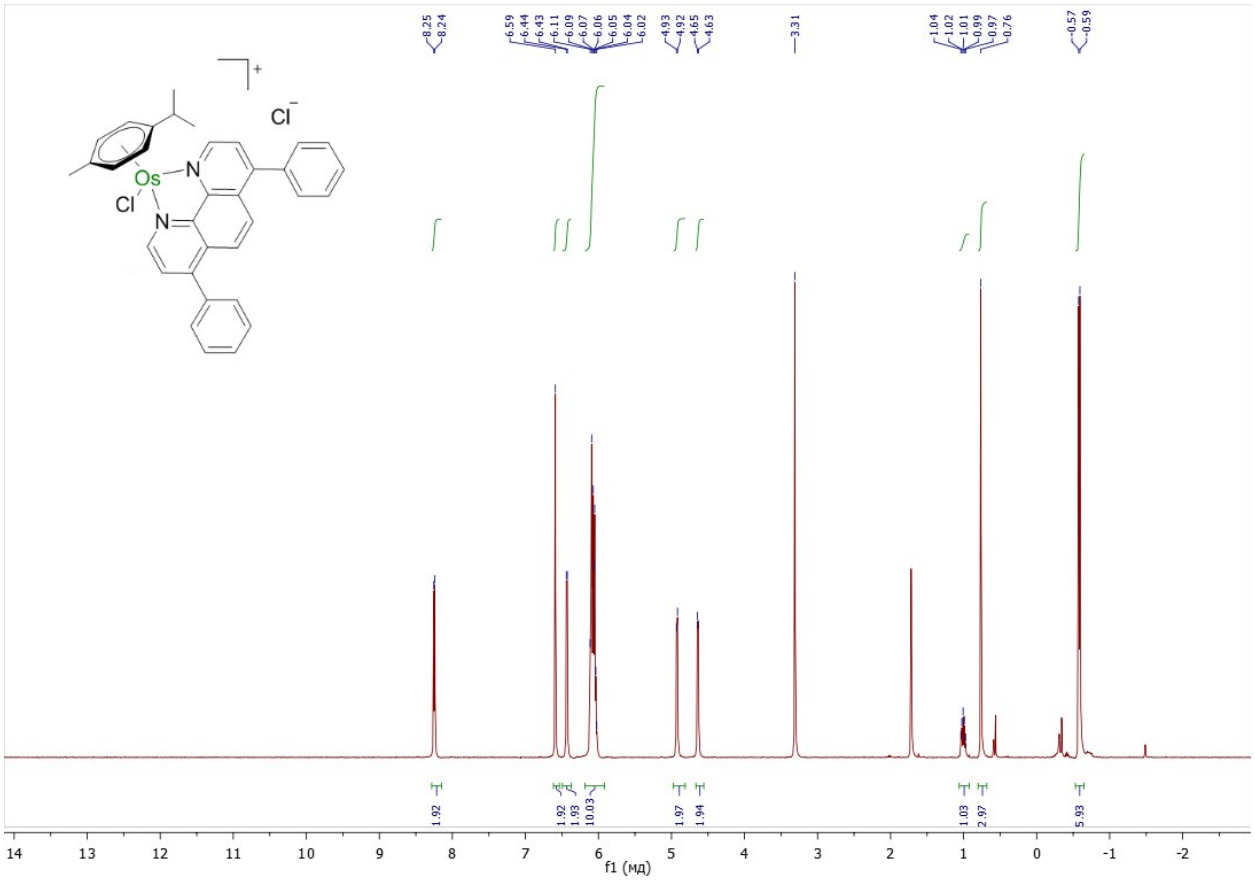
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

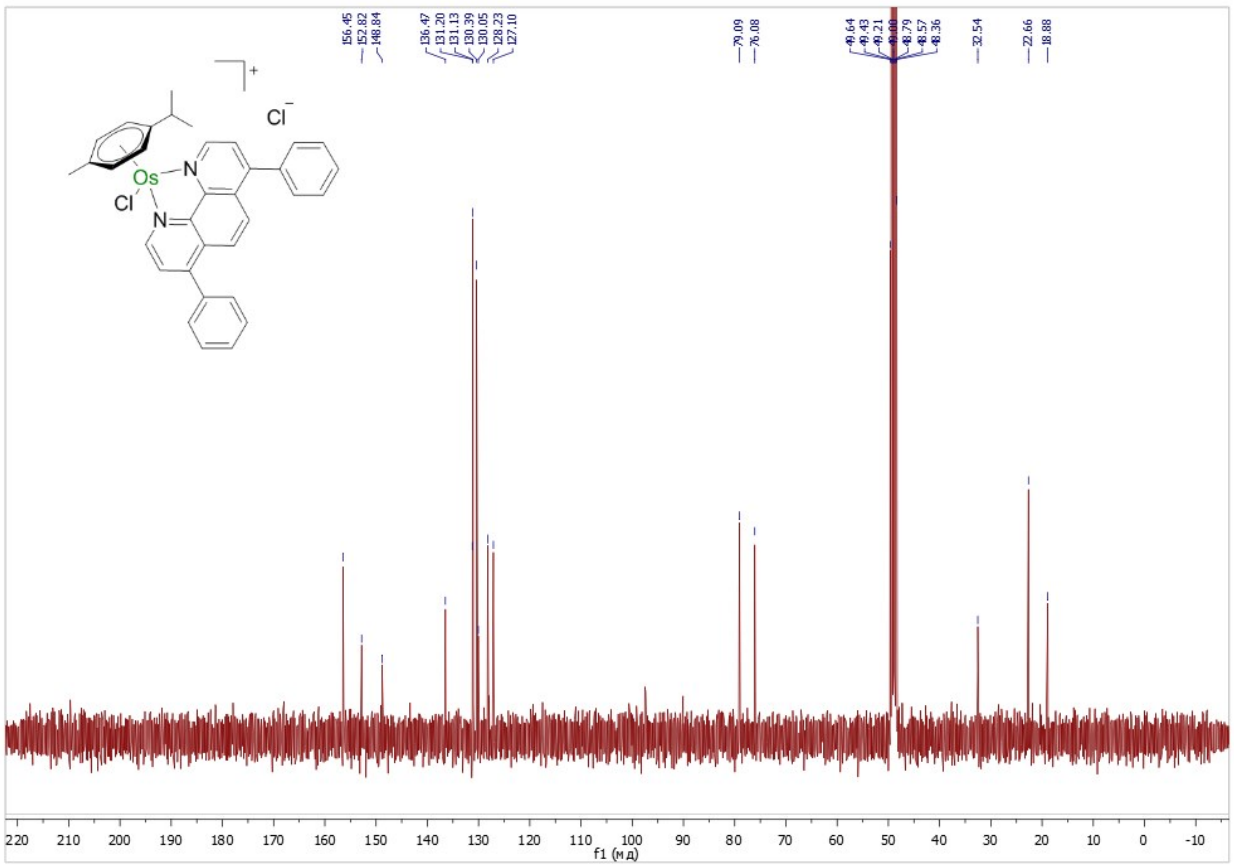


Bruker Compass DataAnalysis 4.0 printed: 08.12.2020 16:49:02 Page 1 of 1

[(η^6-cymene)Os(Bphen)Cl]Cl Os4 ^{1}H NMR (400 MHz, CD_3OD)



[(η^6-cymene)Os(Bphen)Cl]Cl Os4 ^{13}C NMR (101 MHz, CD_3OD)



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Analysis Info

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Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-27	Instrument / Ser#	micrOTOF 10248
Comment	C34H30ClN2Os M 693.1697 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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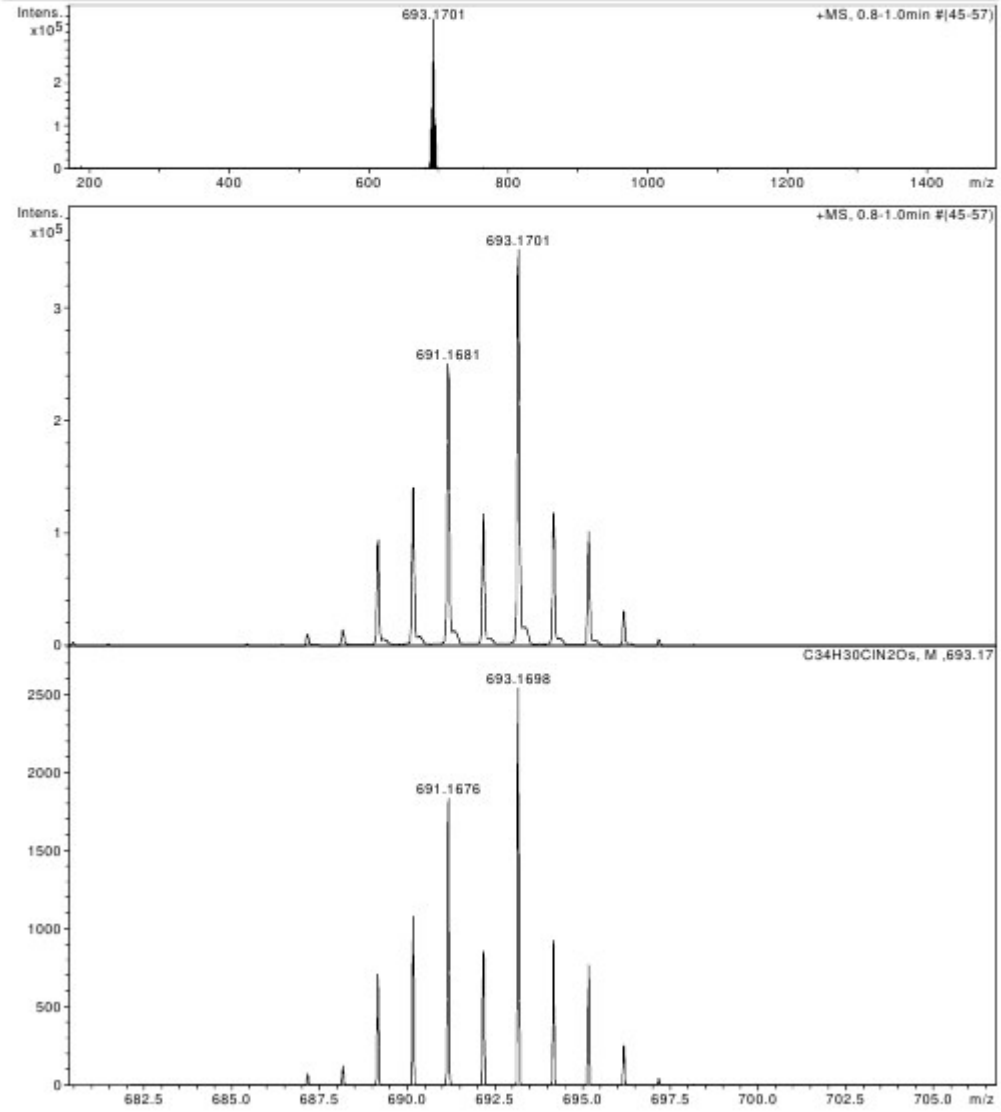
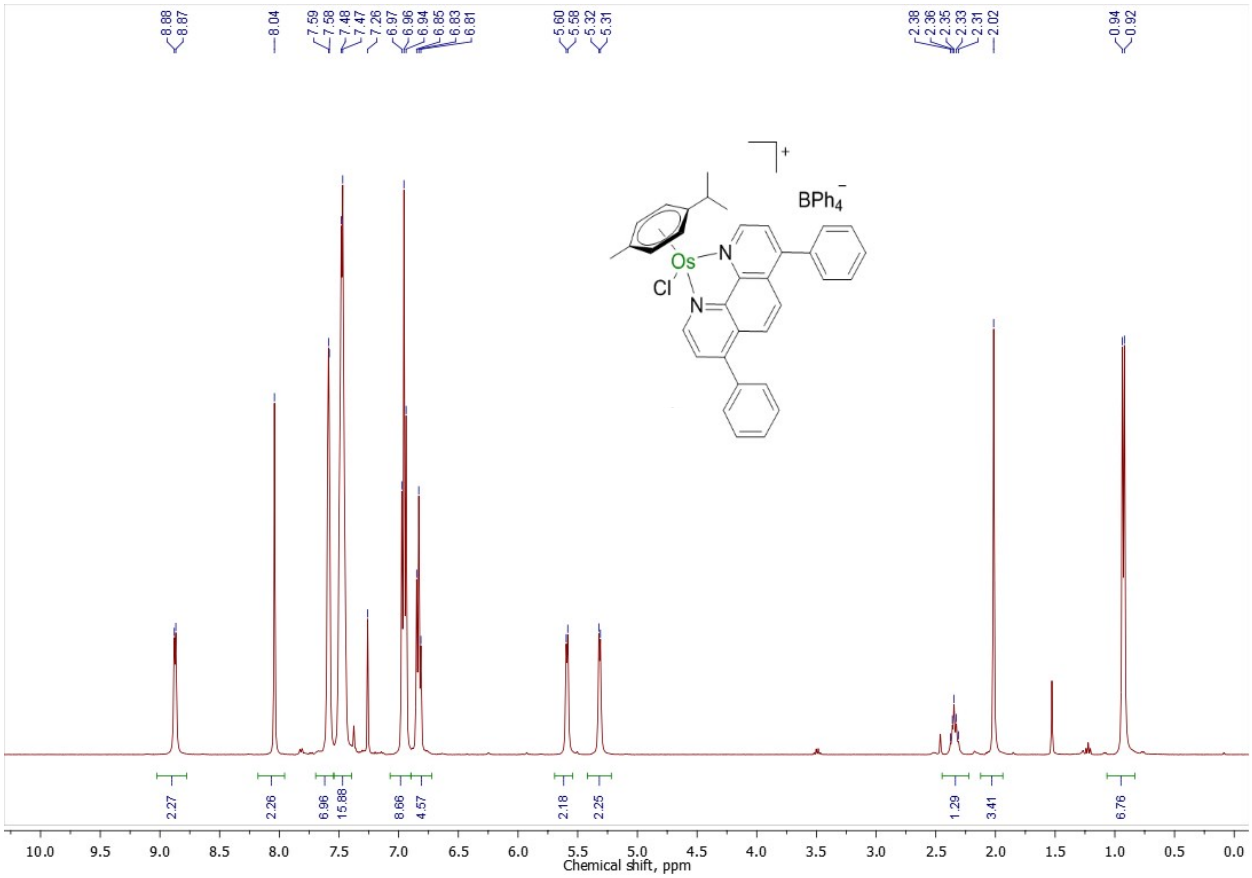
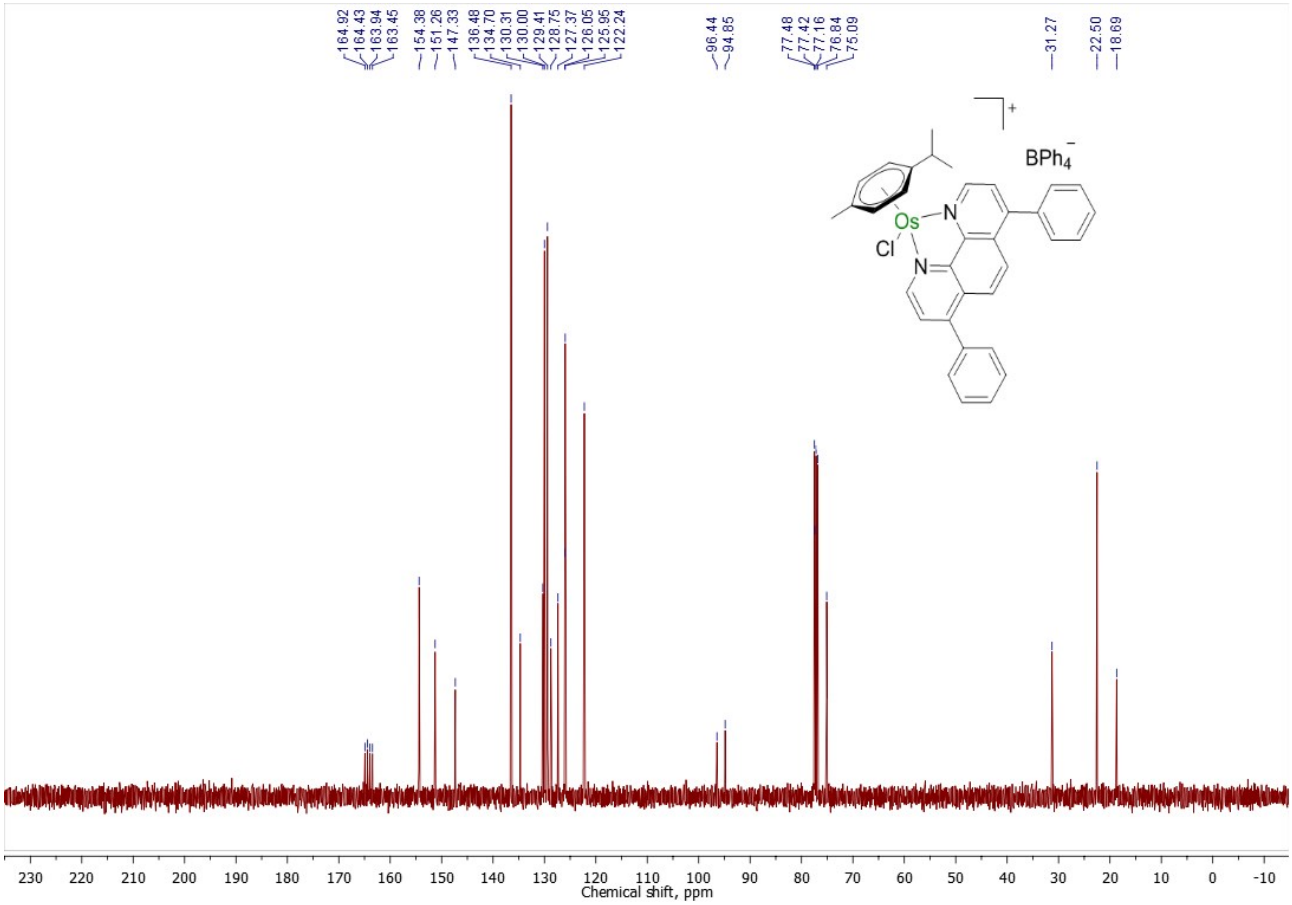
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



[(η^6-cymene)Os(Bphen)Cl]BPh$_4$ Os5 ^{1}H NMR (400 MHz, $CDCl_3$)



[(η^6-cymene)Os(Bphen)Cl]BPh$_4$ Os5 ^{13}C NMR (101 MHz, $CDCl_3$)



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Sample Name	/NGKO LD-39	Instrument / Ser#	micrOTOF 10248
Comment	C34H30N2OsCl m 693.1698 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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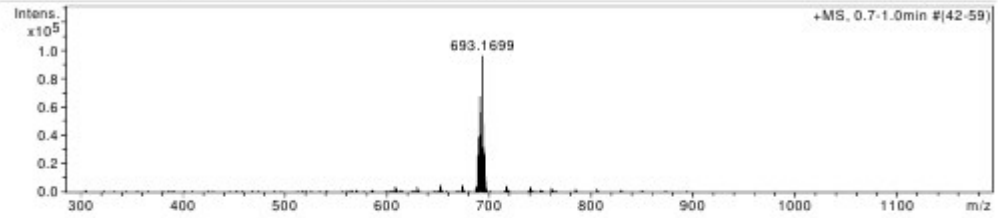
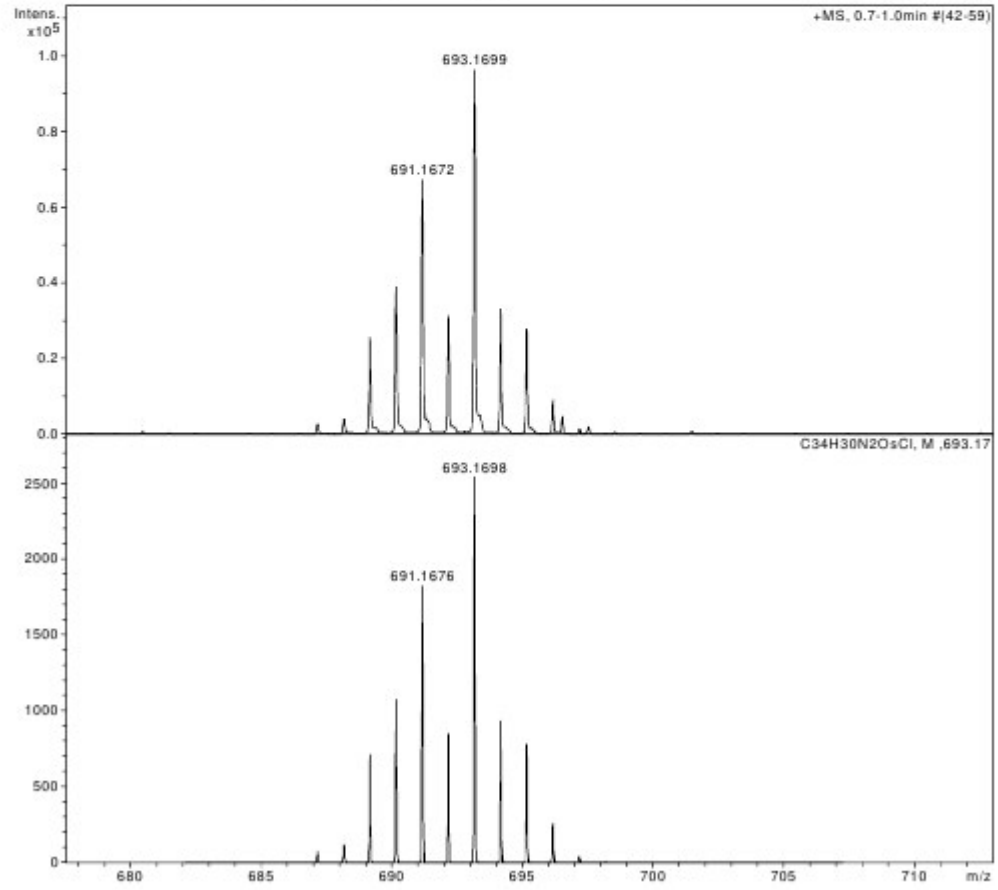
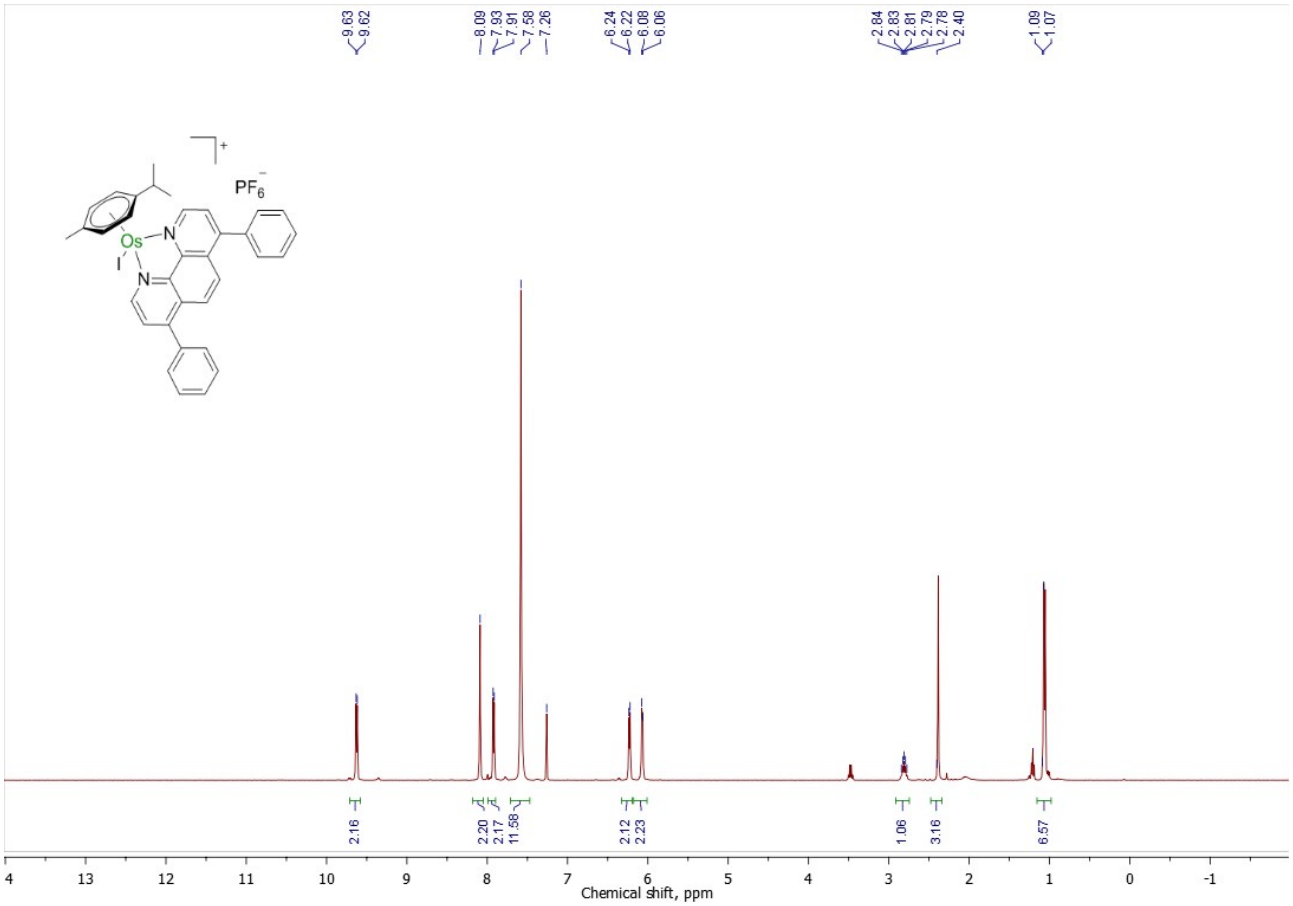
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

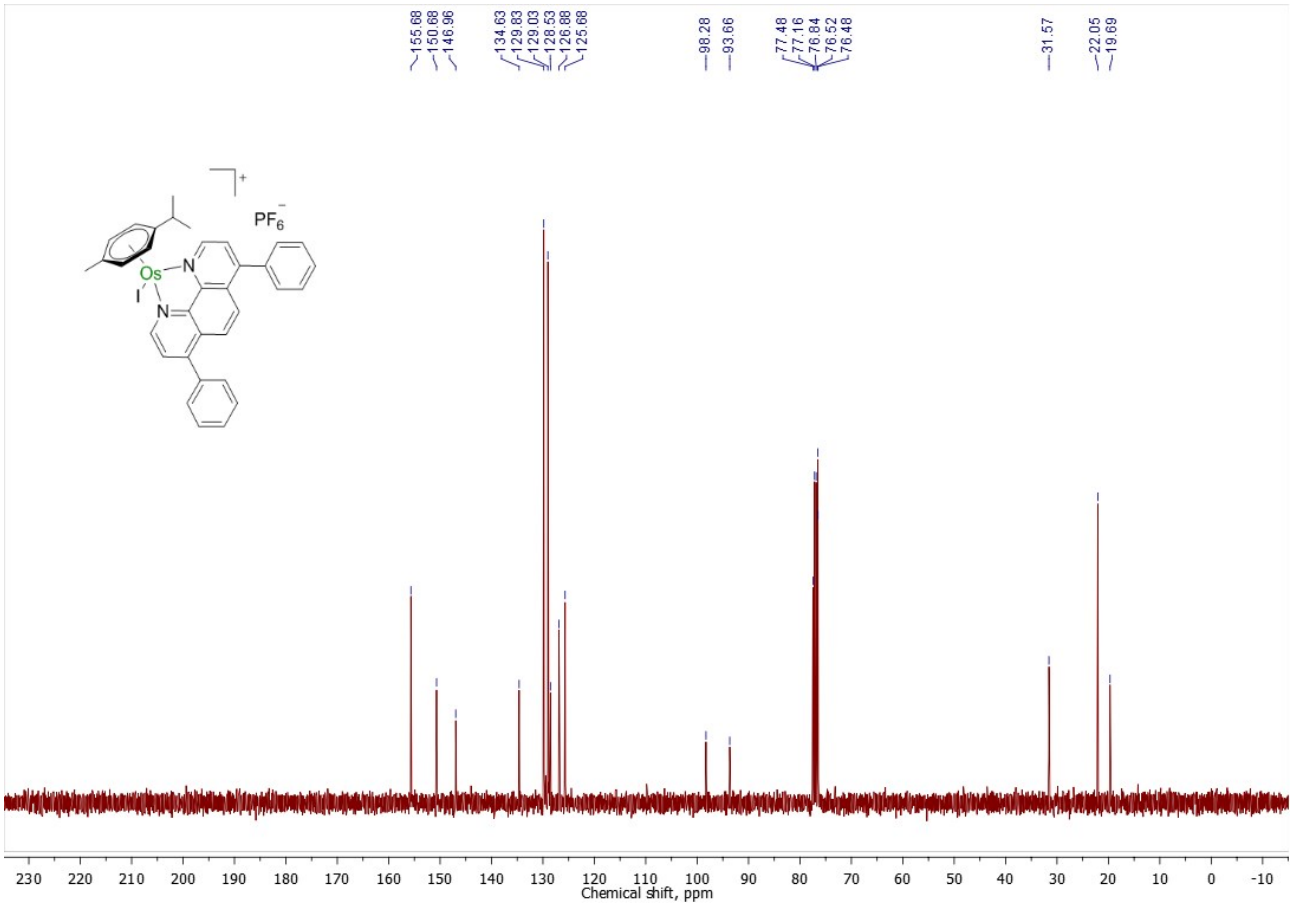




[(η^6-cymene)Os(Bphen)I]PF$_6$ Os6 ^{1}H NMR (400 MHz, $CDCl_3$)



[(η^6-cymene)Os(Bphen)I]PF$_6$ Os6 ^{13}C NMR (101 MHz, $CDCl_3$)



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Sample Name	/NGKO LG-31	Instrument / Ser#	micrOTOF 10248
Comment	C34H30N2O3I calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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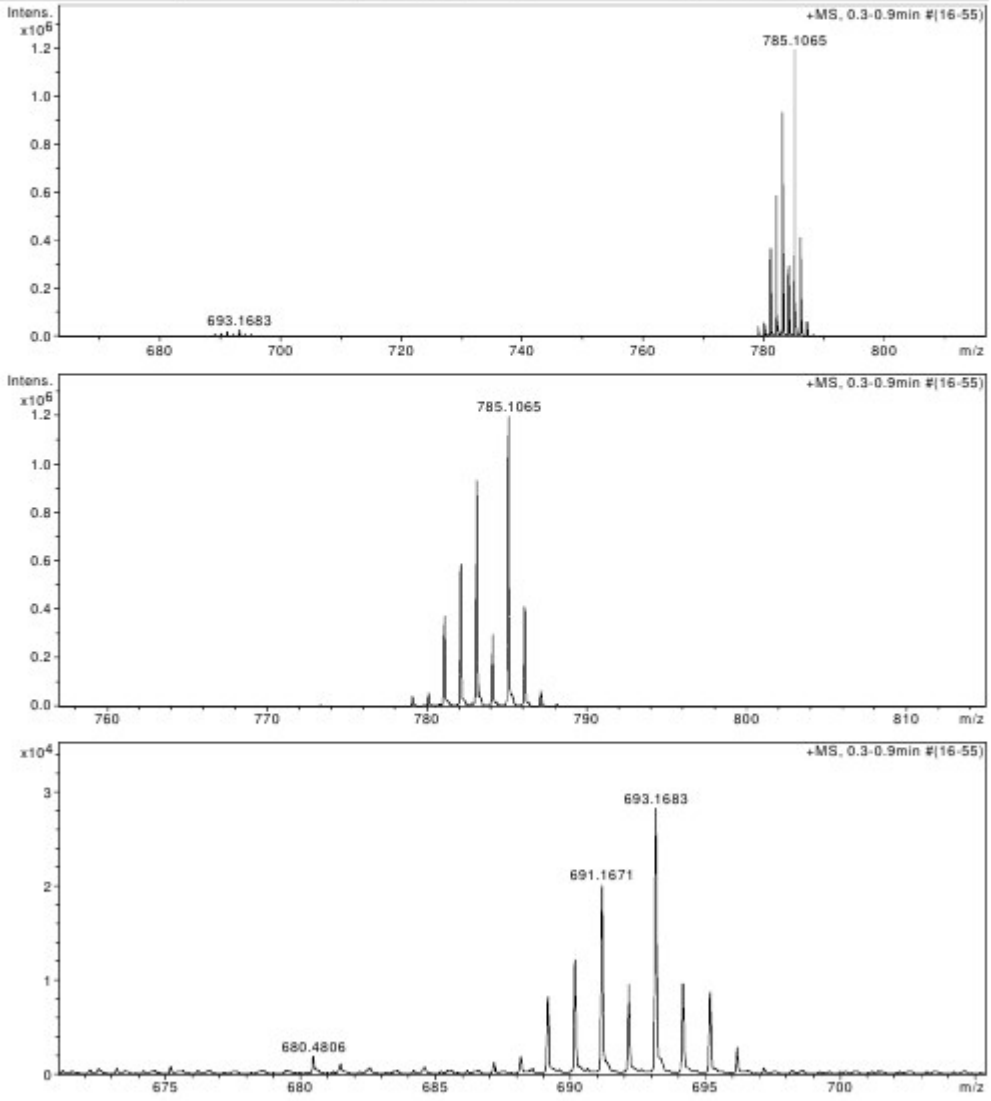

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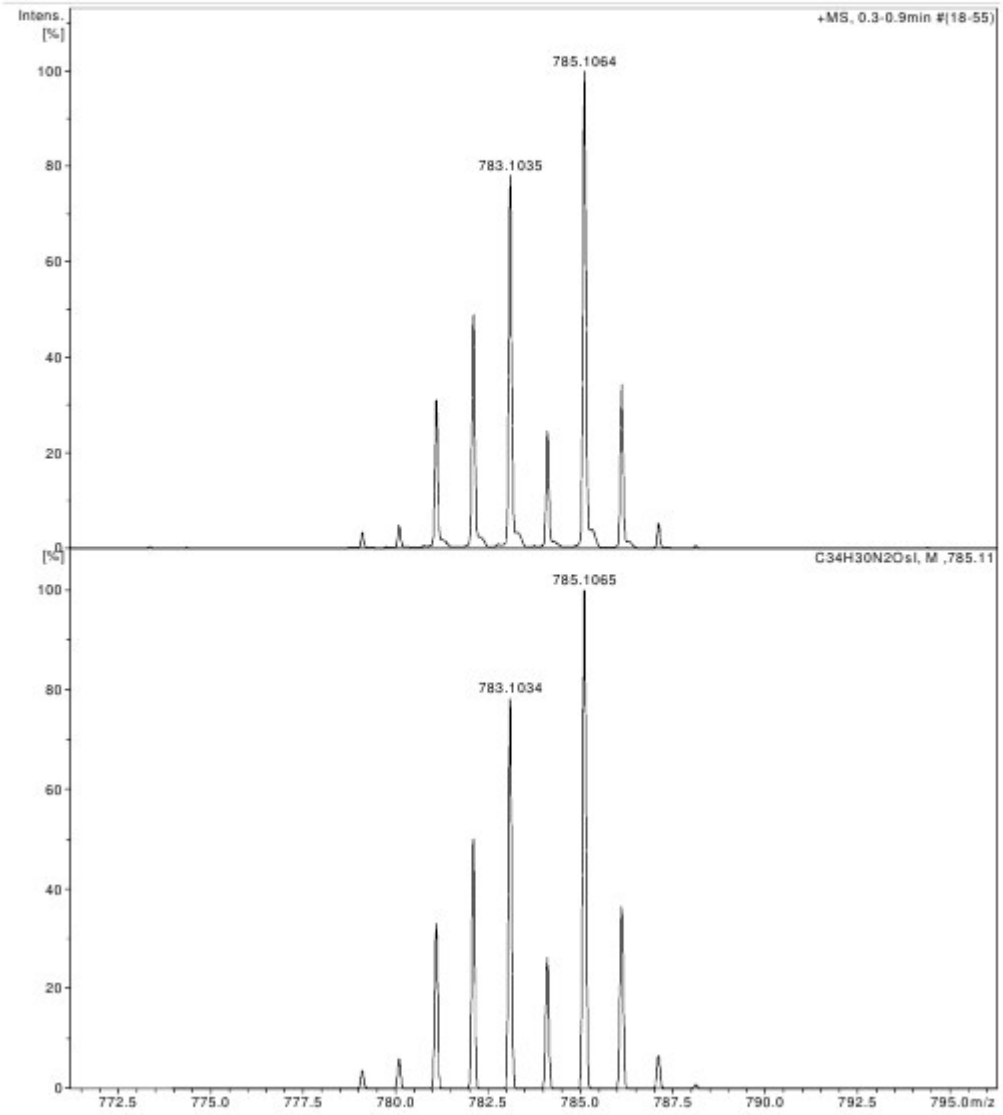
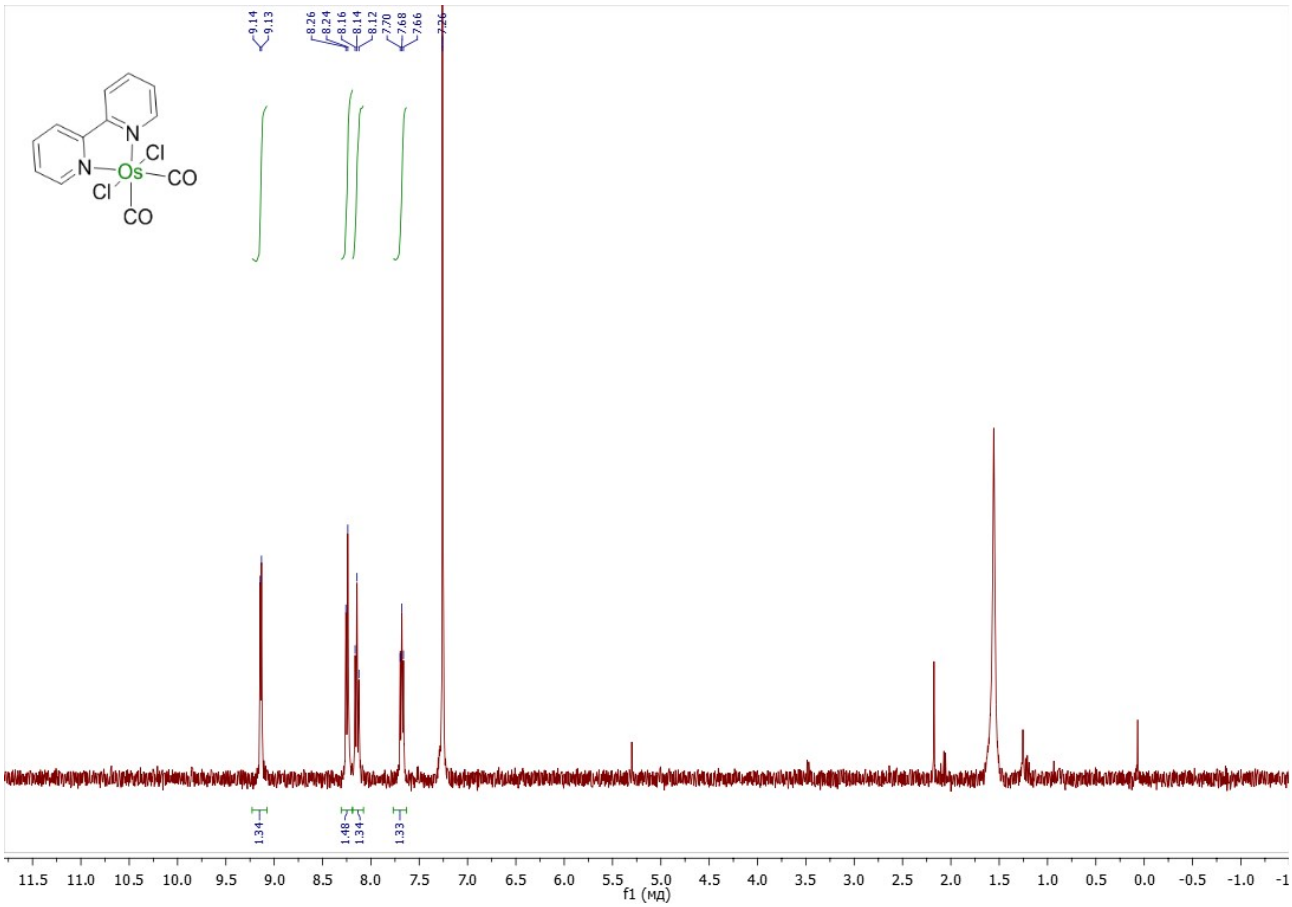
Sample Name	/NGKO LG-31	Instrument / Ser#	micrOTOF 10248
Comment	C34H30N2O3I calibrant added CH3CN		

Acquisition Parameter

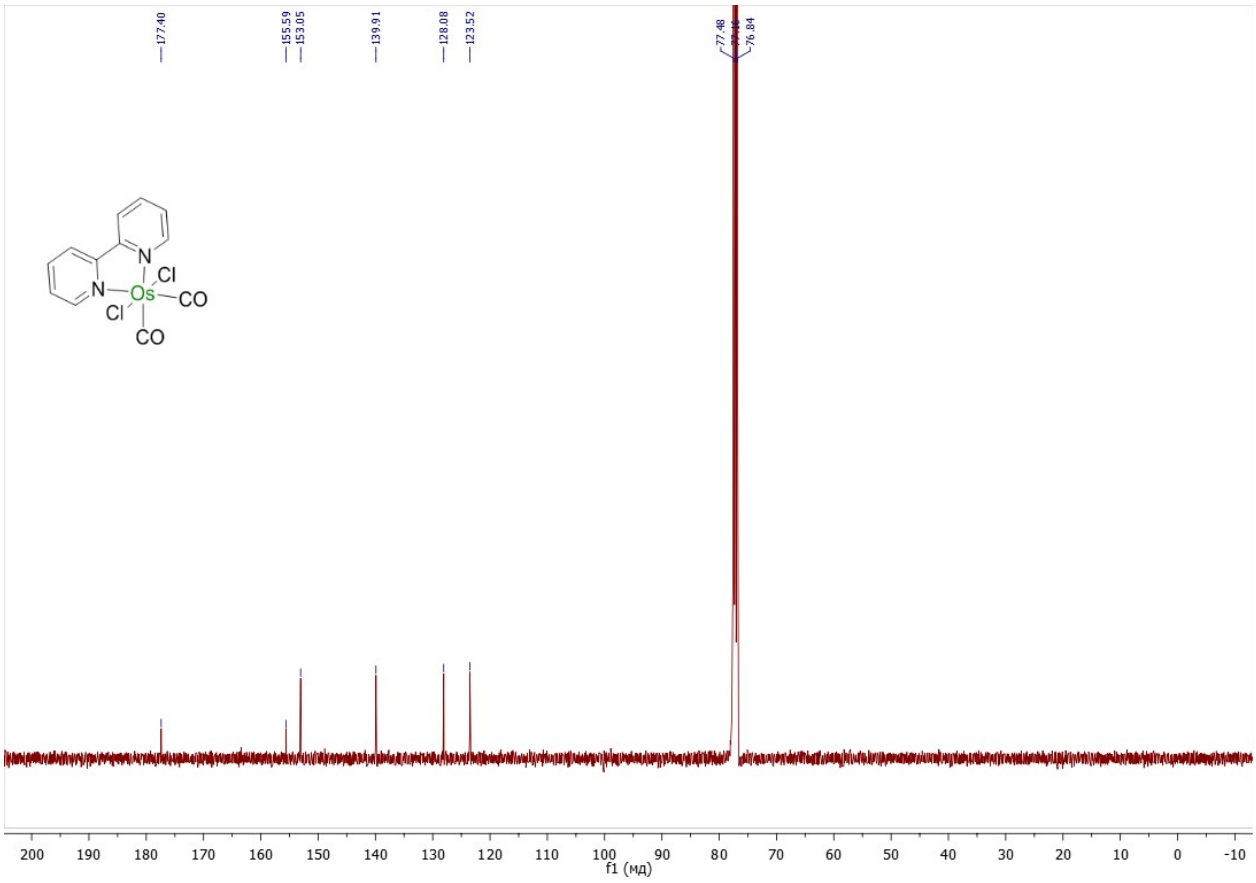
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(2,2'-bipyridine)$OsCl_2(CO)_2$ Os7 ^{1}H NMR (400 MHz, $CDCl_3$)



(2,2'-bipyridine)$OsCl_2(CO)_2$ Os7 ^{13}C NMR (101 MHz, $CDCl_3$)



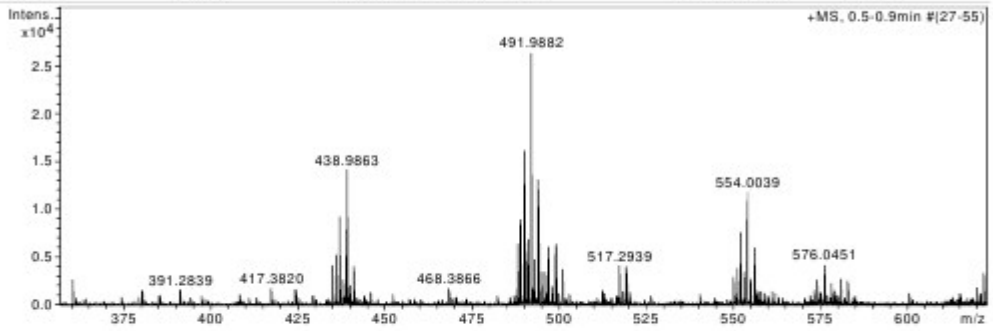
Display Report

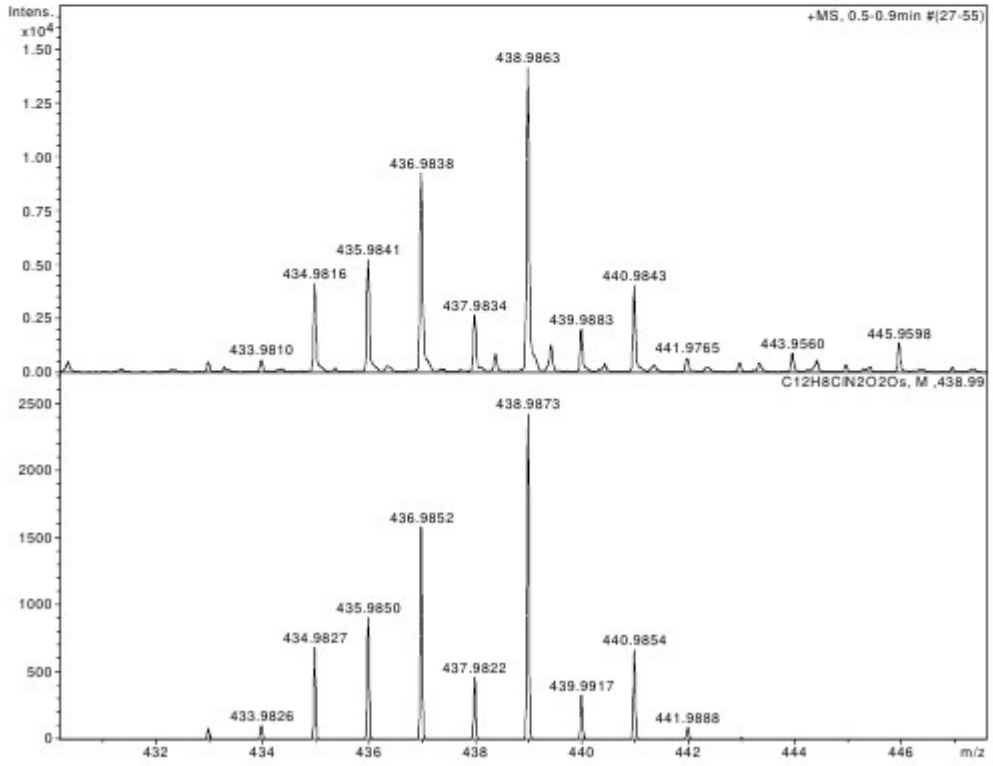
Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Loginov\1117035.d	Acquisition Date	17.11.2020 17:25:47
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-22	Instrument / Ser#	micrOTOF 10248
Comment	C10H8ClOs mH 355.9991clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





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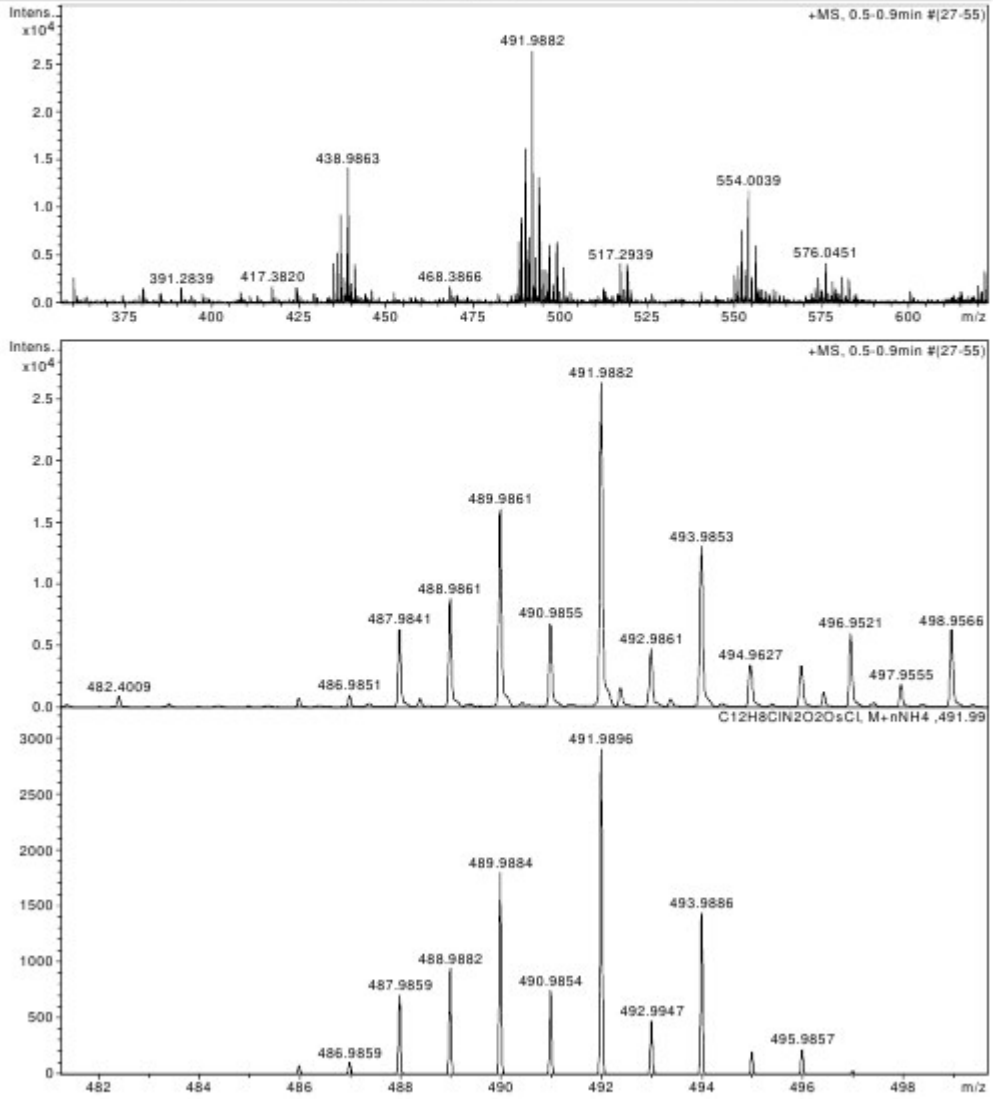
Analysis Info

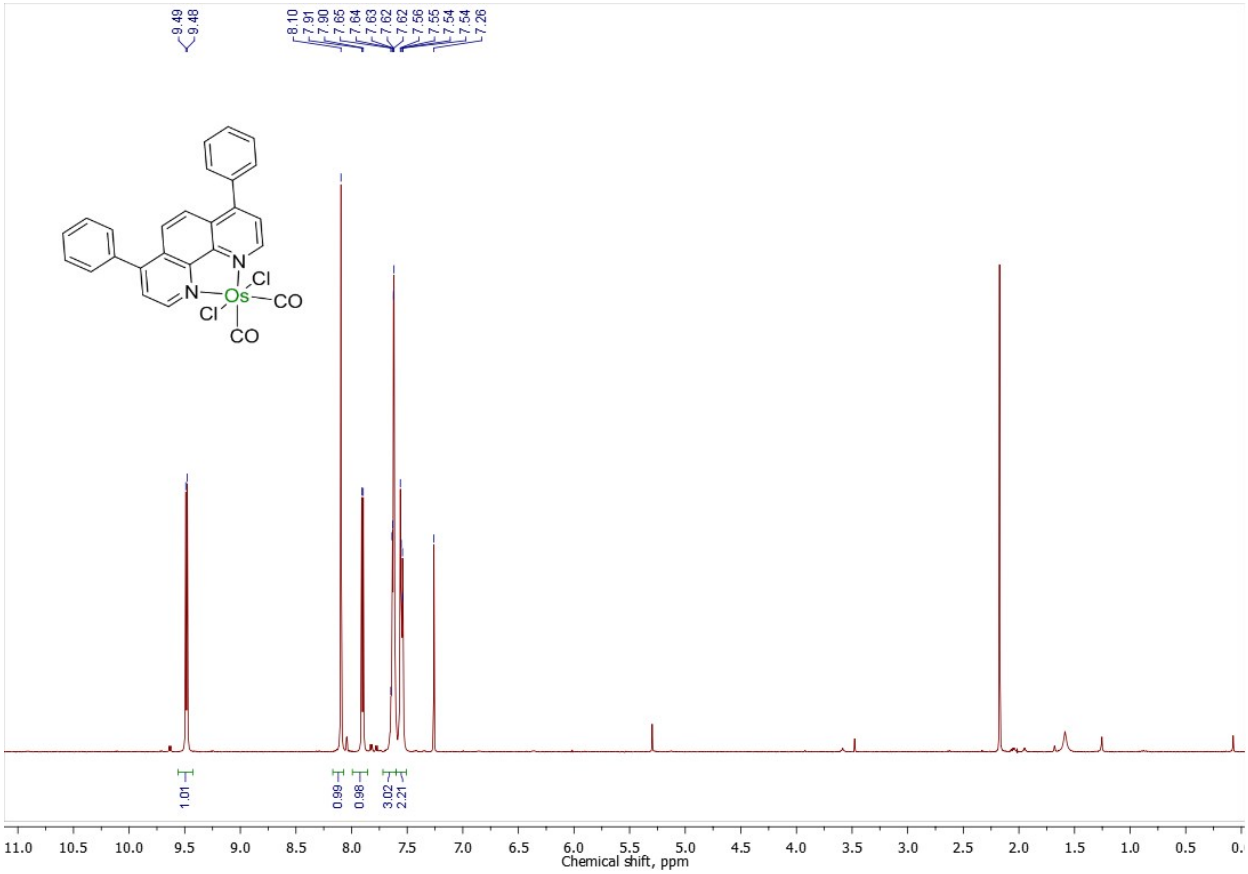
Analysis Name	D:\Data\Kolotyrkina\2020\Loginov\1117035.d	Acquisition Date	17.11.2020 17:25:47
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-22	Instrument / Ser#	micrOTOF 10248
Comment	C10H8ClOs mH 355.9991clb added CH3CN		

Acquisition Parameter

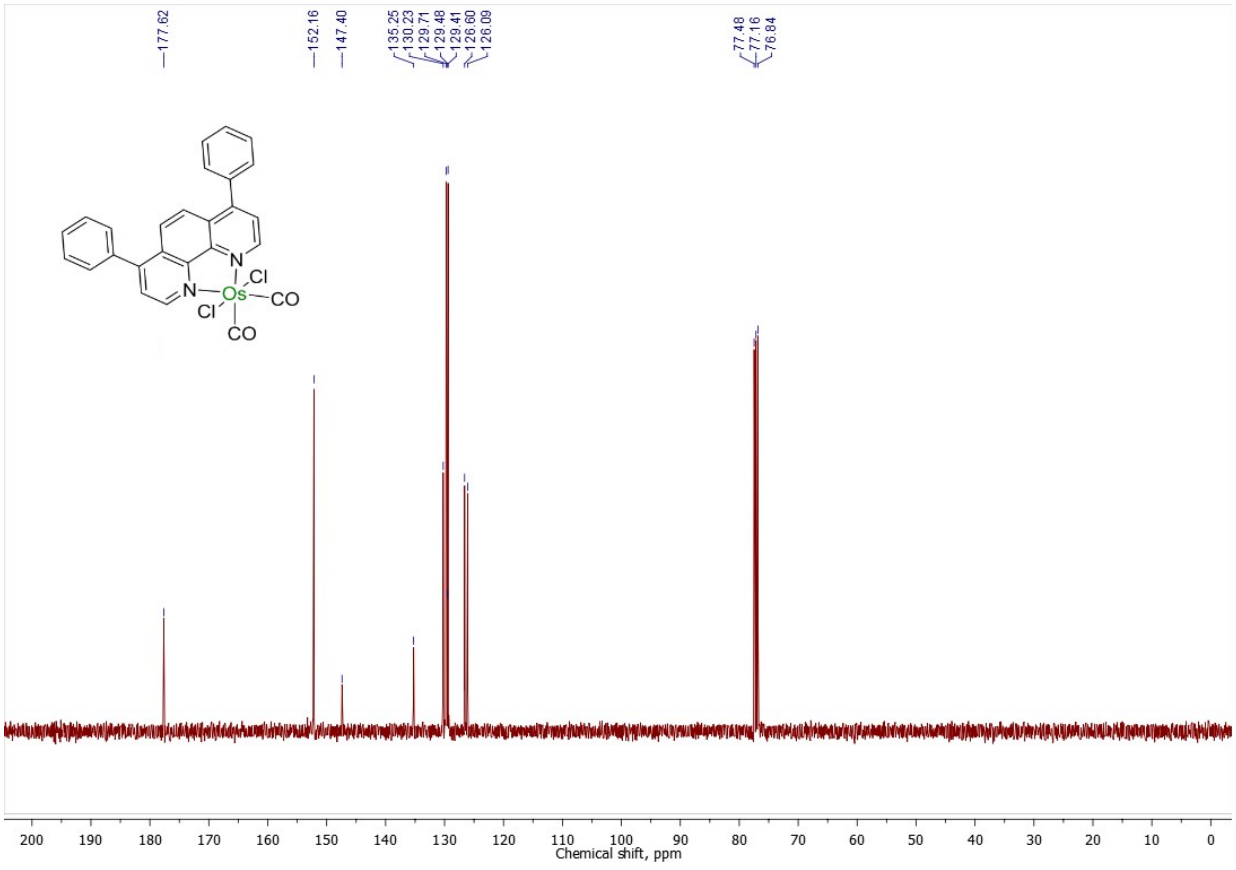
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(Bphen)$OsCl_2(CO)_2$ Os8 ^{1}H NMR (400 MHz, $CDCl_3$)



(Bphen)$OsCl_2(CO)_2$ Os8 ^{13}C NMR (101 MHz, $CDCl_3$)



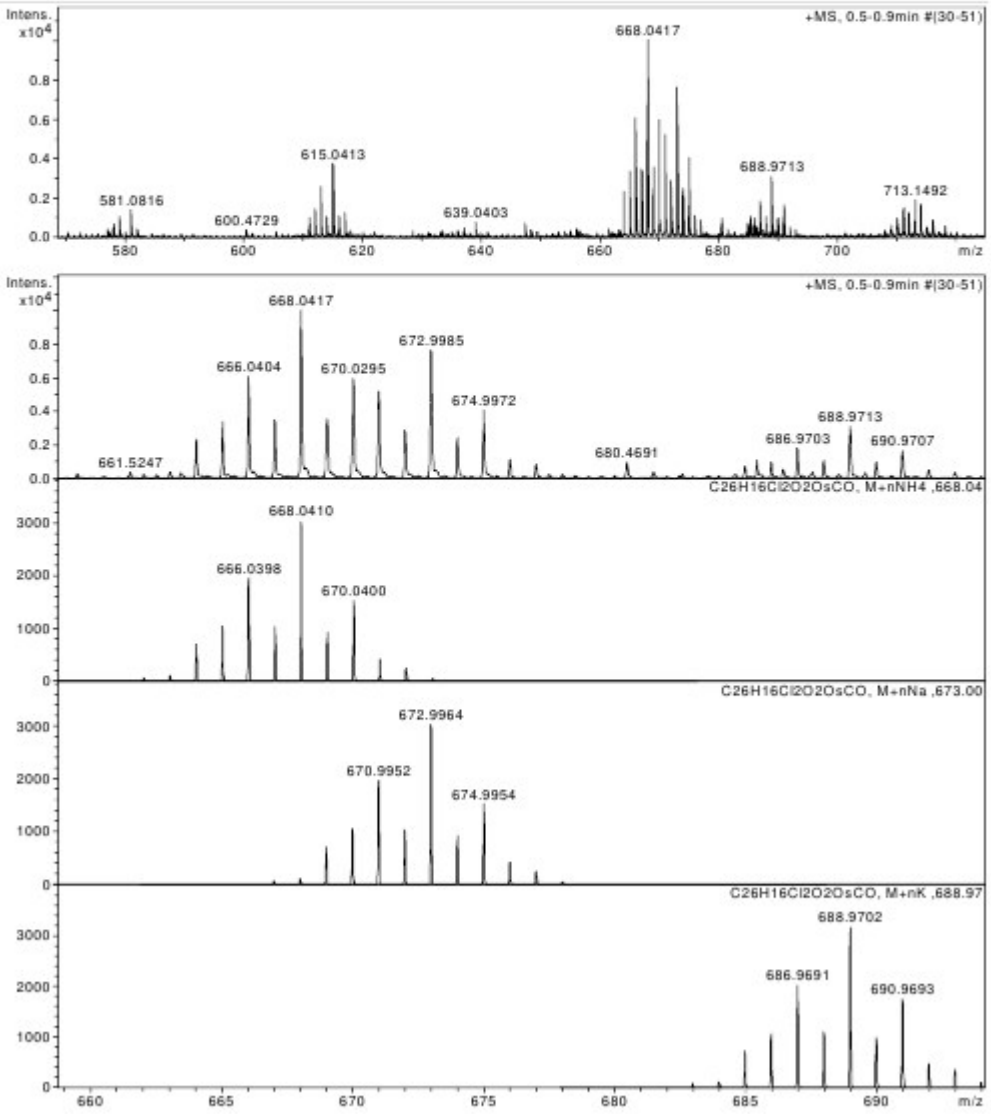
Display Report

Analysis Info

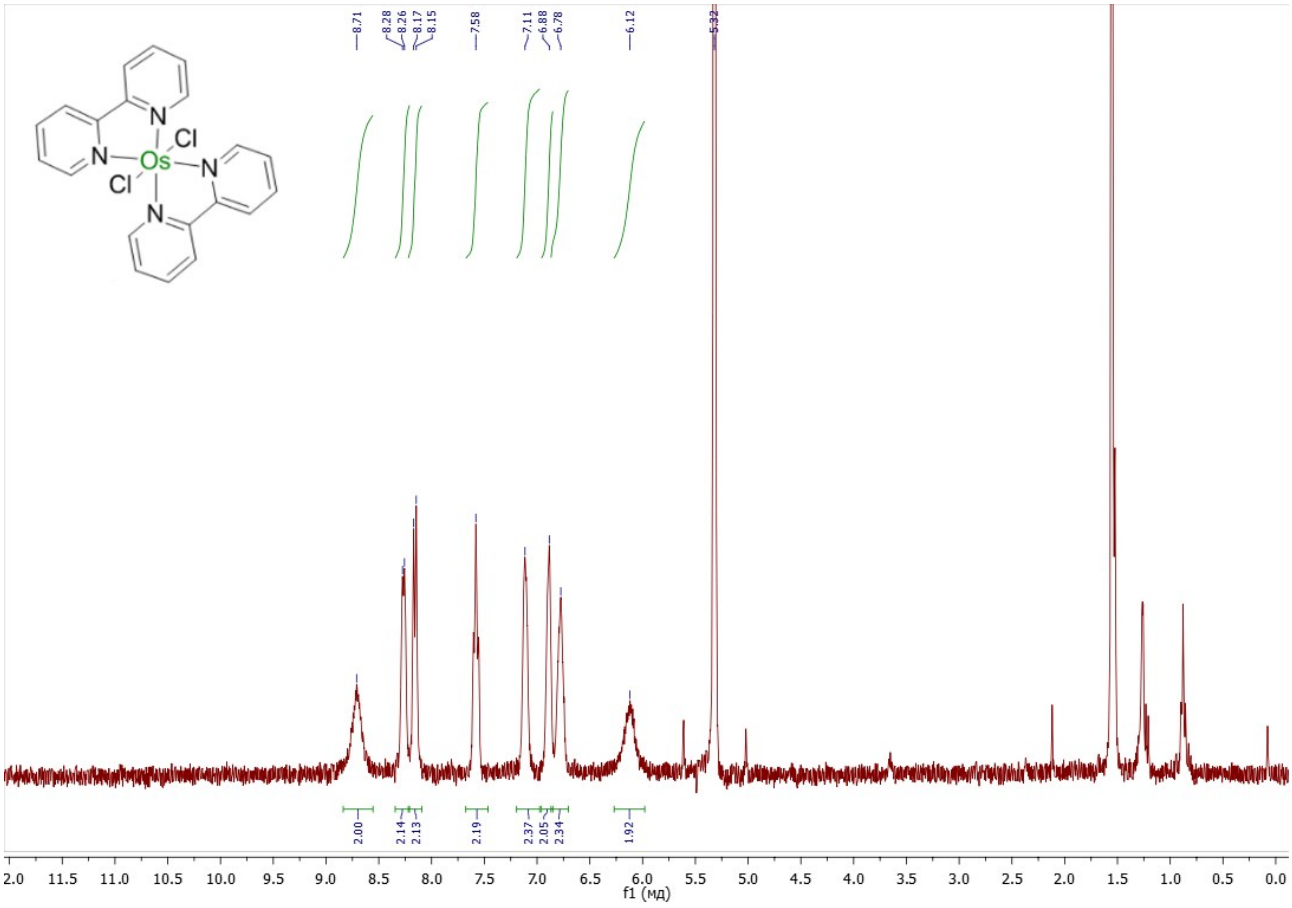
Analysis Name	D:\Data\Kolotyrkina\2020\Loginov\1201026.d	Acquisition Date	01.12.2020 15:39:09
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-26	Instrument / Ser#	micrOTOF 10248
Comment	C26H16Cl2O2Os M 622.0117 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(2,2'-bipyridine)$_2$OsCl$_2$ Os9 ^{1}H NMR (300 MHz, CD_2Cl_2)



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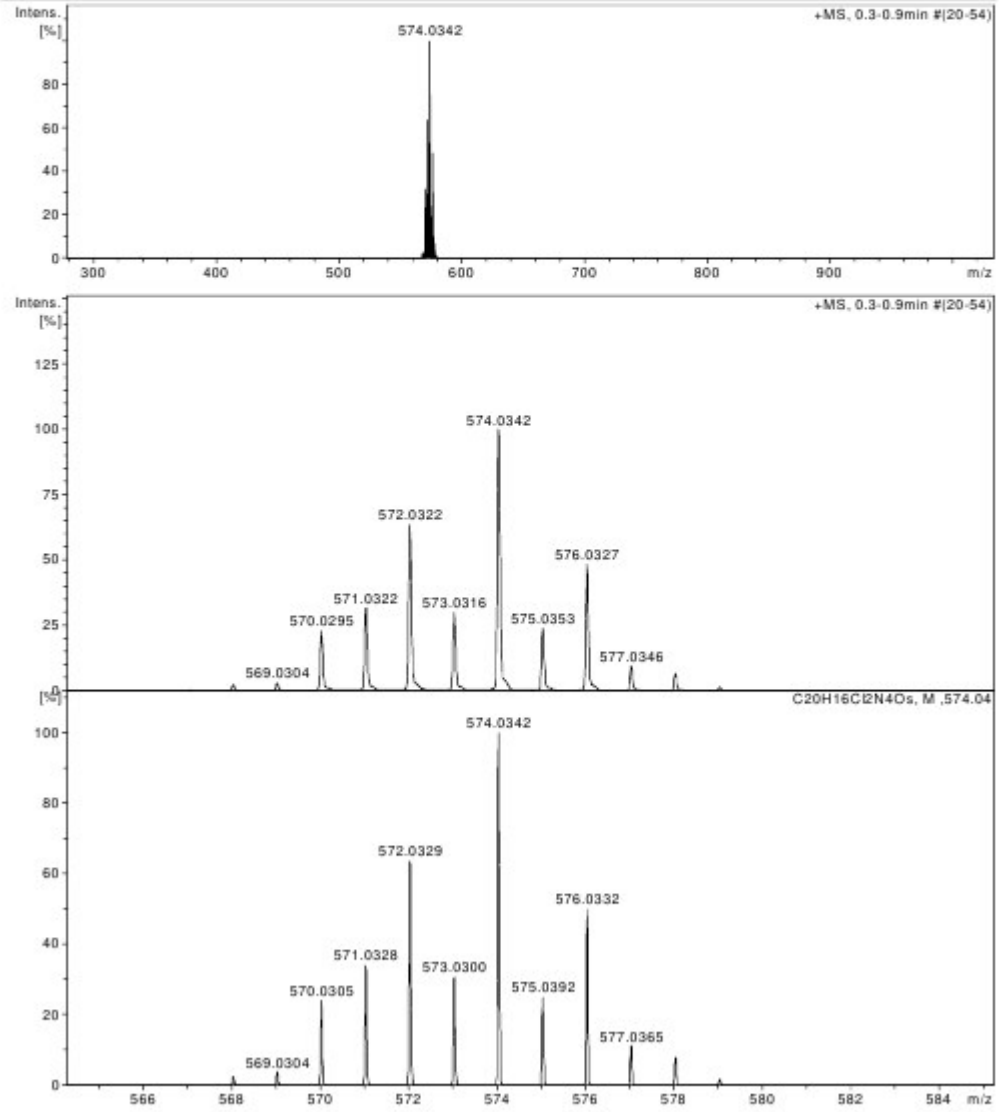
Analysis Info

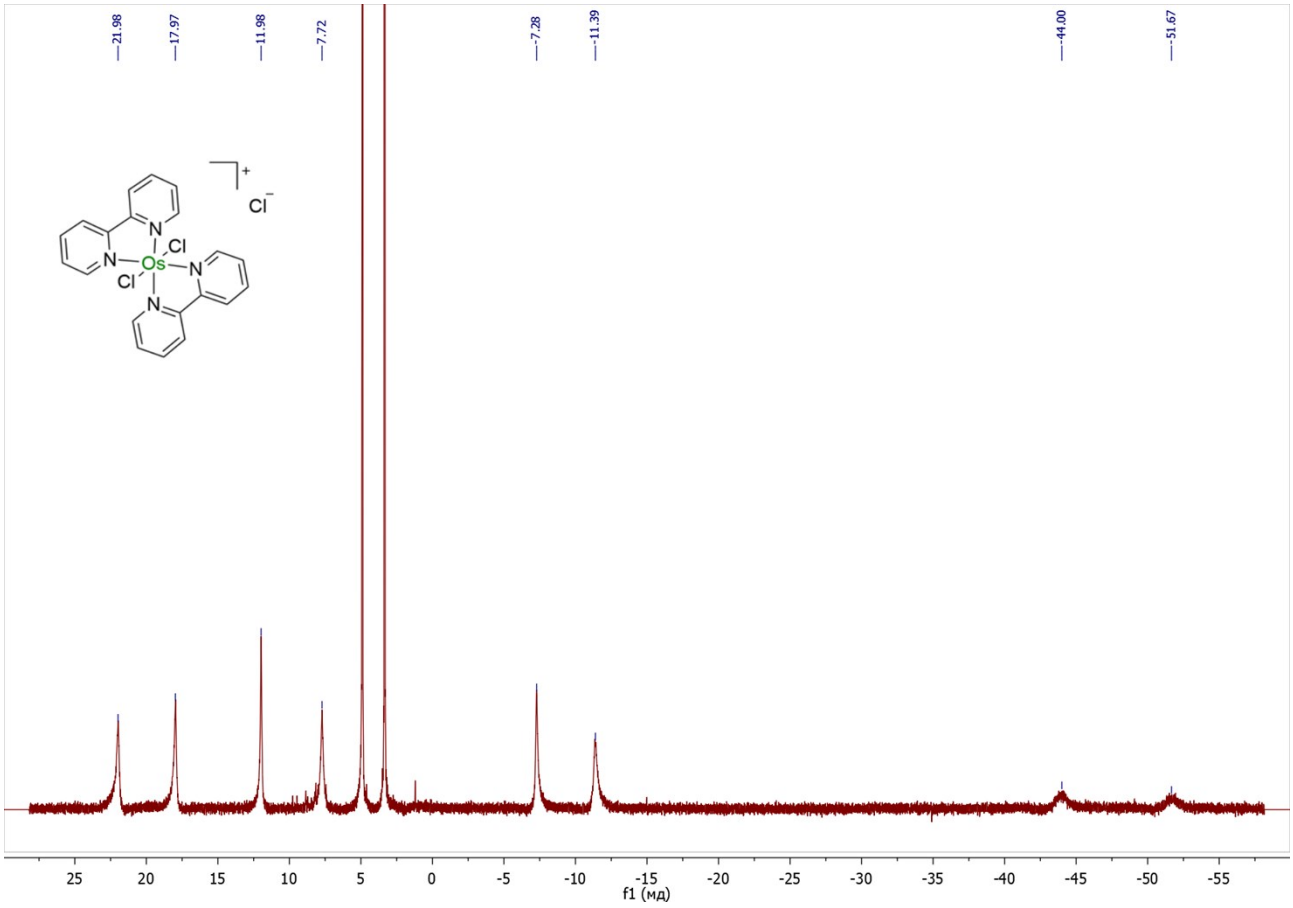
Analysis Name	D:\Data\Kolotyrkina\2020\Loginov\1124031.d	Acquisition Date	24.11.2020 17:03:08
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-24	Instrument / Ser#	micrOTOF 10248
Comment	C20H16Cl2N4Os m 518.0218 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(2,2'-bipyridine)$_2$OsCl$_3$ Os10 ^{1}H NMR (400 MHz, CD_3OD)



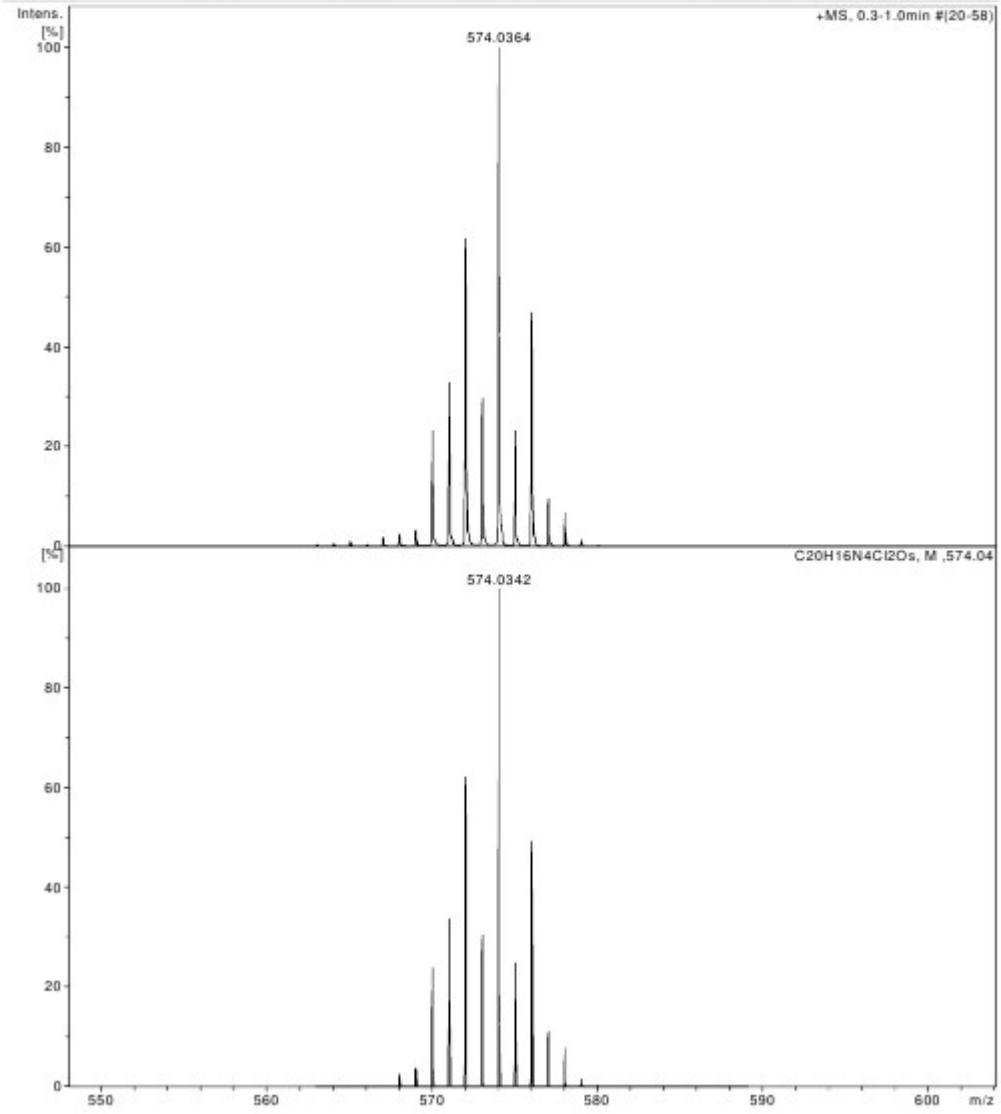
Display Report

Analysis Info

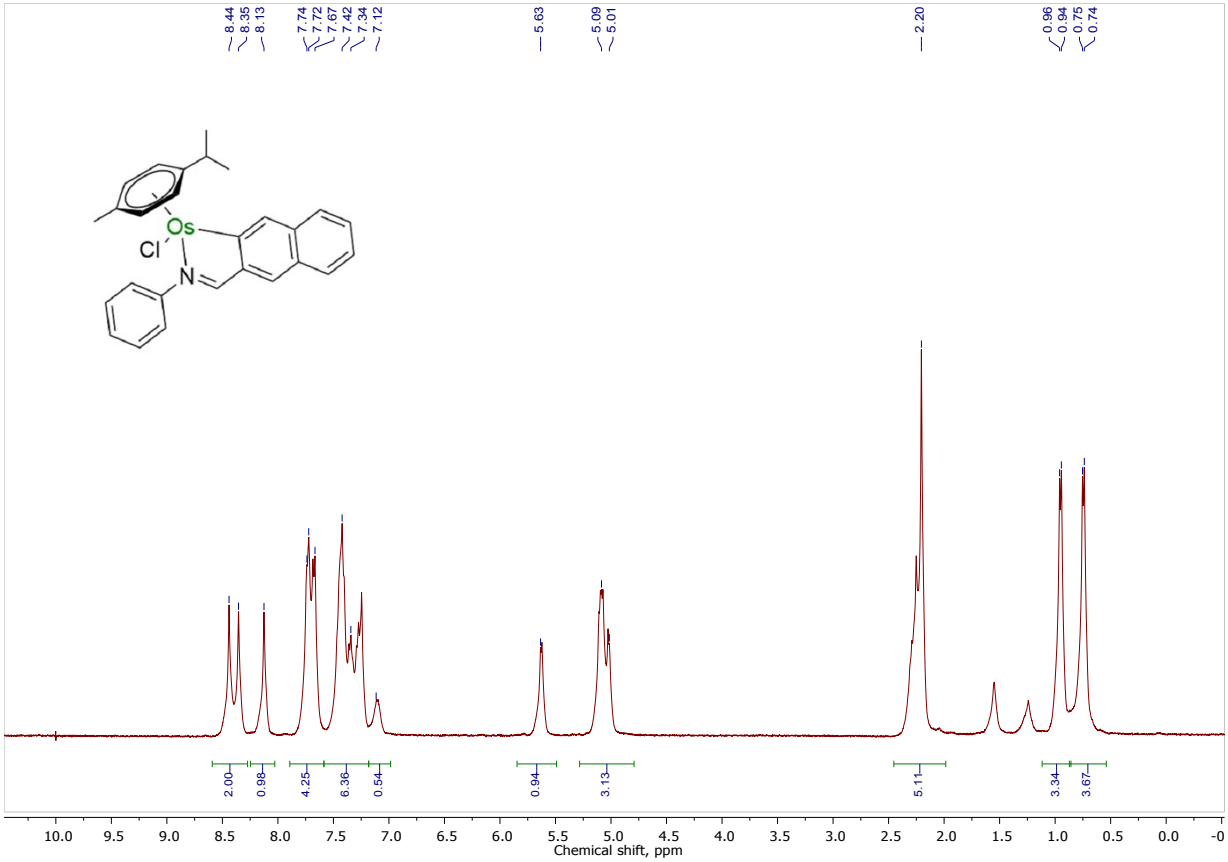
Analysis Name	D:\Data\Kolotyrkina\2021\Loginov\0119026.d	Acquisition Date	19.01.2021 13:30:09
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-33	Instrument / Ser#	micrOTOF 10248
Comment	C20H16N4Cl2Os calibrant added CH3CN		

Acquisition Parameter

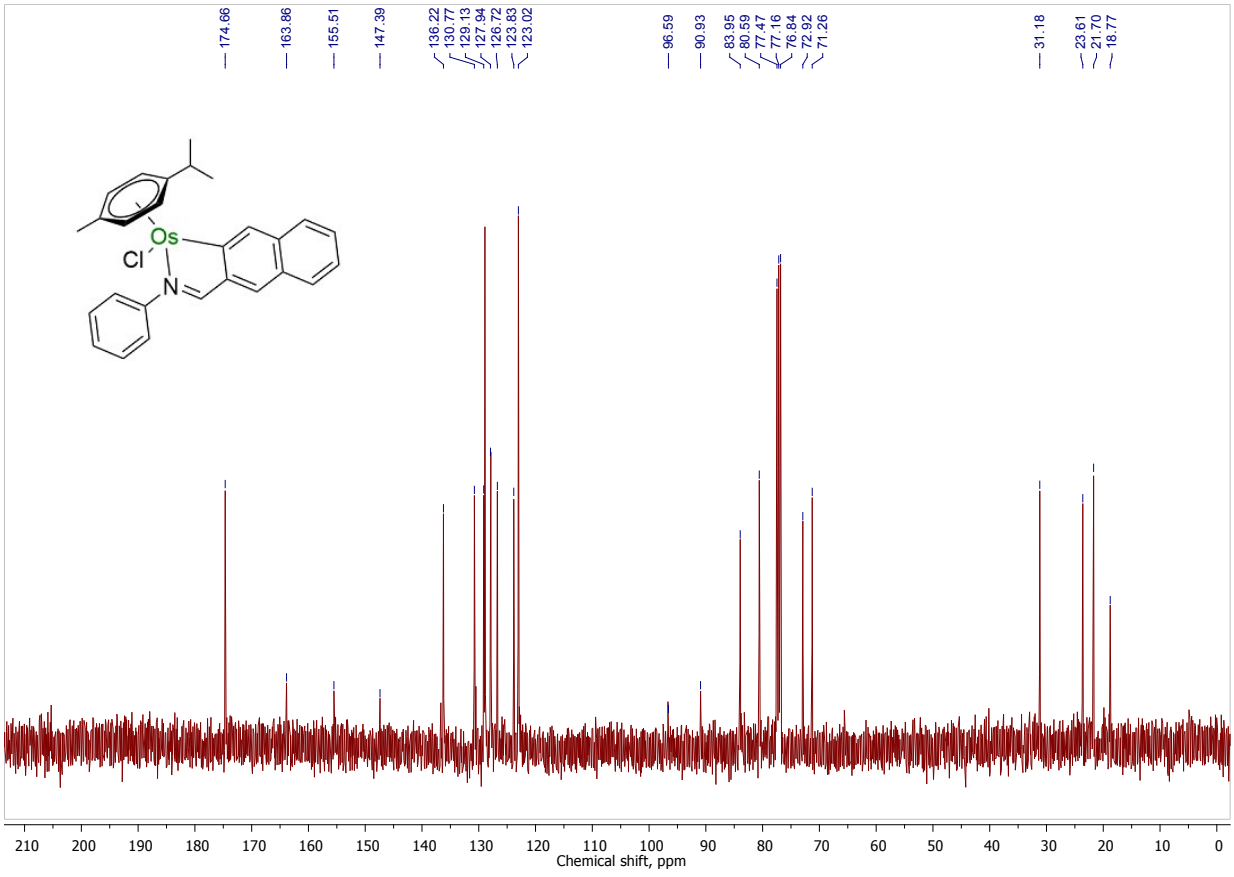
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



[(η⁶-cymene)Os(N,C-napht)Cl] Os11 ^{1}H NMR (400 MHz, $CDCl_3$)



[(η⁶-cymene)Os(N,C-napht)Cl] Os11 ^{13}C NMR (101 MHz, $CDCl_3$)



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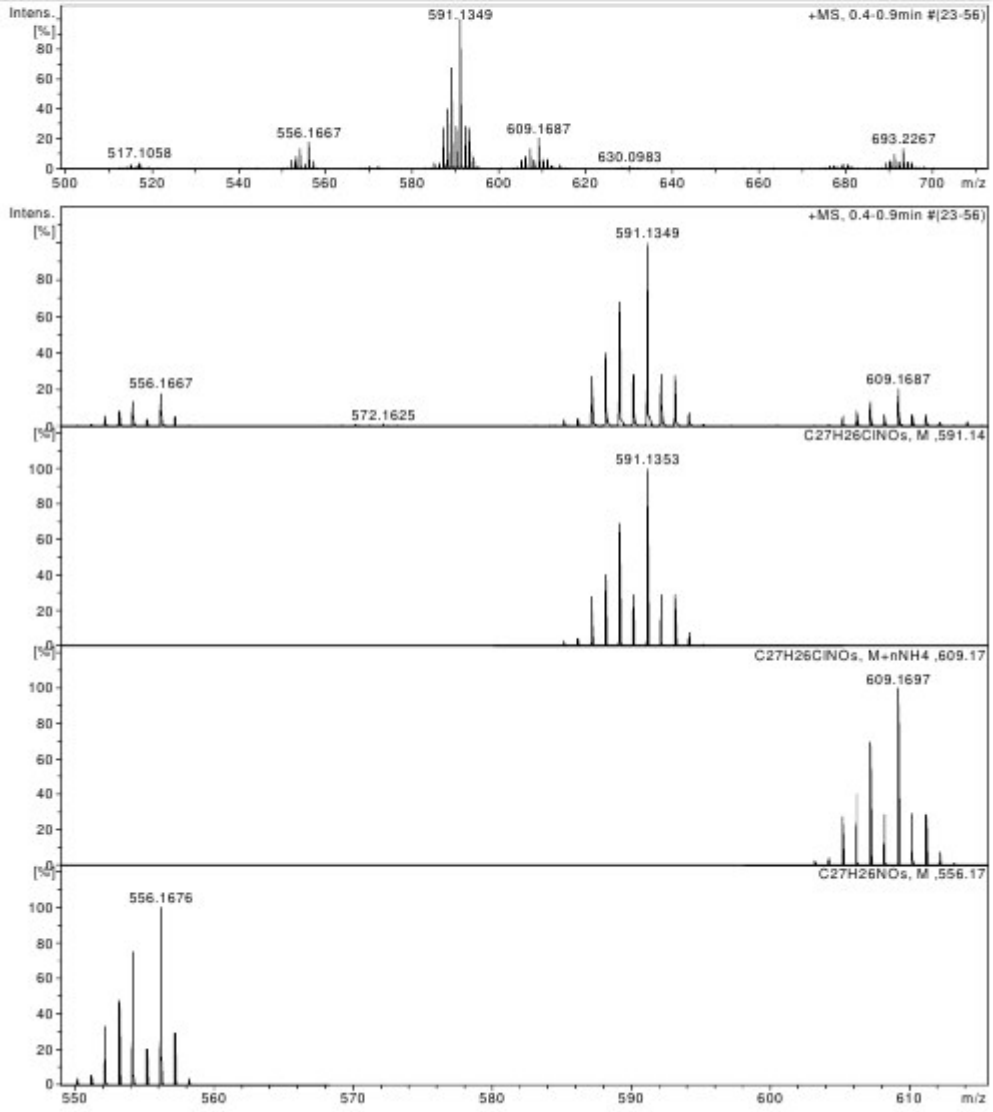
Analysis Info

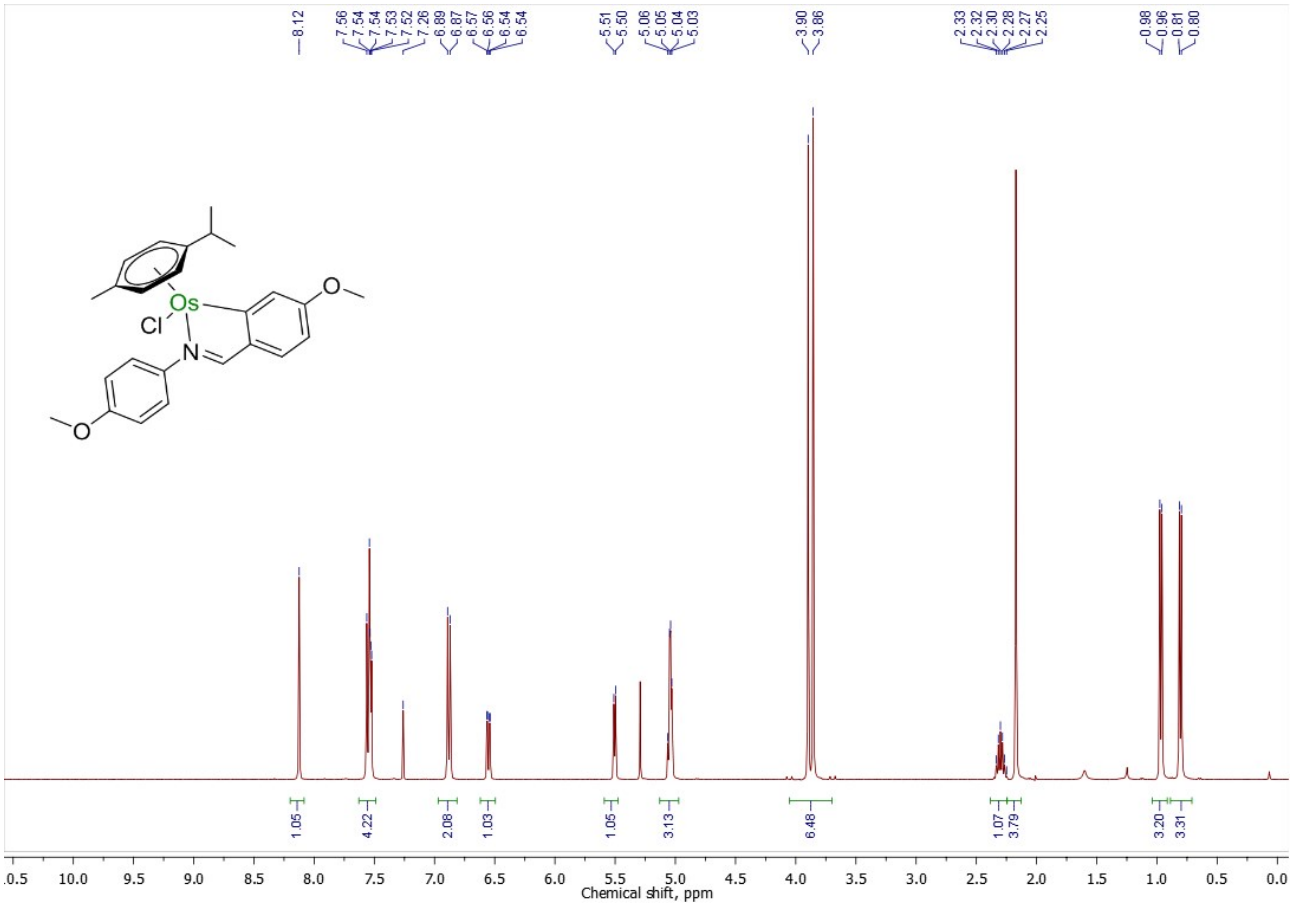
Analysis Name	D:\Data\Kolotyrkina\2020\Loginov\1208041.d	Acquisition Date	08.12.2020 16:50:53
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-29	Instrument / Ser#	micrOTOF 10248
Comment	C27H26NOsCl calibrant added CH3CN		

Acquisition Parameter

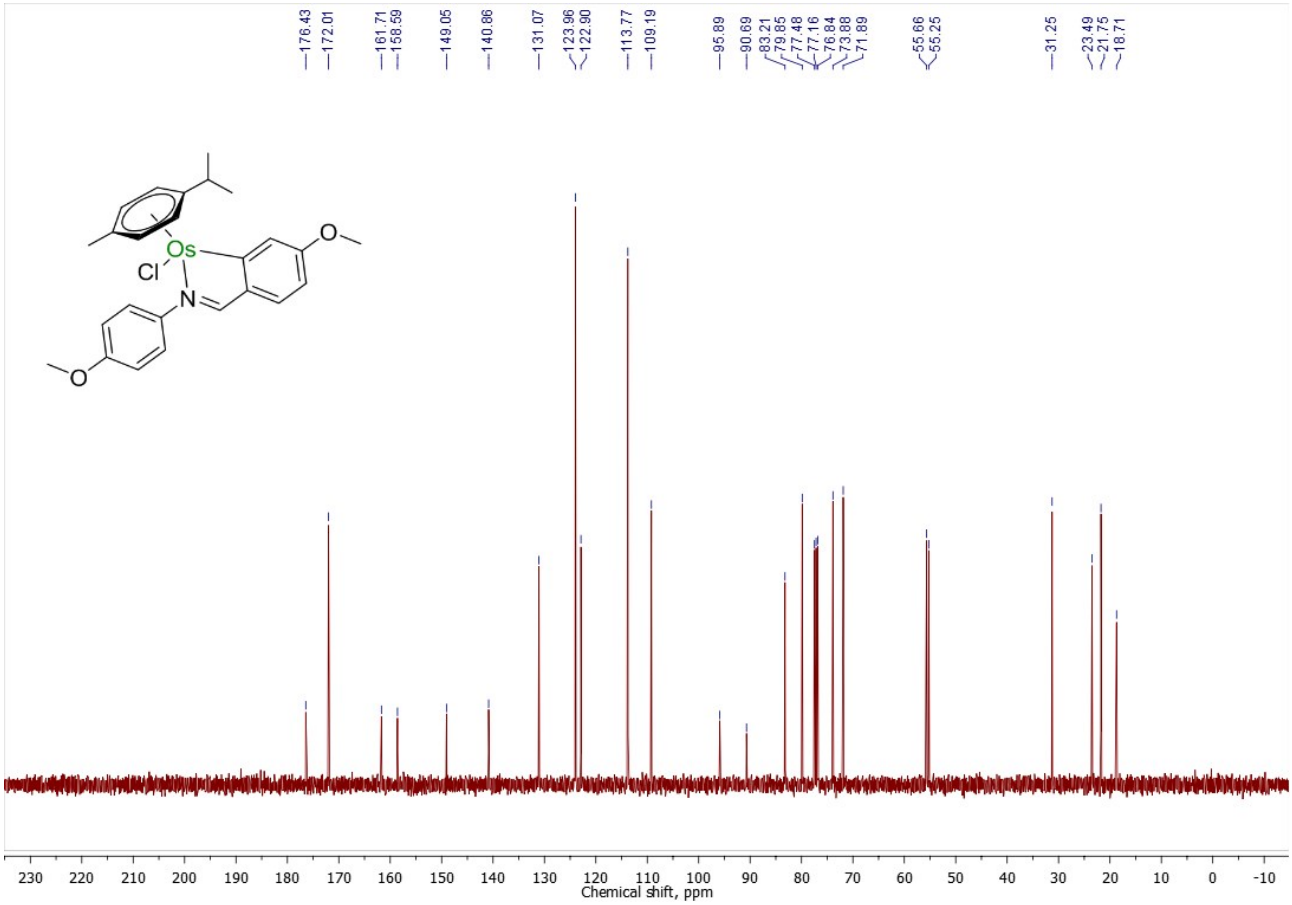
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



[(η^6-cymene)Os(N,C-anis)Cl] Os12 ^{1}H NMR (400 MHz, $CDCl_3$)



[(η^6-cymene)Os(N,C-anis)Cl] Os12 ^{13}C NMR (101 MHz, $CDCl_3$)


176.43
172.01
161.71
158.59
149.05
140.86
131.07
123.96
122.90
113.77
109.19
95.89
90.69
83.21
79.85
77.48
77.16
76.84
73.88
71.89
55.66
55.25
31.25
23.49
21.75
18.71
Os
Cl
N
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift, ppm

Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Loginov\1117036.d	Acquisition Date	17.11.2020 17:39:23
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/NGKO LD-23	Instrument / Ser#	micrOTOF 10248
Comment	C25H28NO2Os mH 567.1808 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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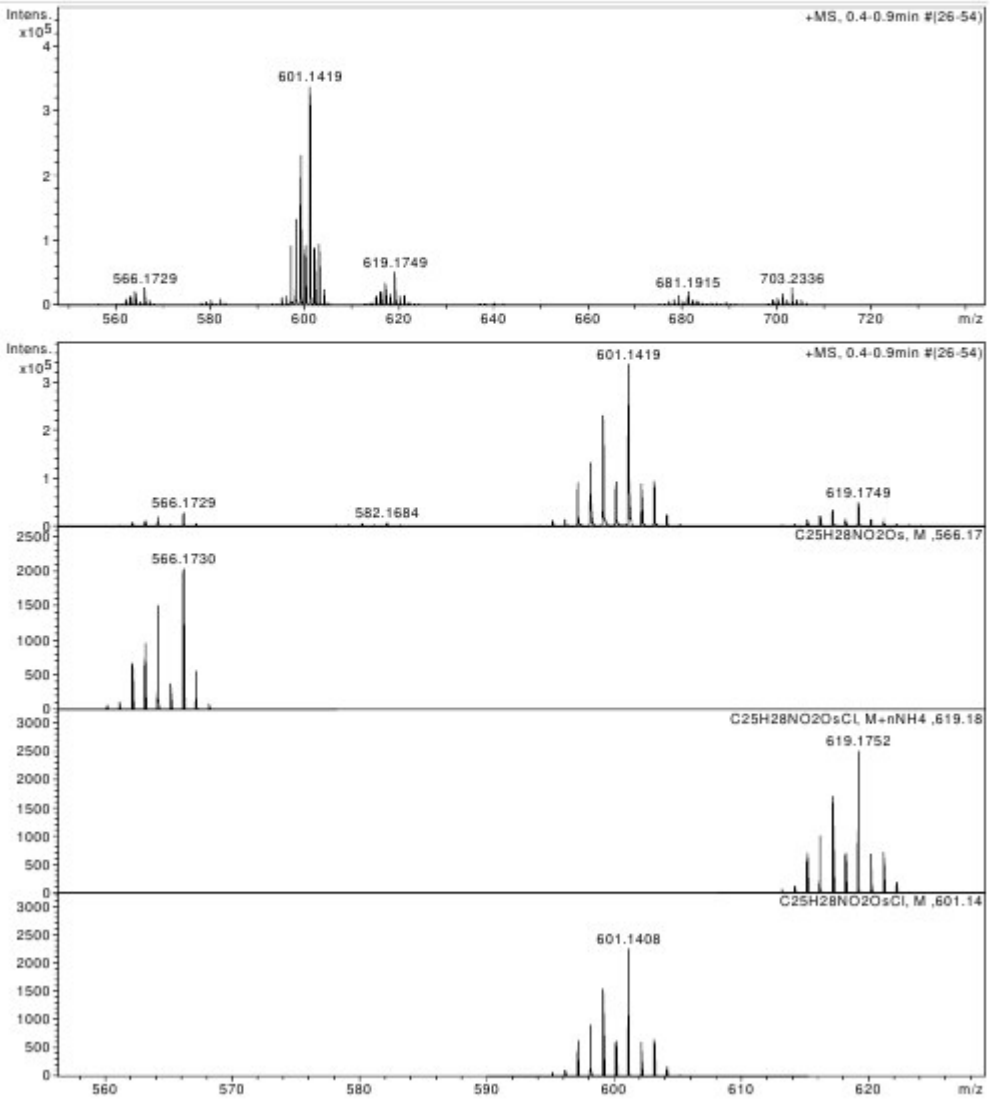
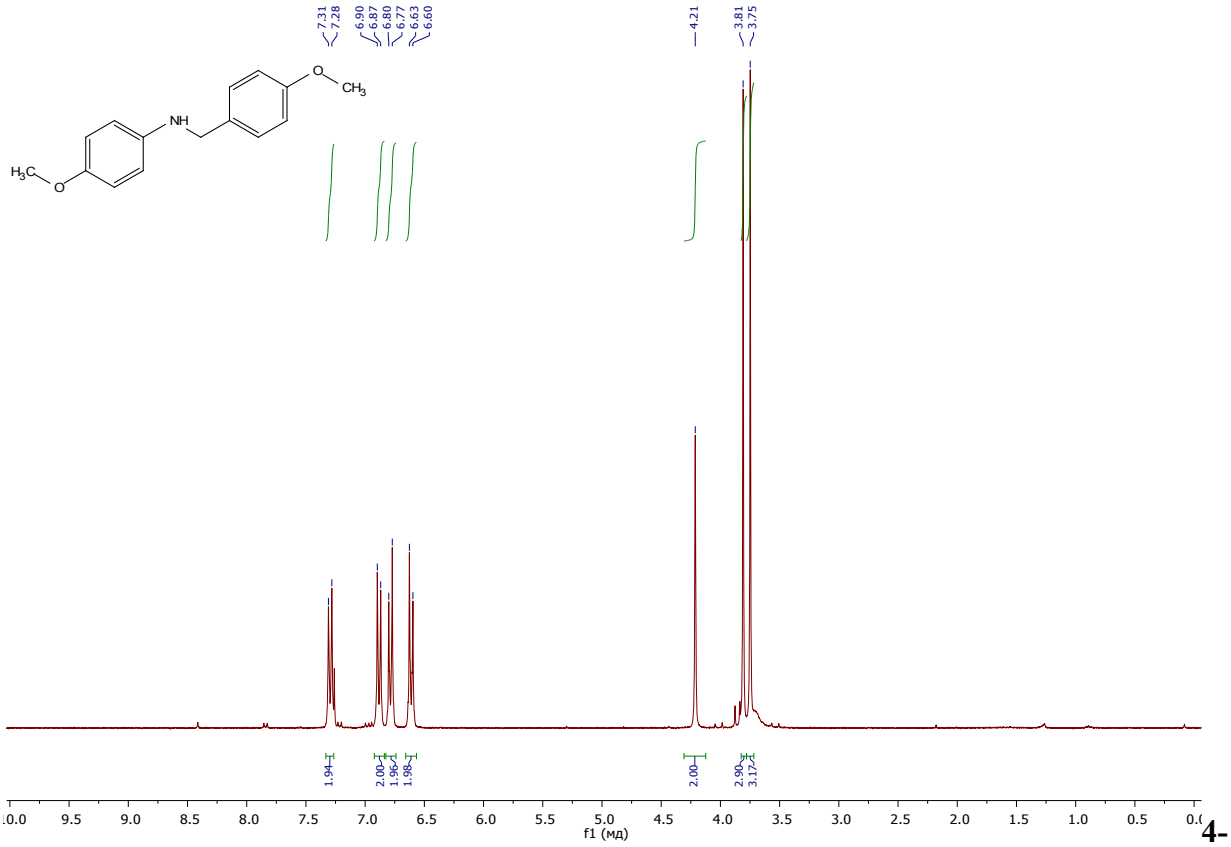
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

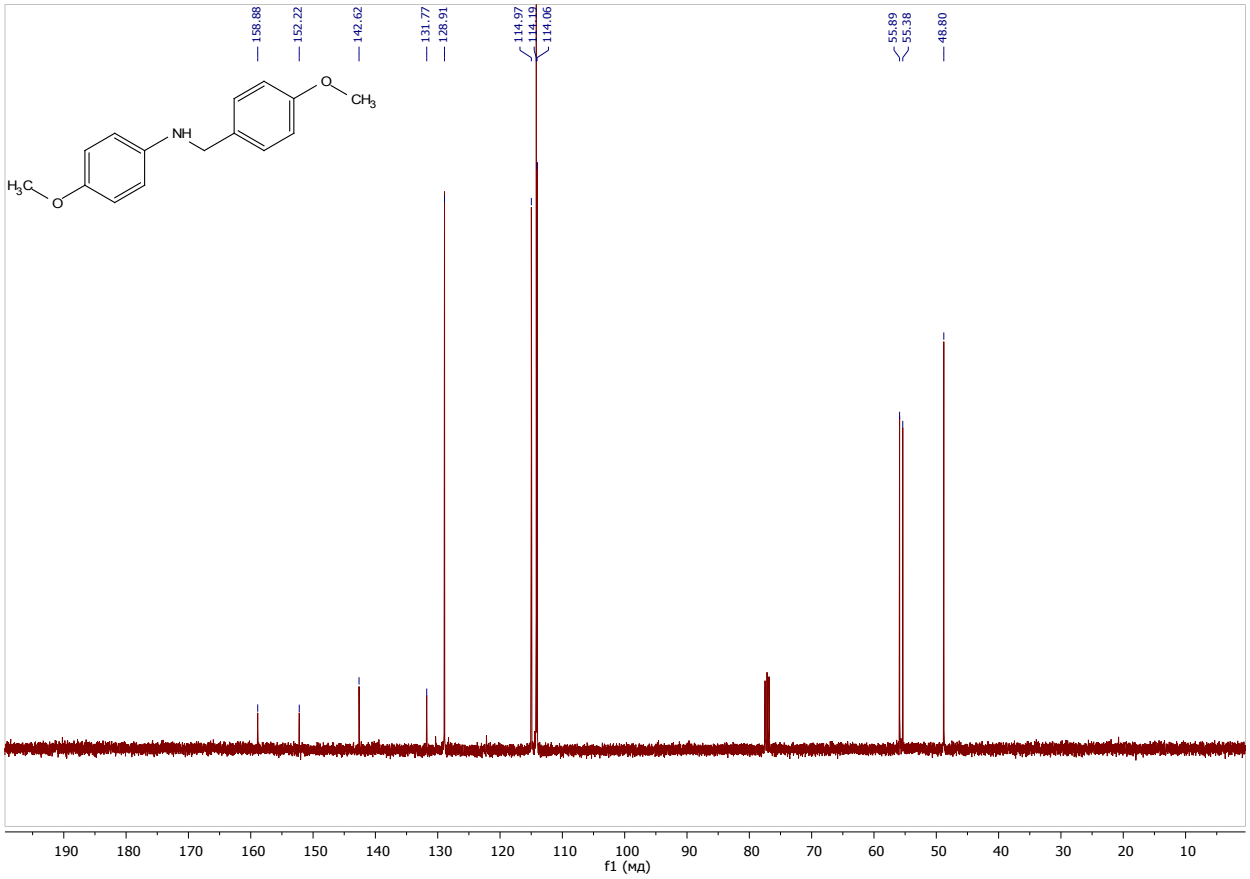


9. ^{1}H and ^{13}C NMR spectra of the RA products.

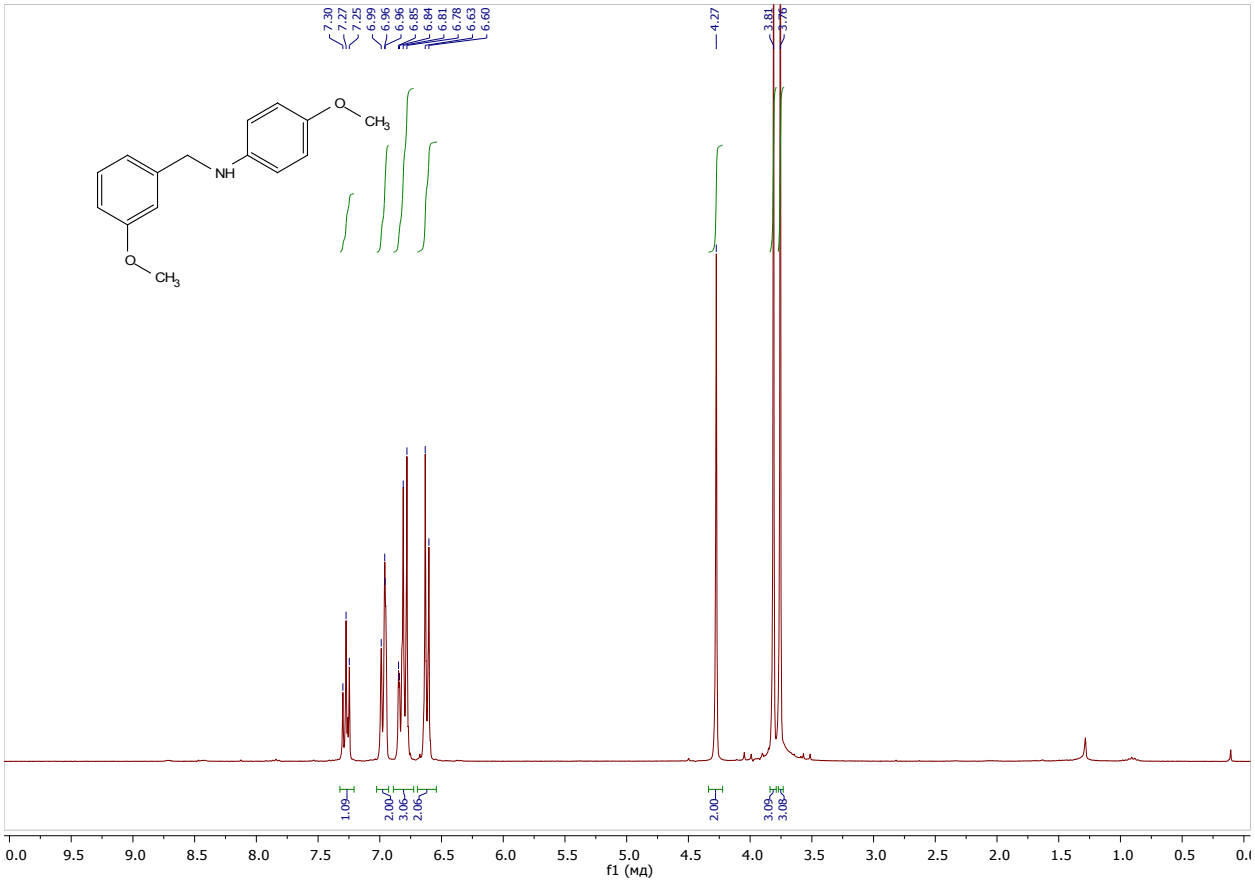
4-methoxy-N-(4-methoxybenzyl)aniline (1) ^{1}H NMR (300 MHz, $CDCl_3$)



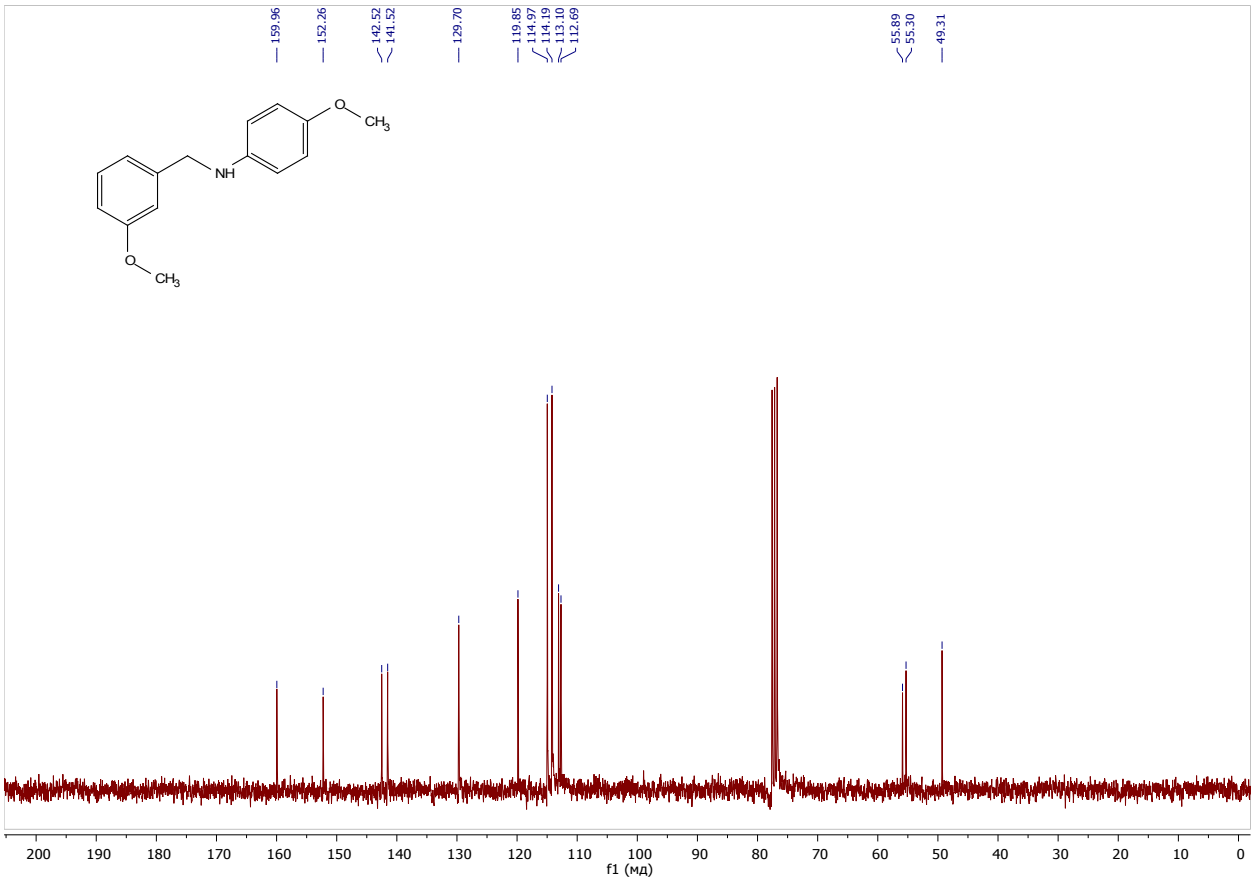
4-methoxy-N-(4-methoxybenzyl)aniline (1) ^{13}C NMR (101 MHz, $CDCl_3$)



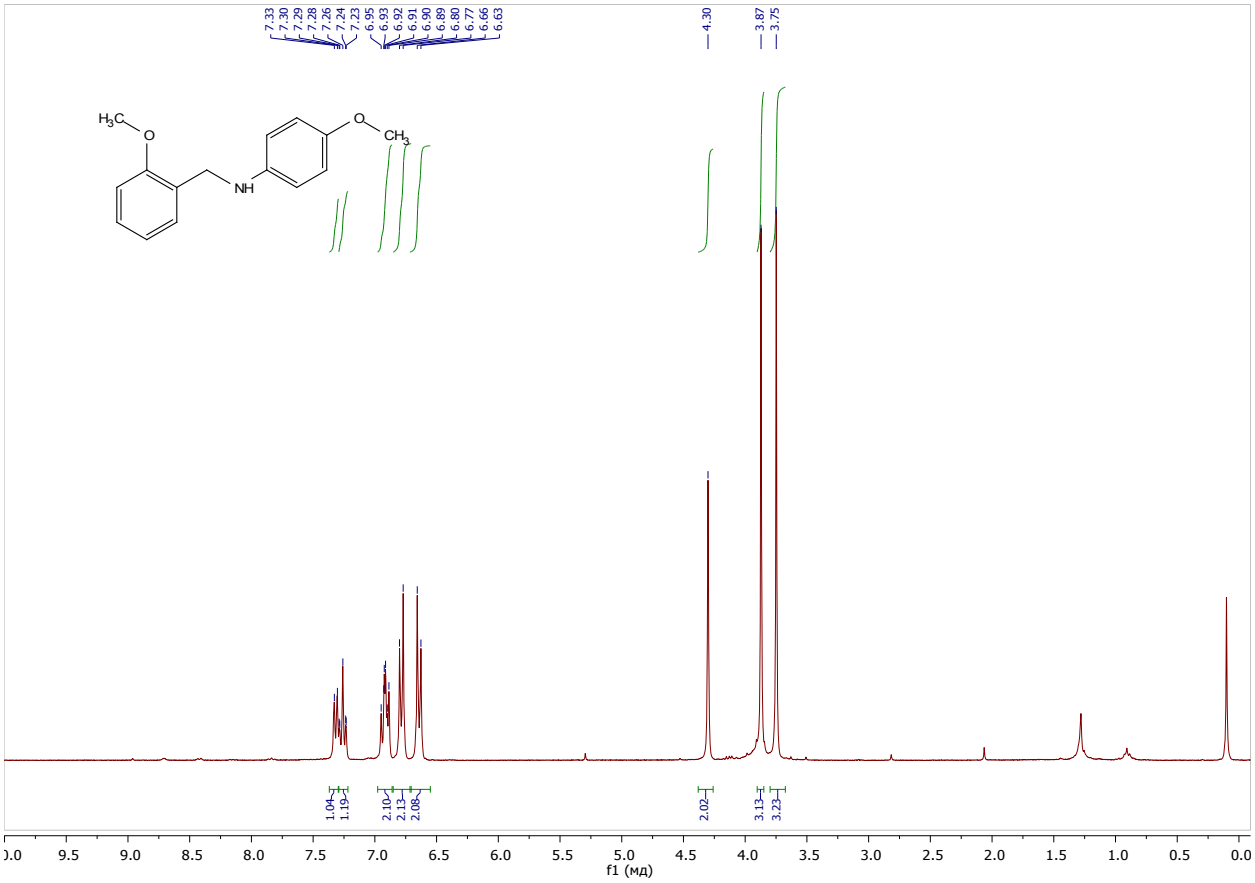
4-methoxy-N-(3-methoxybenzyl)aniline (2) ^{1}H NMR (300 MHz, $CDCl_3$)



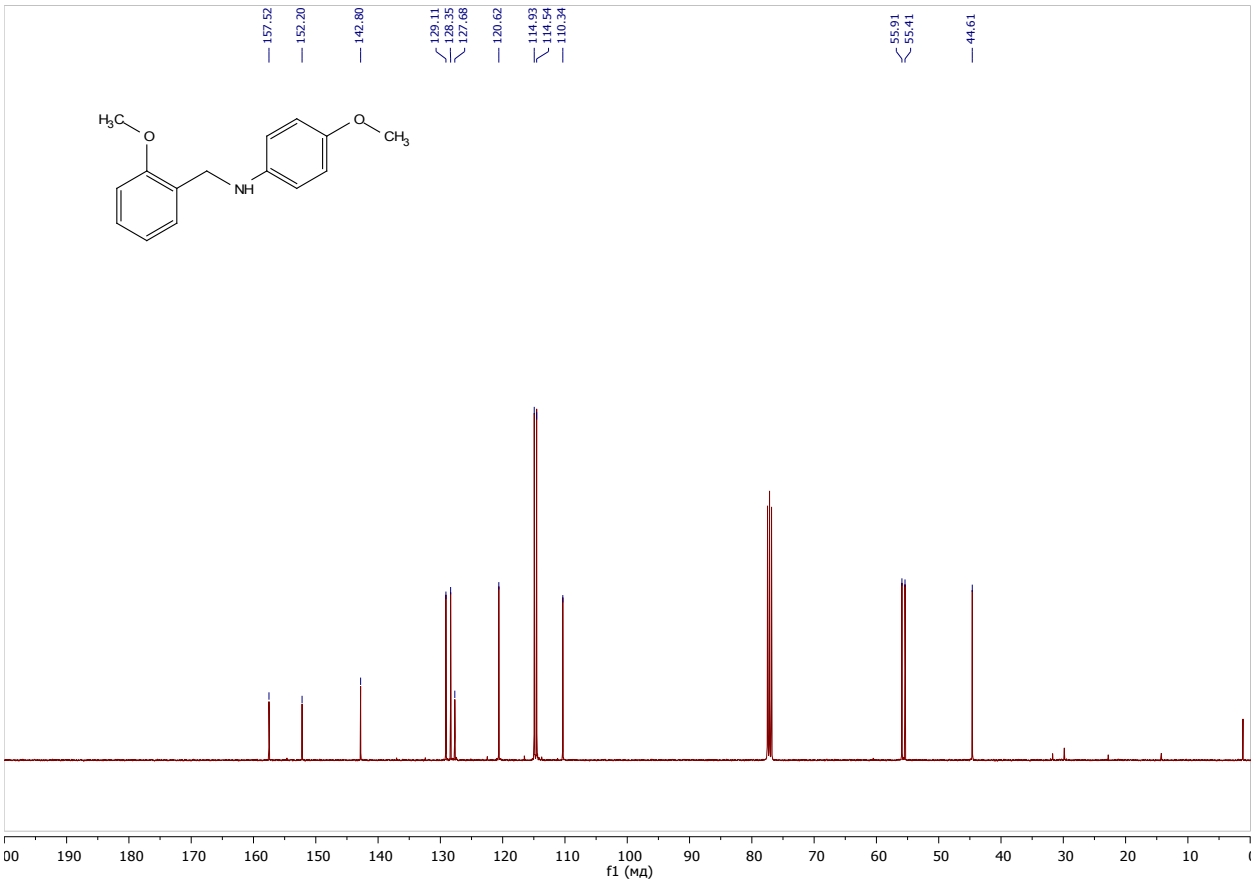
4-methoxy-N-(3-methoxybenzyl)aniline (2) ^{13}C NMR (101 MHz, $CDCl_3$)



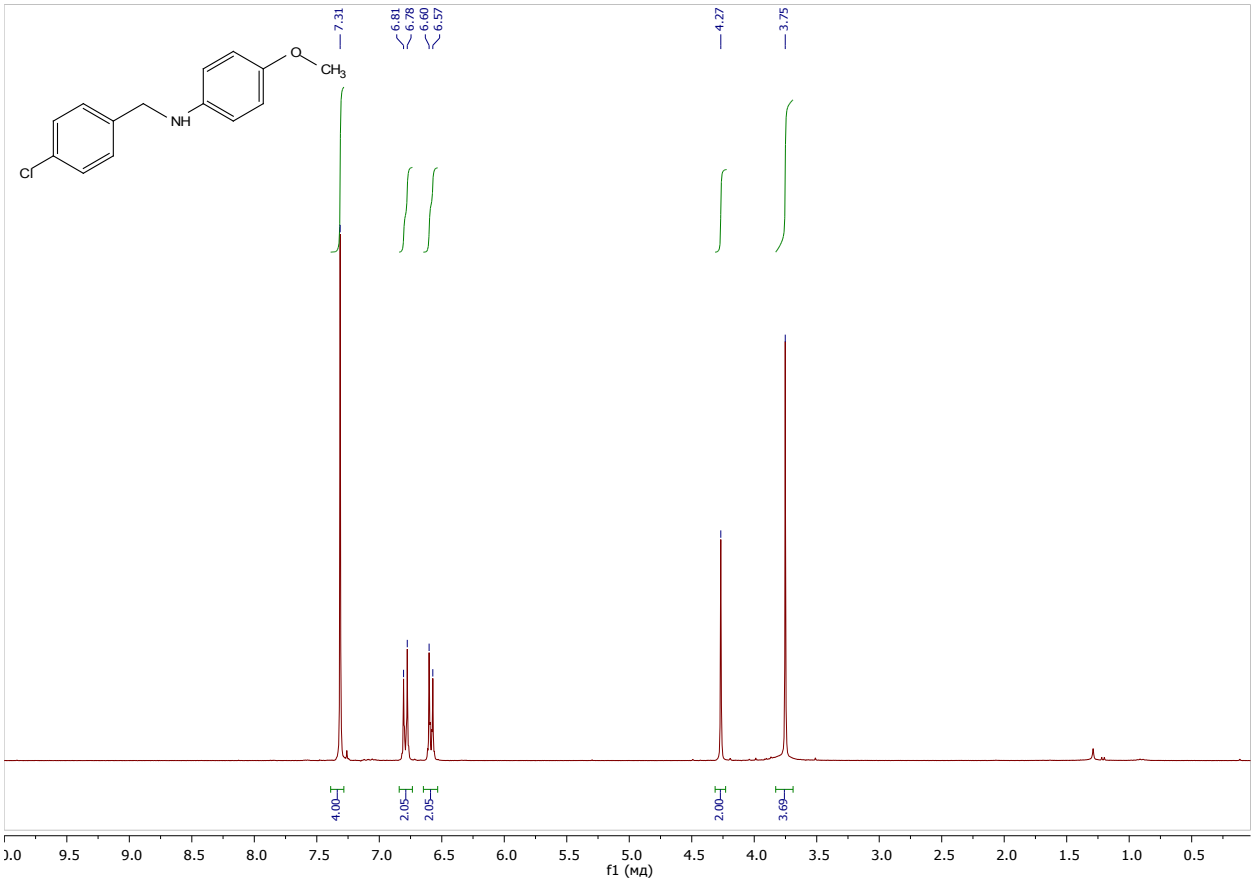
4-methoxy-N-(2-methoxybenzyl)aniline (3) ^{1}H NMR (300 MHz, $CDCl_3$)



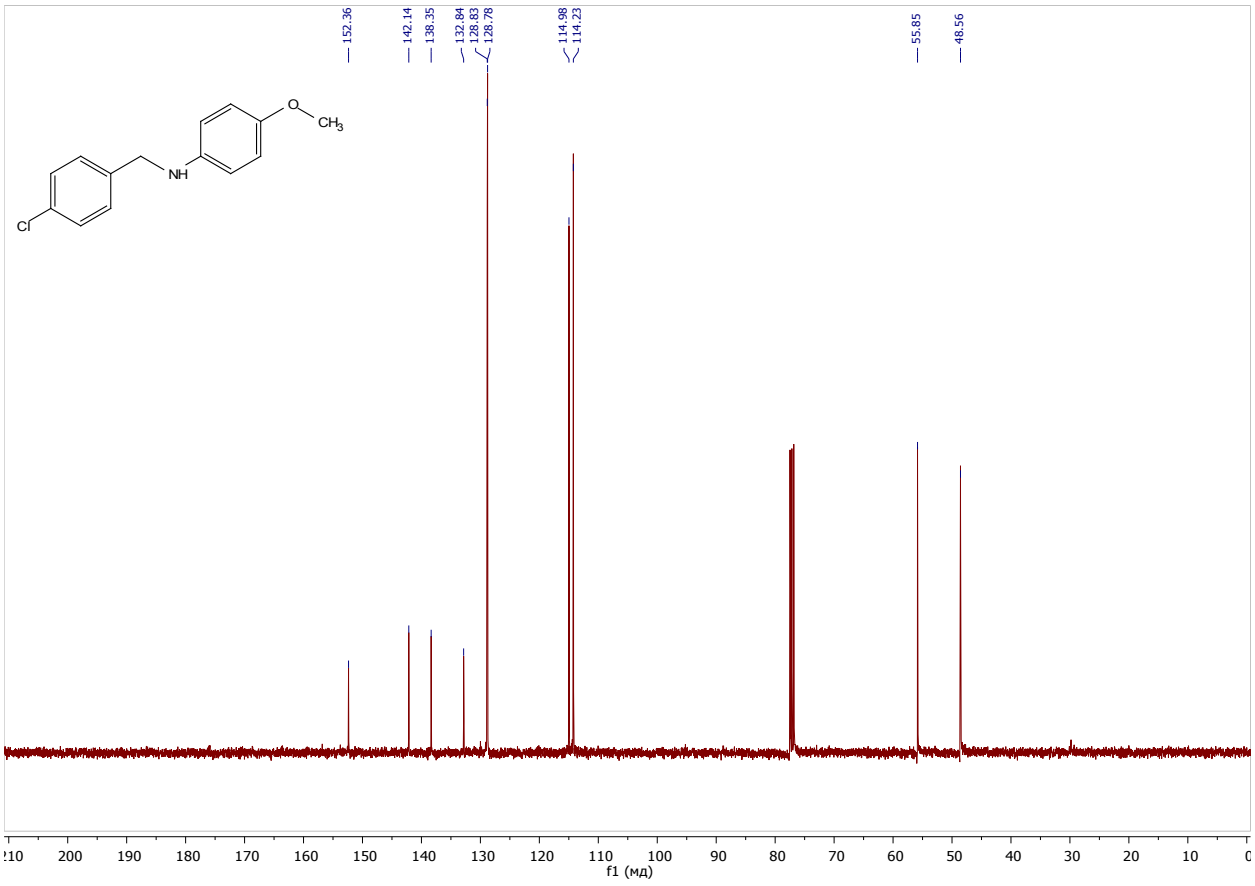
4-methoxy-N-(2-methoxybenzyl)aniline (3) ^{13}C NMR (101 MHz, $CDCl_3$)



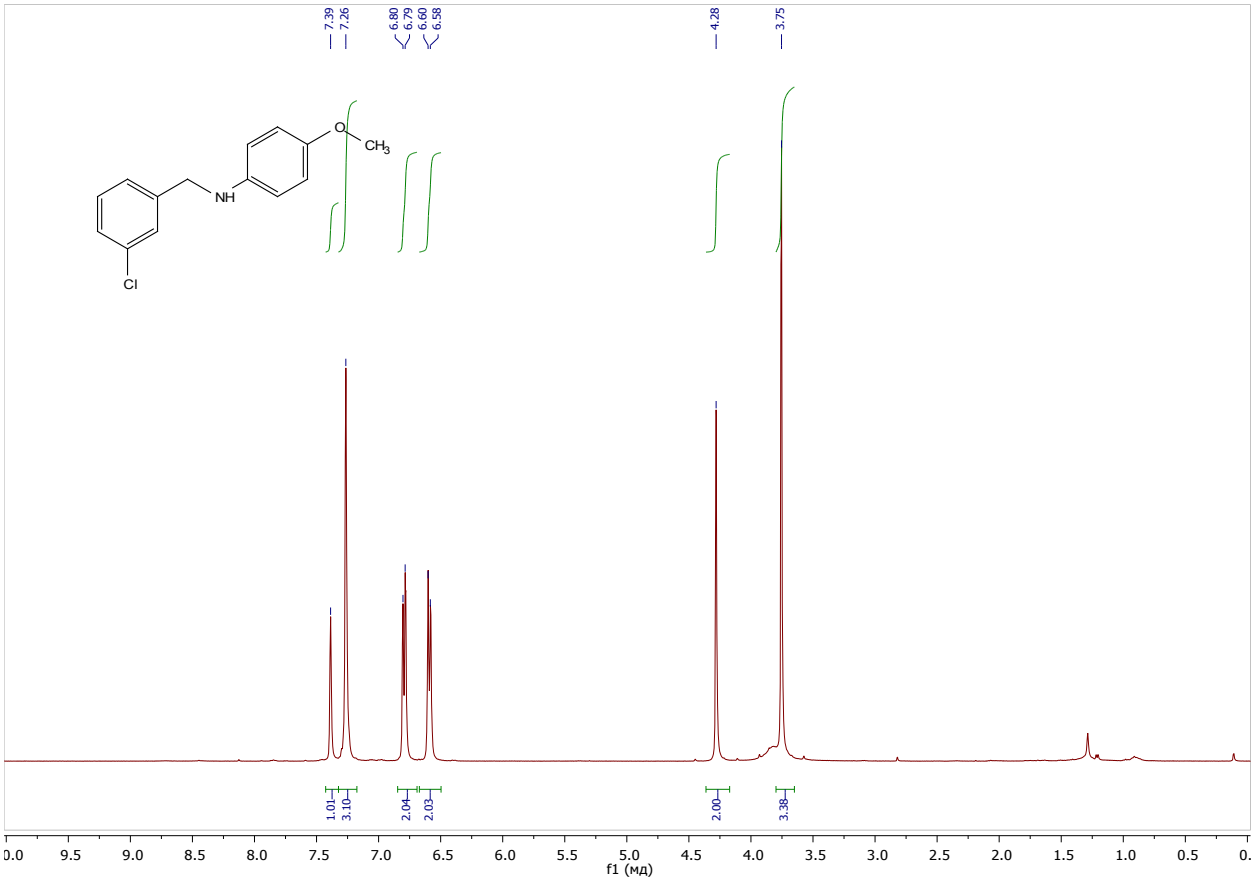
N-(4-chlorobenzyl)-4-methoxyaniline (4) ^{1}H NMR (300 MHz, $CDCl_3$)



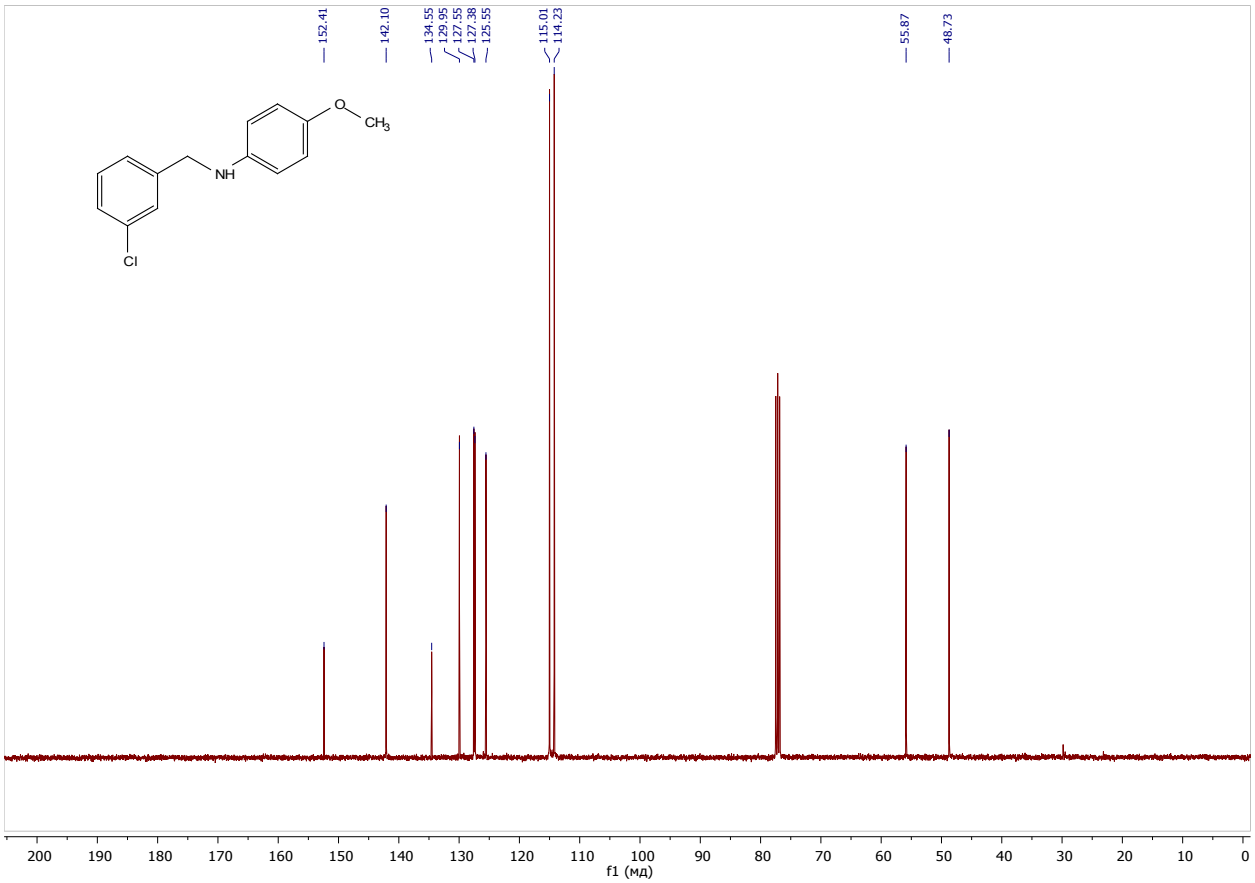
N-(4-chlorobenzyl)-4-methoxyaniline (4) ^{13}C NMR (101 MHz, $CDCl_3$)



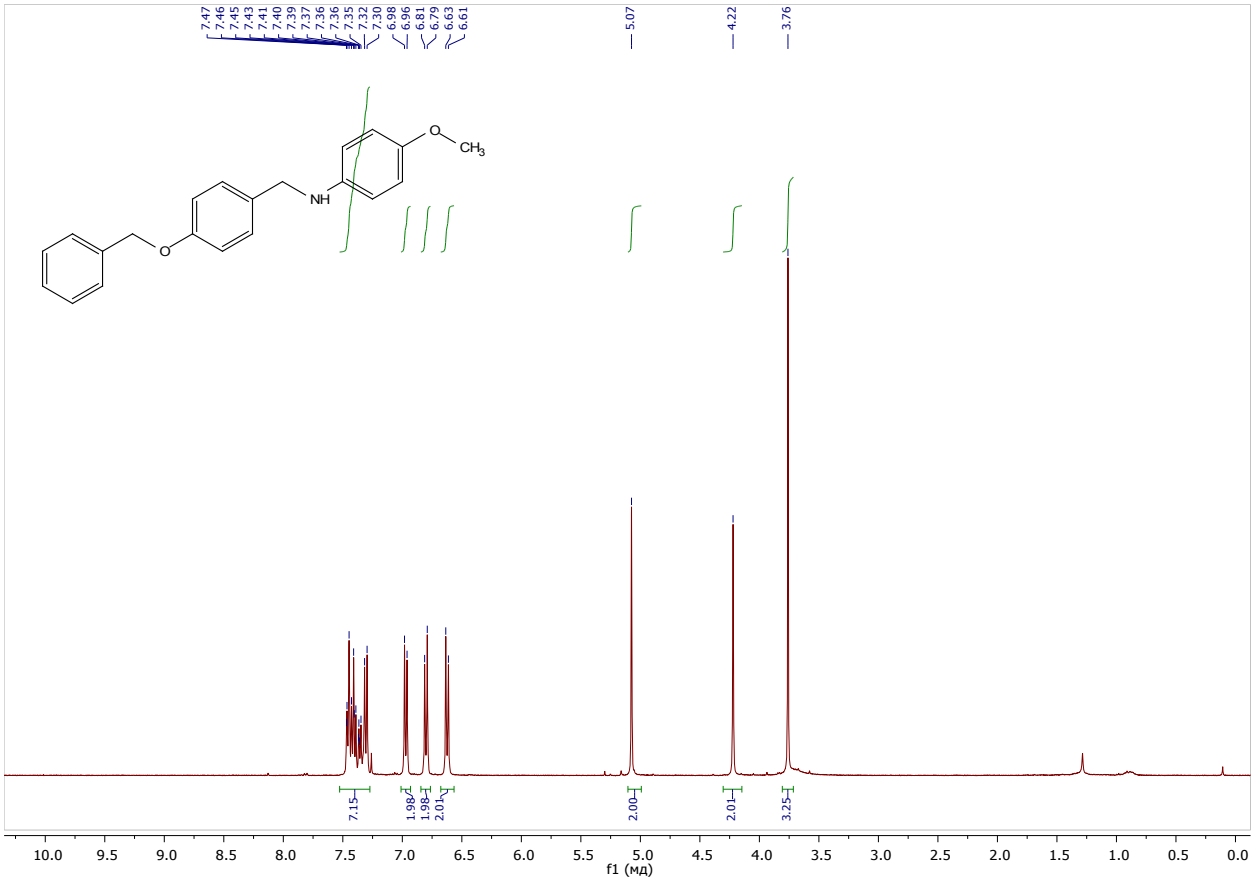
N-(3-chlorobenzyl)-4-methoxyaniline (5) ^{1}H NMR (400 MHz, $CDCl_3$)



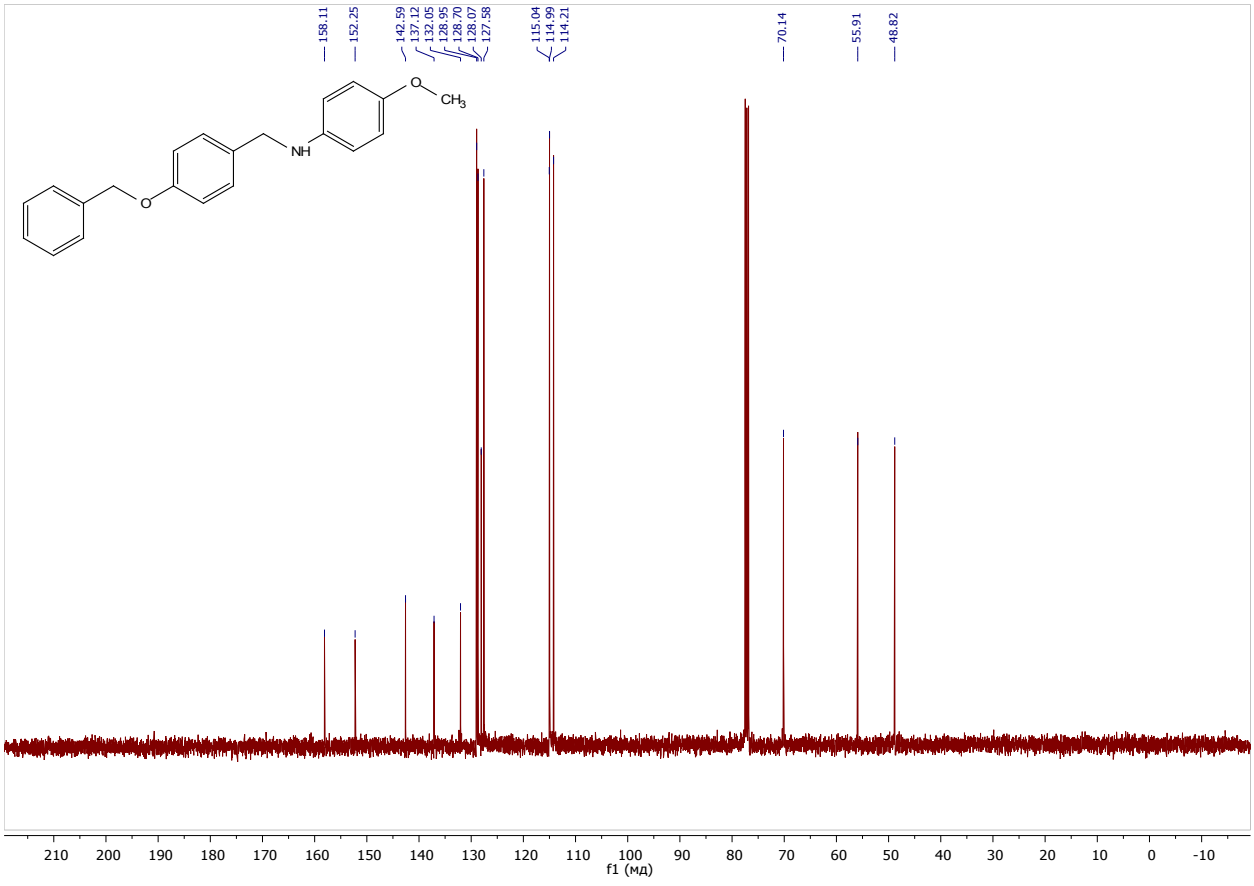
N-(3-chlorobenzyl)-4-methoxyaniline (5) ^{13}C NMR (101 MHz, $CDCl_3$)



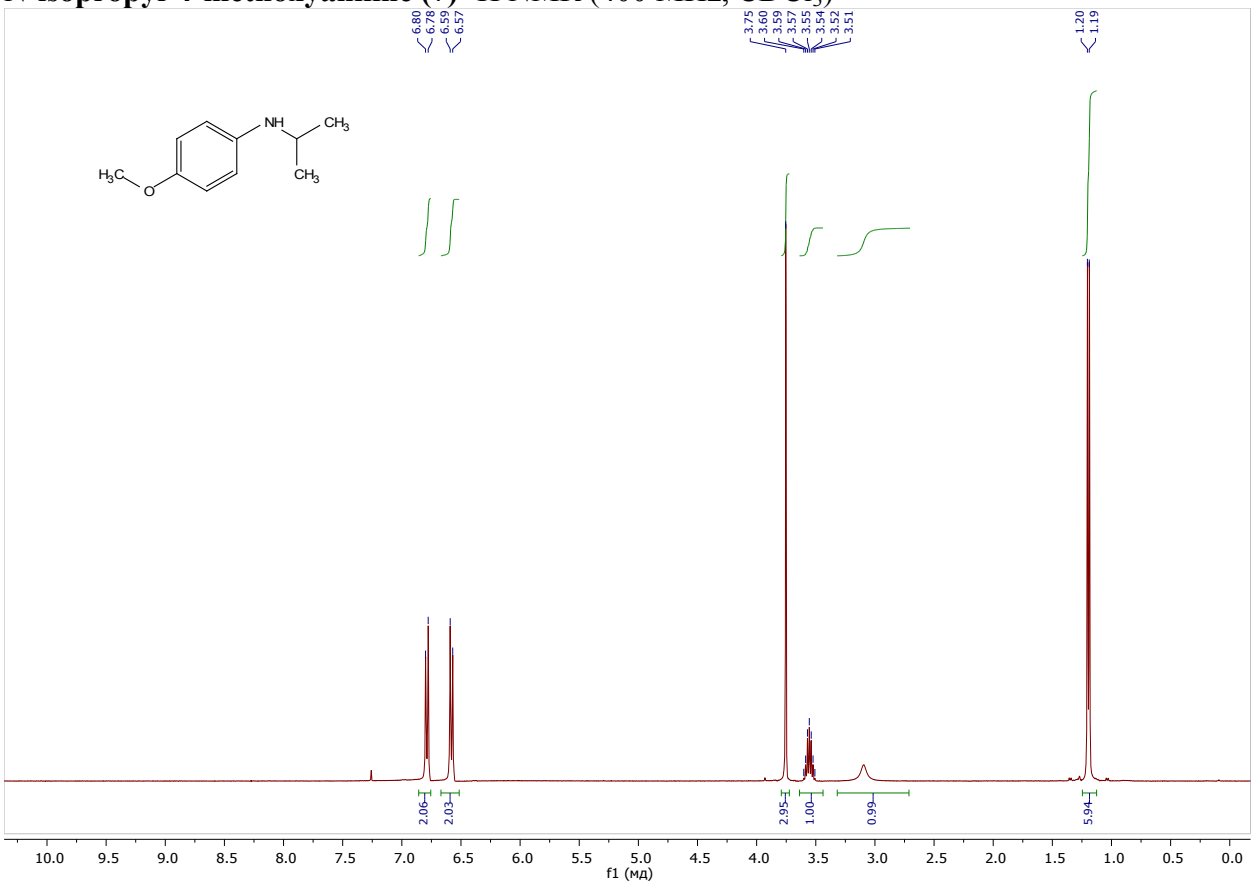
N-(4-(benzyloxy)benzyl)-4-methoxyaniline (6) ^{1}H NMR (400 MHz, $CDCl_3$)



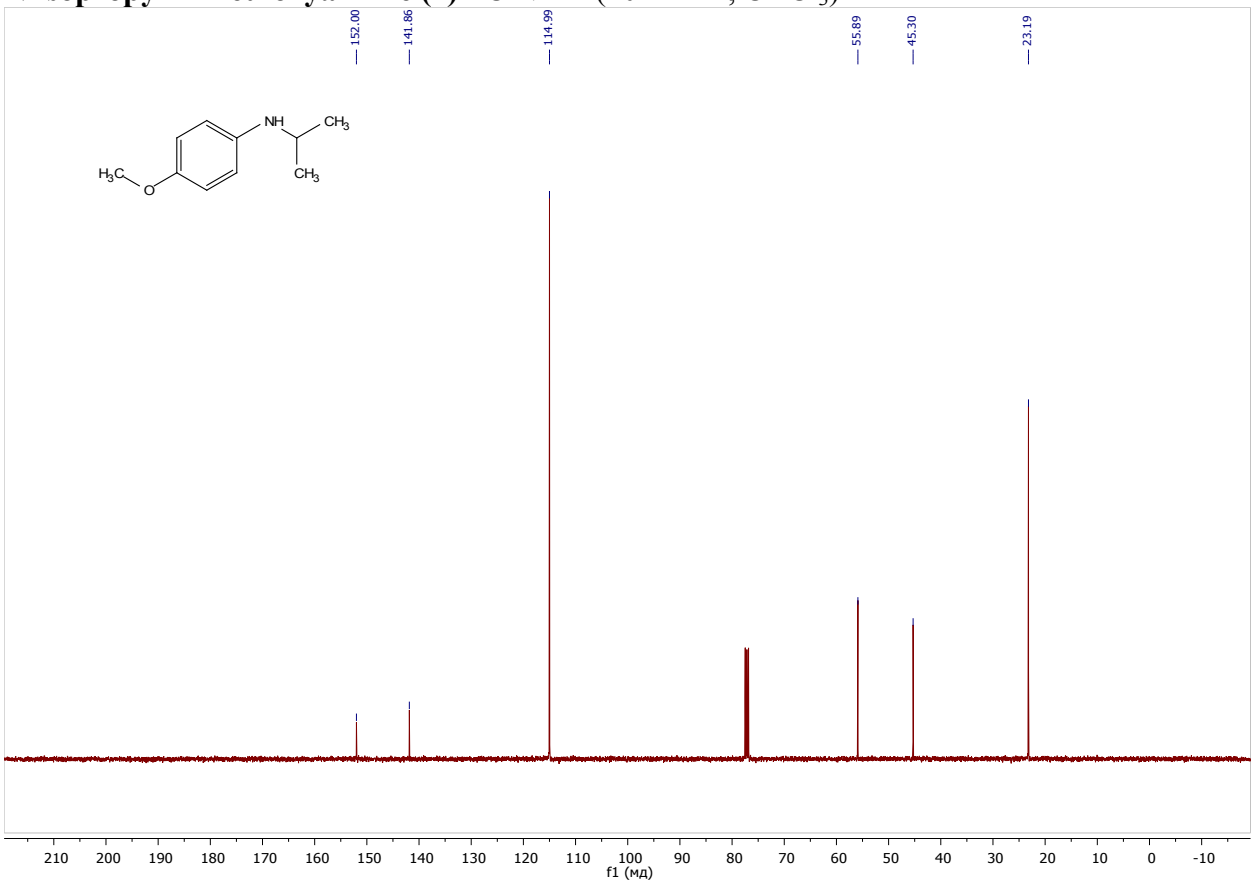
N-(4-(benzyloxy)benzyl)-4-methoxyaniline (6) ^{13}C NMR (101 MHz, $CDCl_3$)



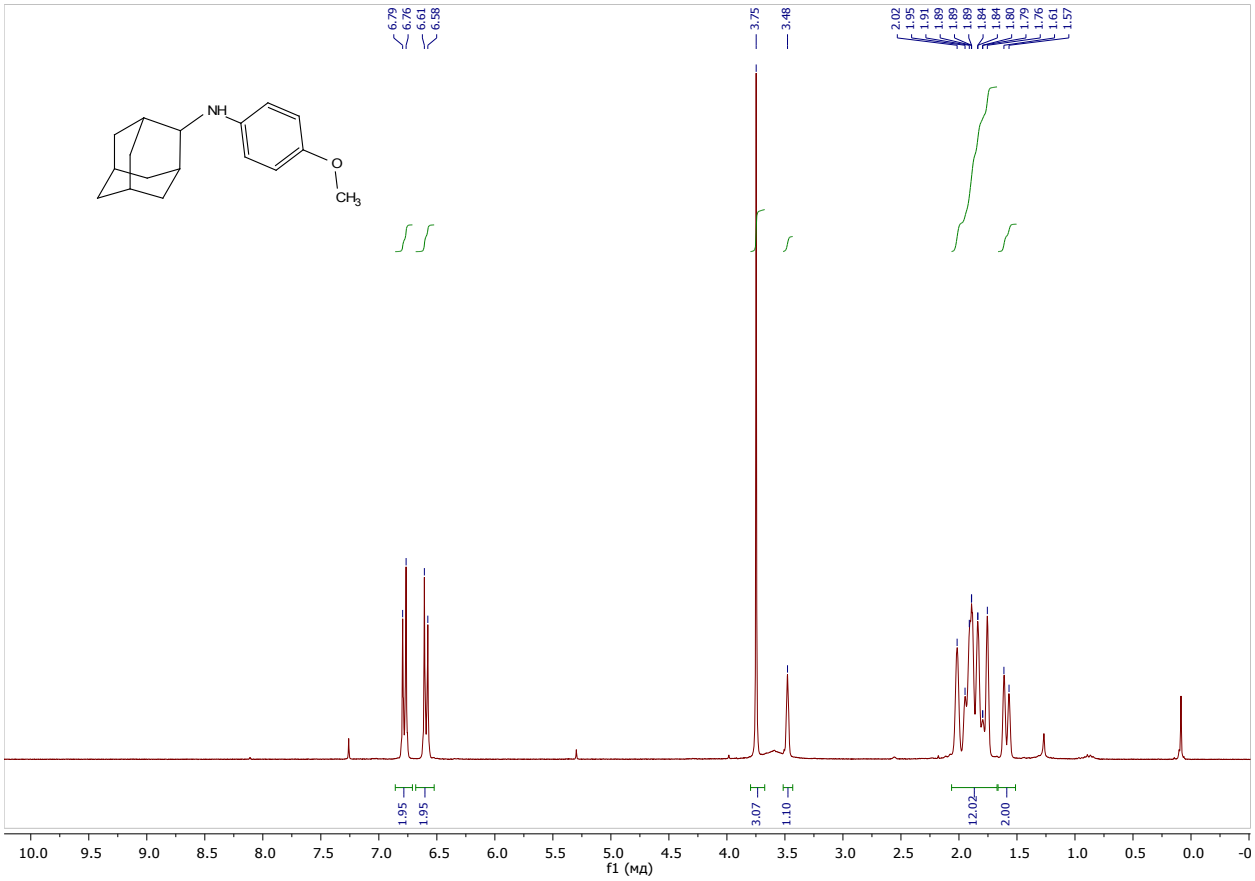
N-isopropyl-4-methoxyaniline (7) ^{1}H NMR (400 MHz, $CDCl_3$)



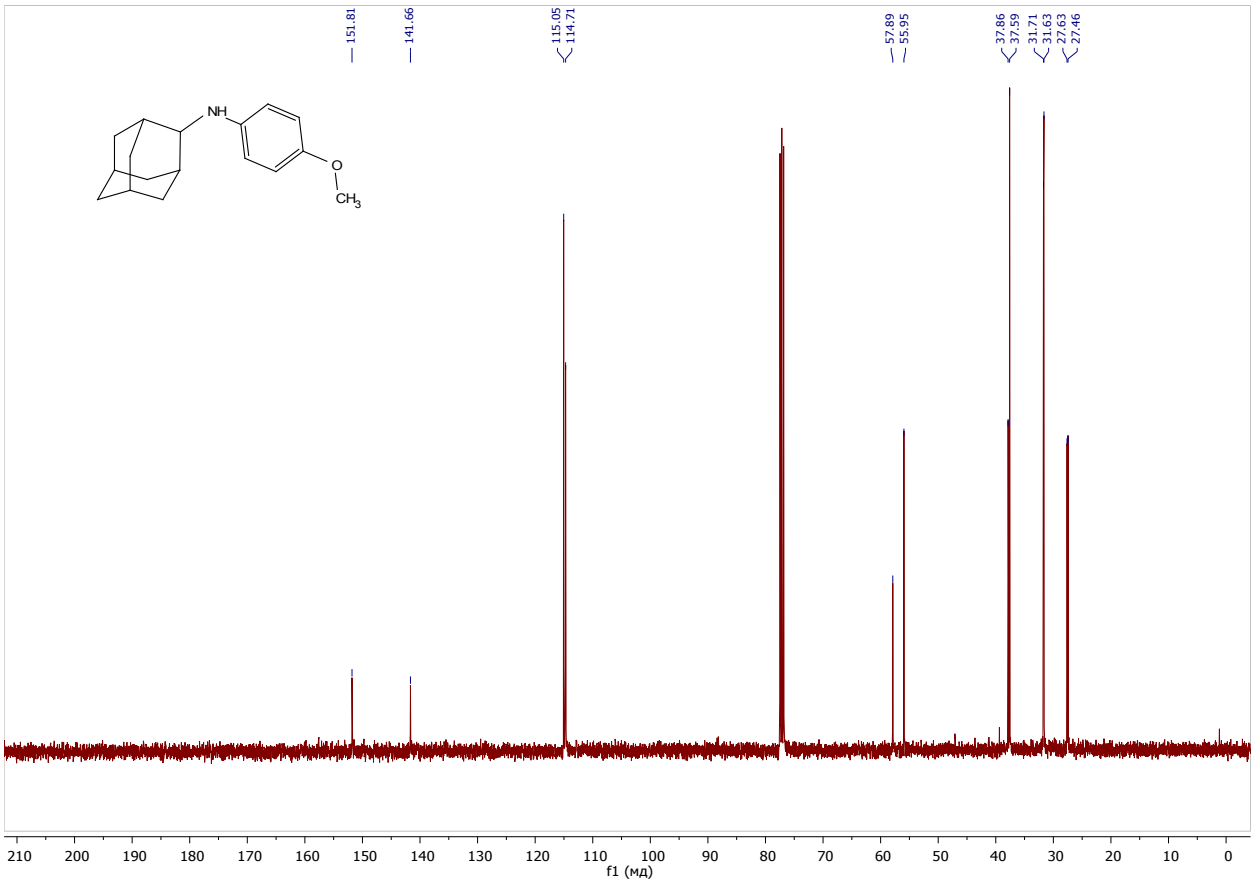
N-isopropyl-4-methoxyaniline (7) ^{13}C NMR (101 MHz, $CDCl_3$)



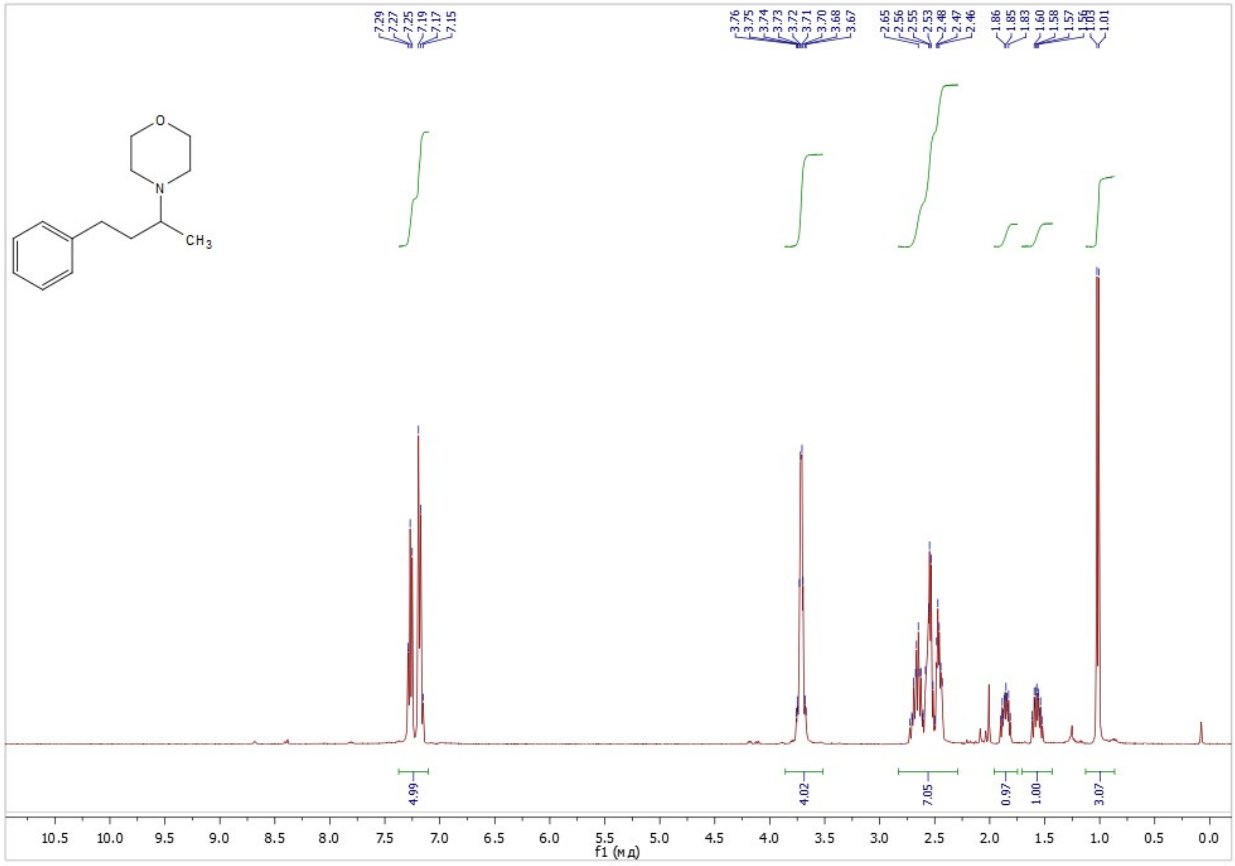
N-(4-methoxyphenyl)adamantan-2-amine (8) ^{1}H NMR (300 MHz, $CDCl_3$)



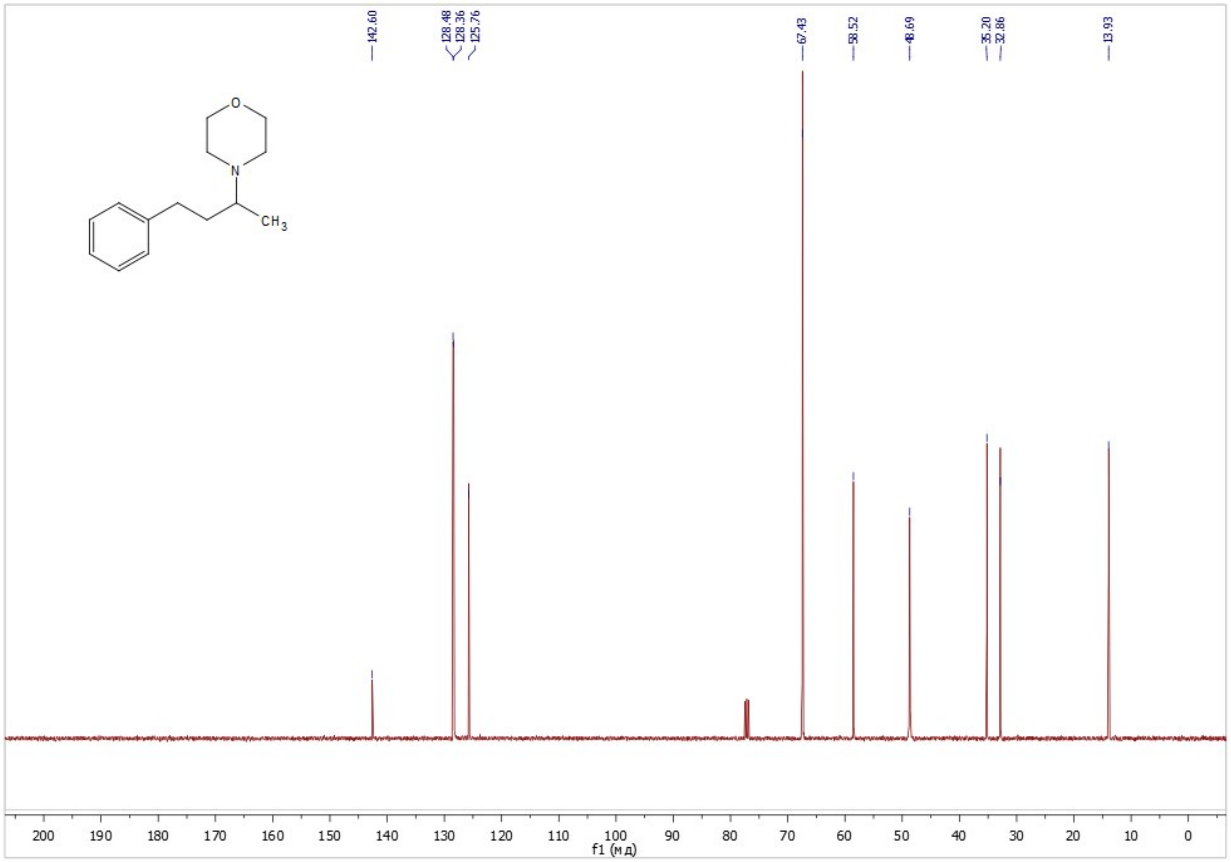
N-(4-methoxyphenyl)adamantan-2-amine (8) ^{13}C NMR (101 MHz, $CDCl_3$)



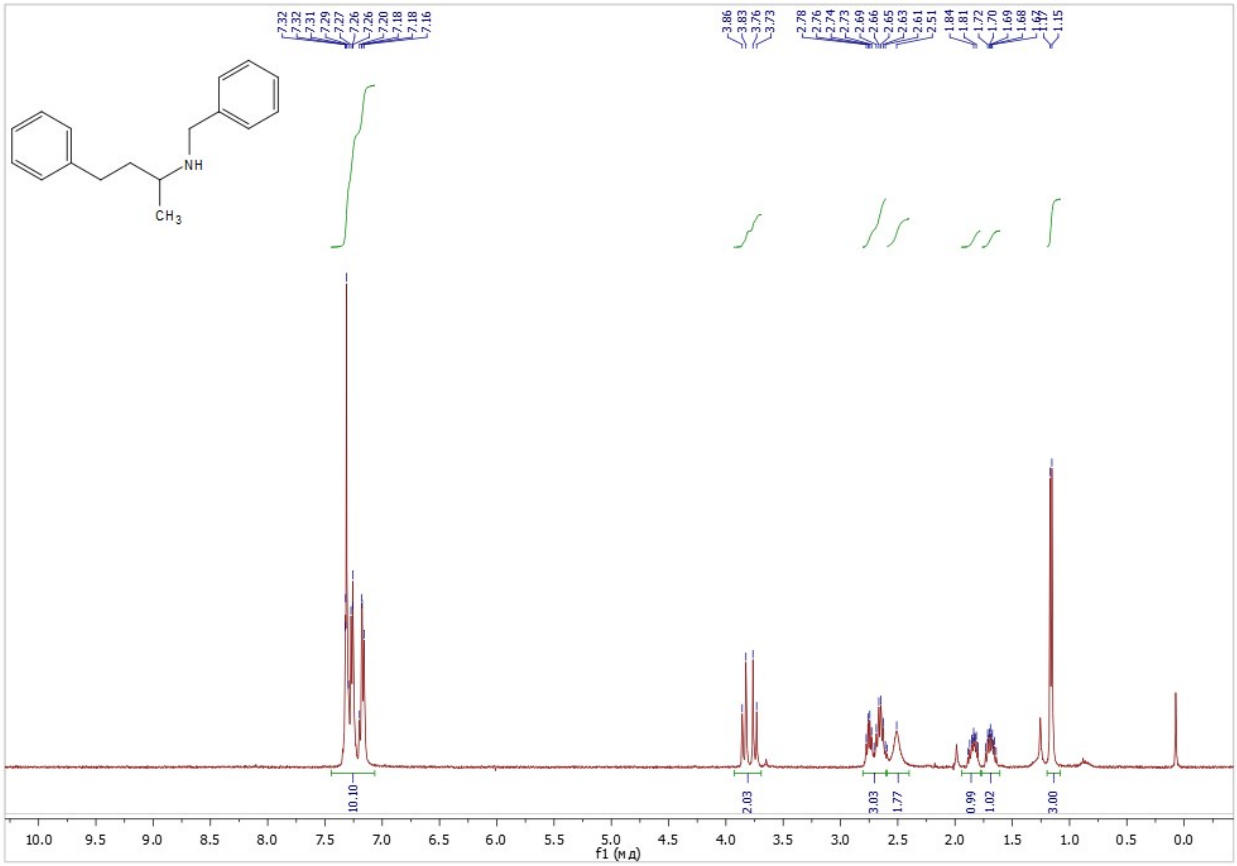
4-(4-phenylbutan-2-yl)-morpholine (9) ^{1}H NMR (400 MHz, $CDCl_3$)



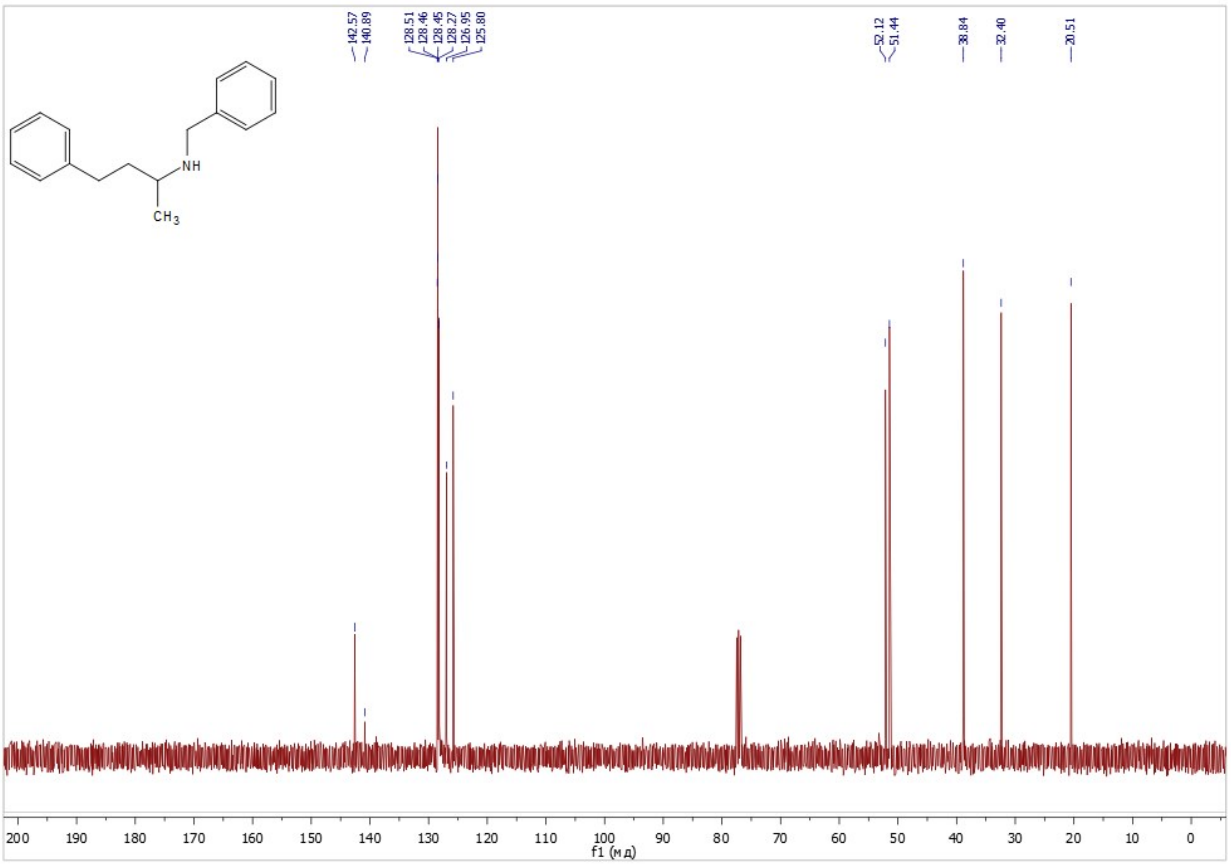
4-(4-phenylbutan-2-yl)-morpholine (9) ^{13}C NMR (101 MHz, $CDCl_3$)



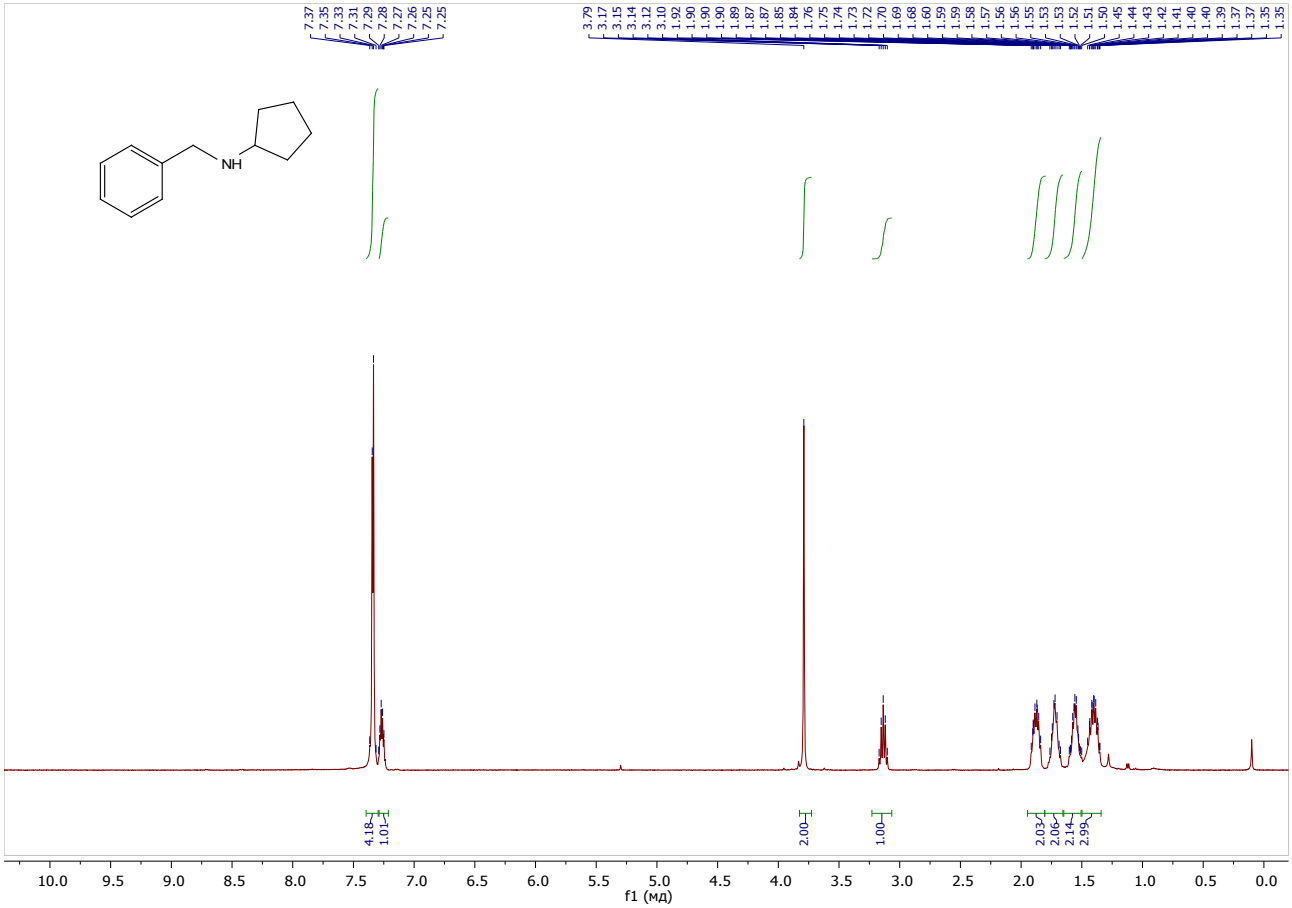
N-benzyl-4-phenylbutan-2-amine (10) ^{1}H NMR (400 MHz, $CDCl_3$)



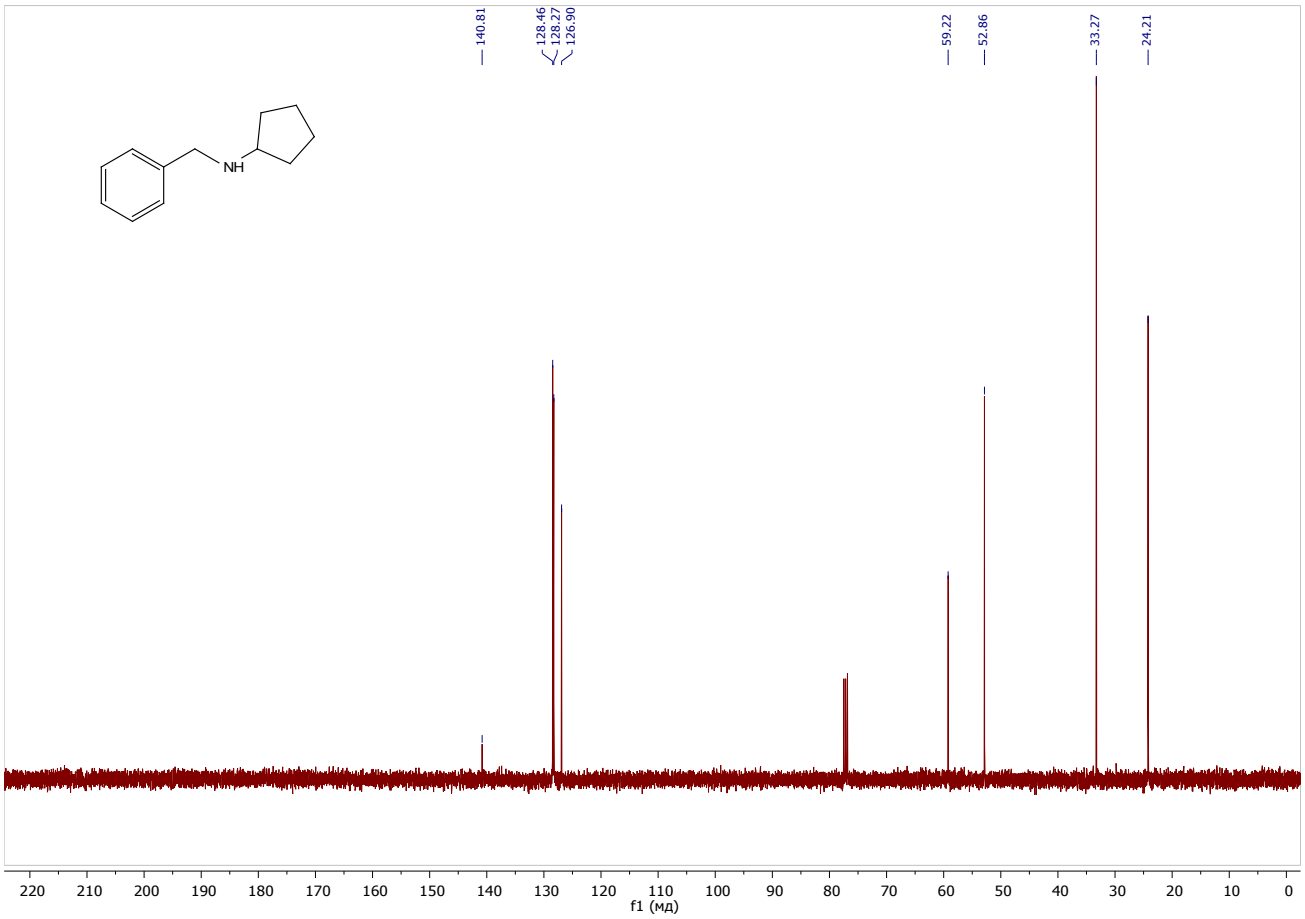
N-benzyl-4-phenylbutan-2-amine (10) ^{13}C NMR (101 MHz, $CDCl_3$)



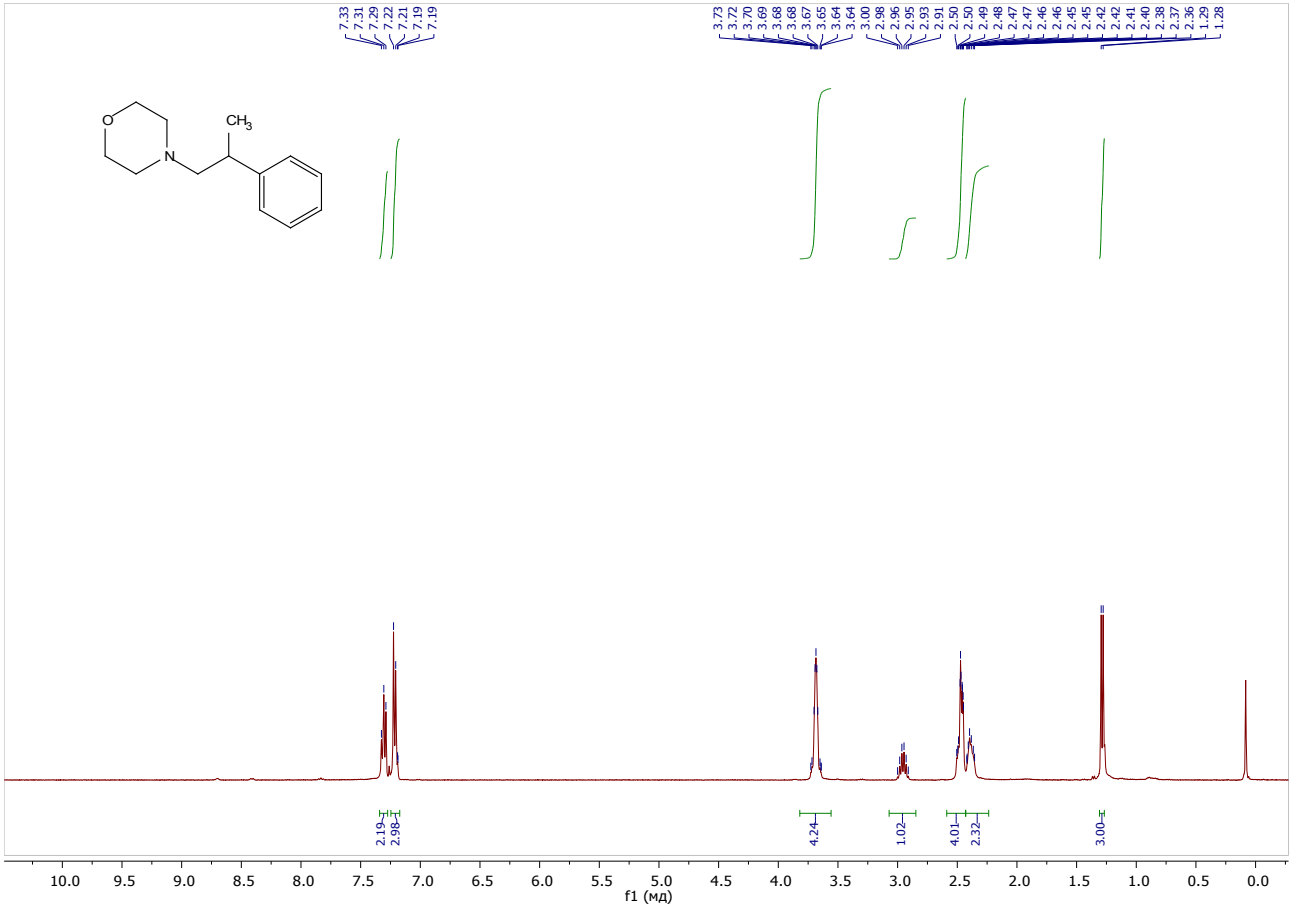
N-benzylcyclopentanamine (11) ^{1}H NMR (400 MHz, $CDCl_3$)



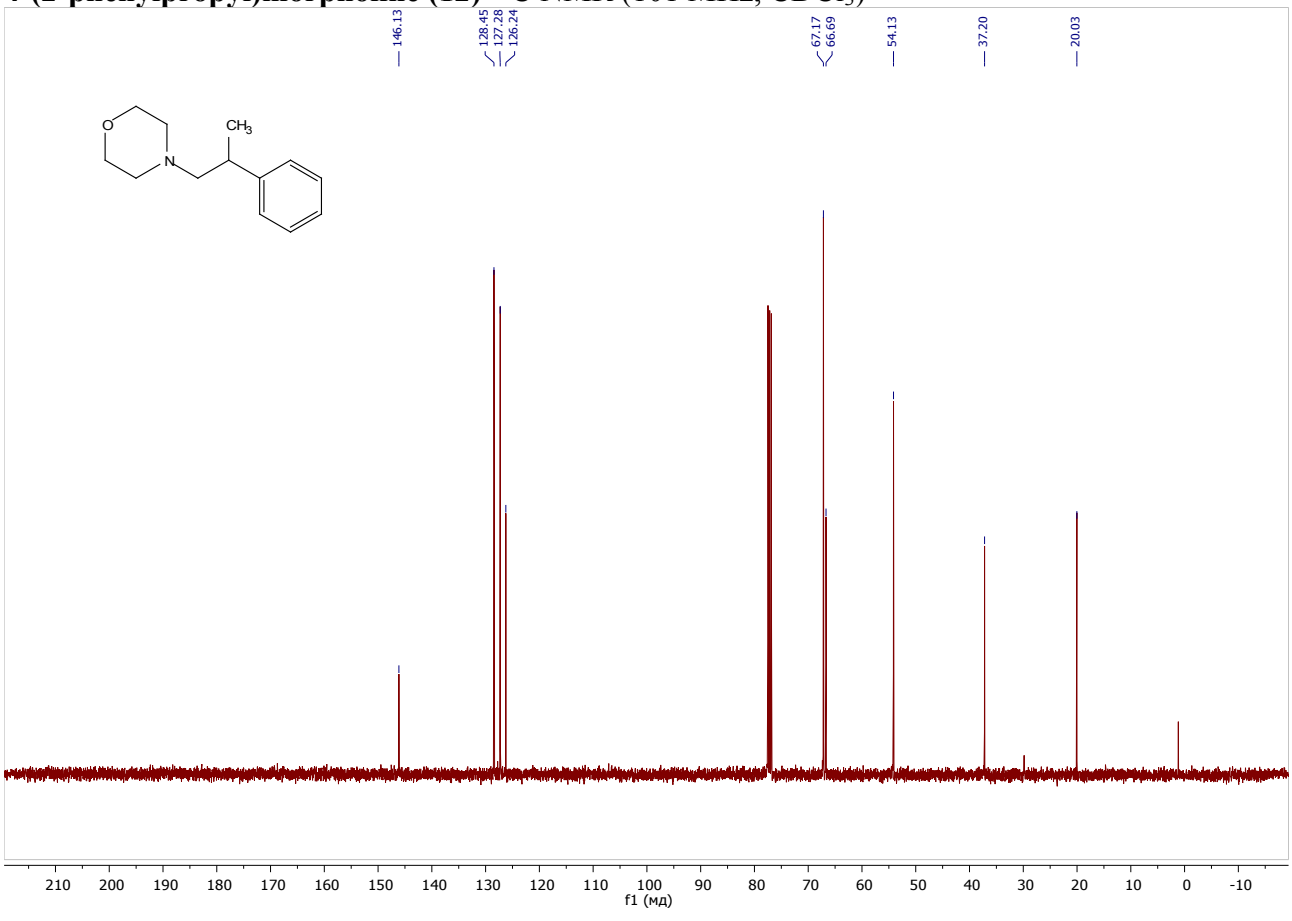
N-benzylcyclopentanamine (11) ^{13}C NMR (101 MHz, $CDCl_3$)



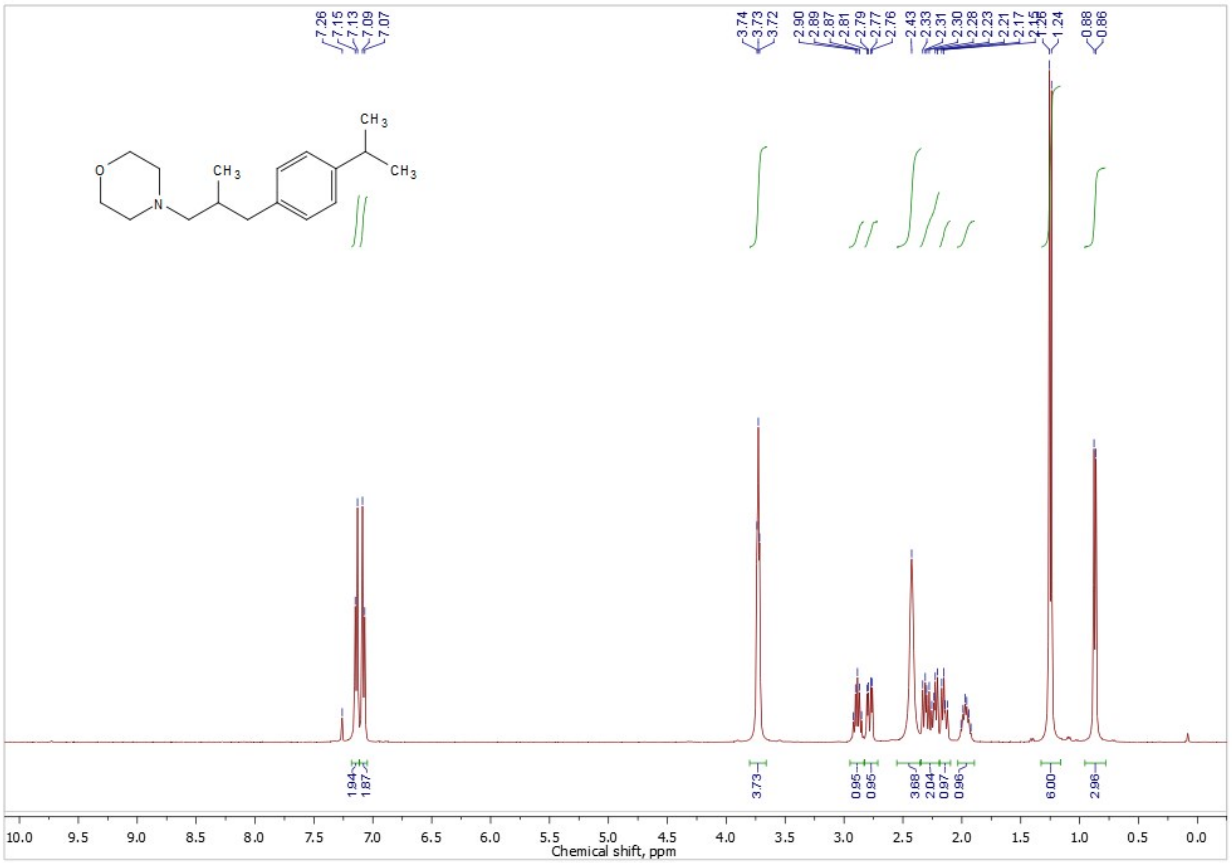
4-(2-phenylpropyl)morpholine (12) ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$)



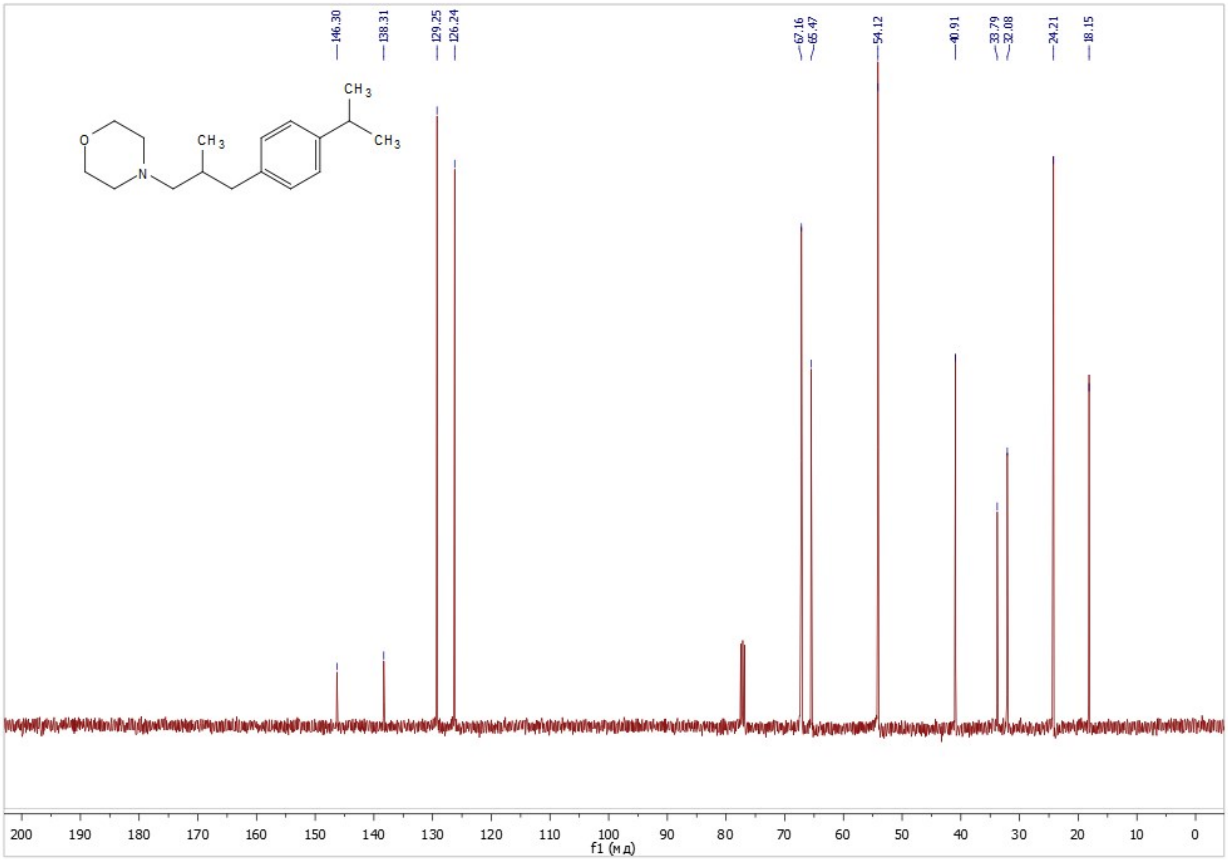
4-(2-phenylpropyl)morpholine (12) ^{13}C NMR (101 MHz, $CDCl_3$)



4-(3-(4-isopropylphenyl)-2-methylpropyl)morpholine (13) ^{1}H NMR (400 MHz, $CDCl_3$)



4-(3-(4-isopropylphenyl)-2-methylpropyl)morpholine (13) ^{13}C NMR (101 MHz, $CDCl_3$)



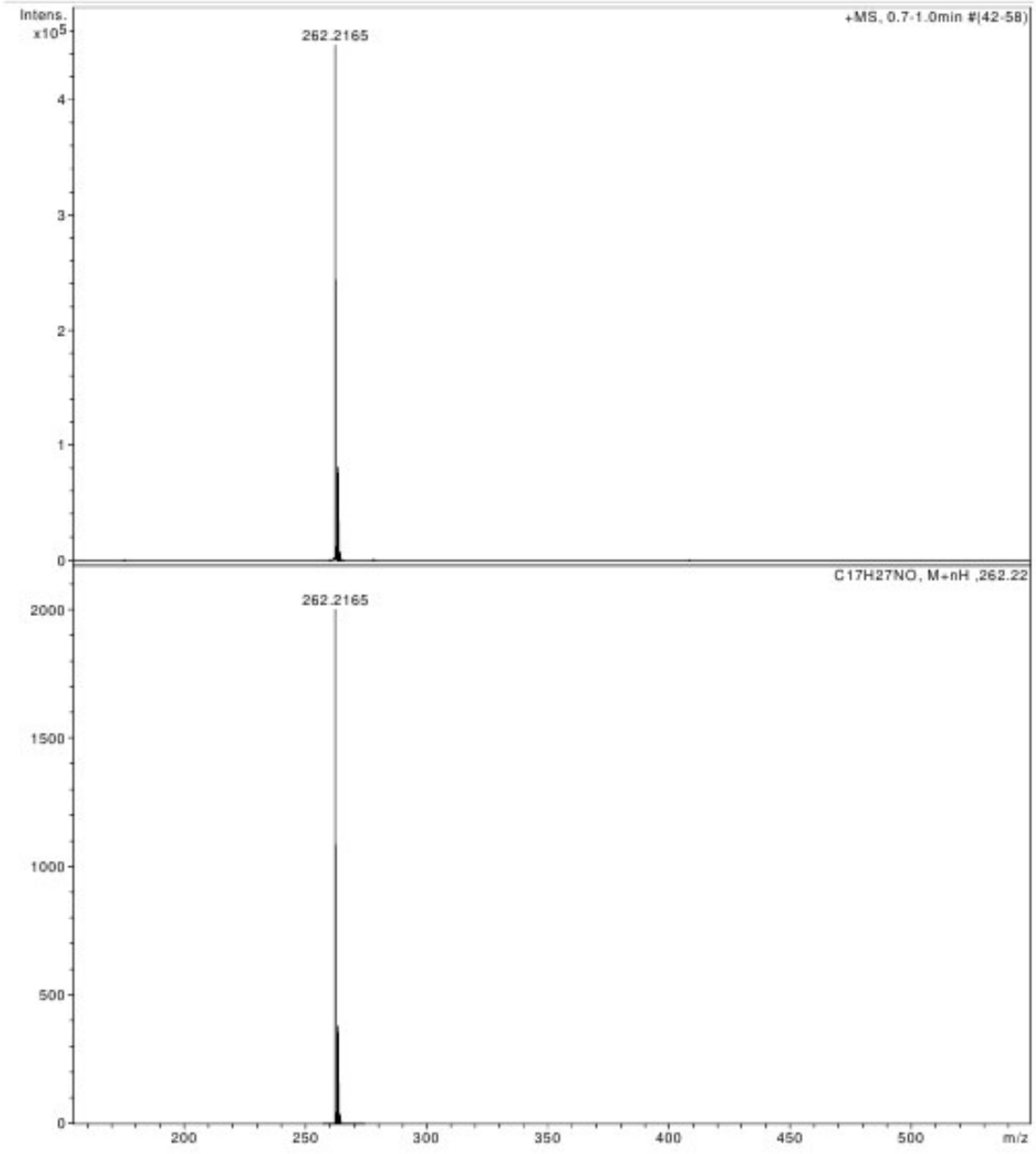
Display Report

Analysis Info

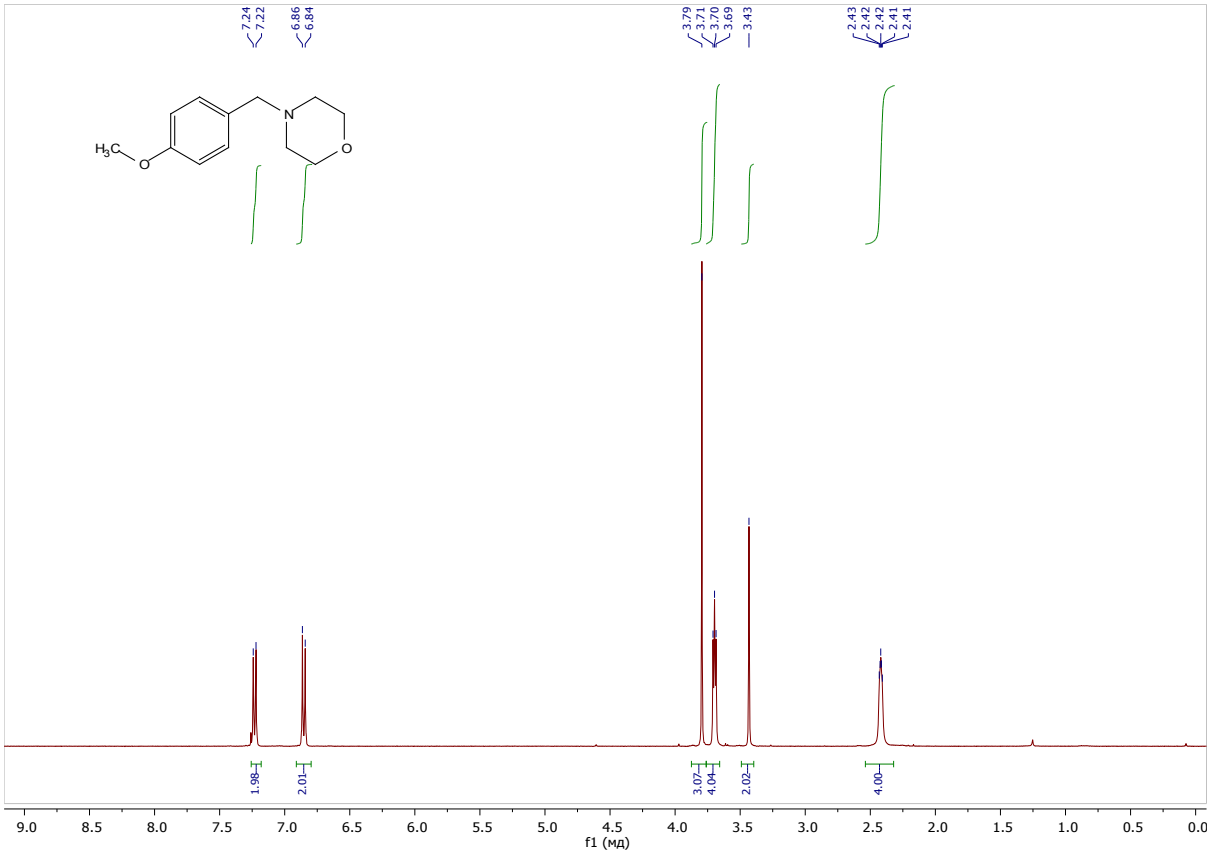
Analysis Name	D:\Data\Kolotyrkina\2021\Novikov\0414023.d	Acquisition Date	14.04.2021 16:14:00
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/MNOV LB-05-iPr	Instrument / Ser#	micrOTOF 10248
Comment	C17H27NO mH 262.2165 calibrant added CH3CN		

Acquisition Parameter

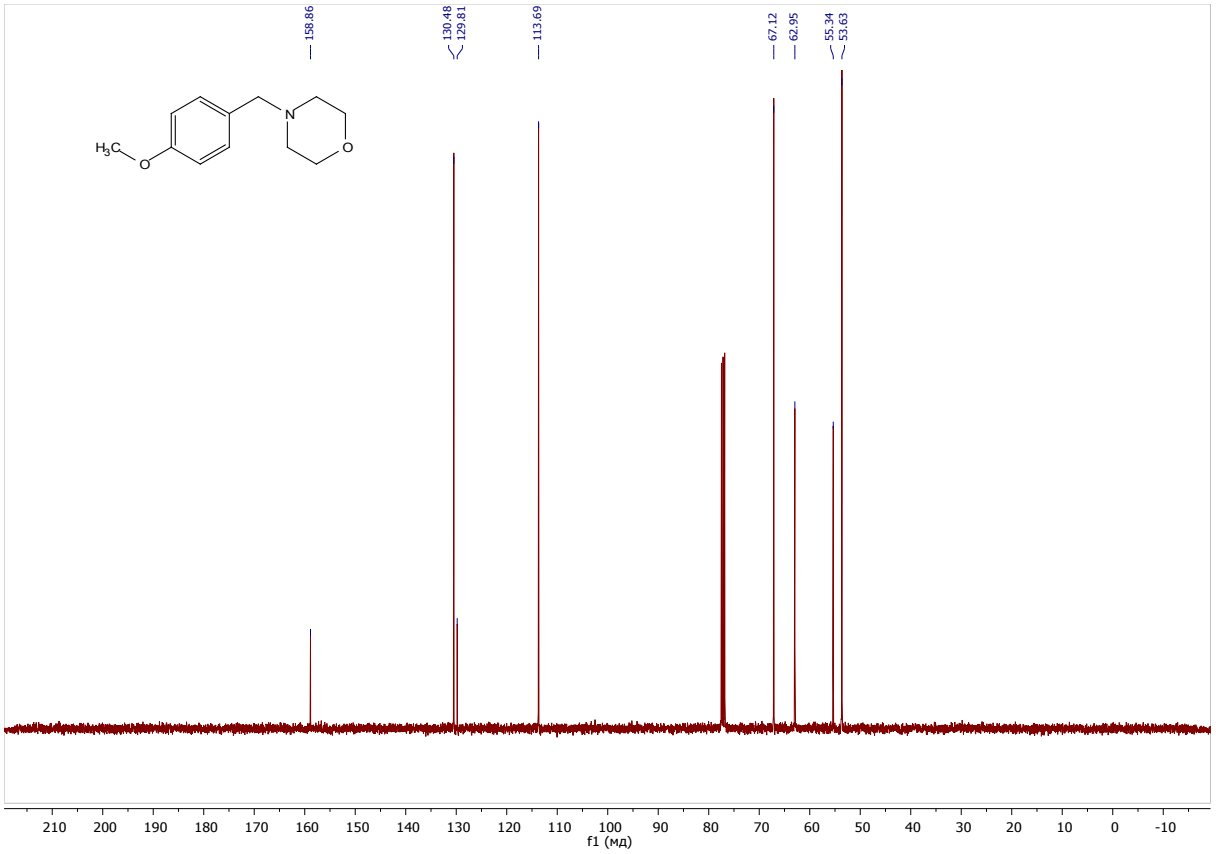
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



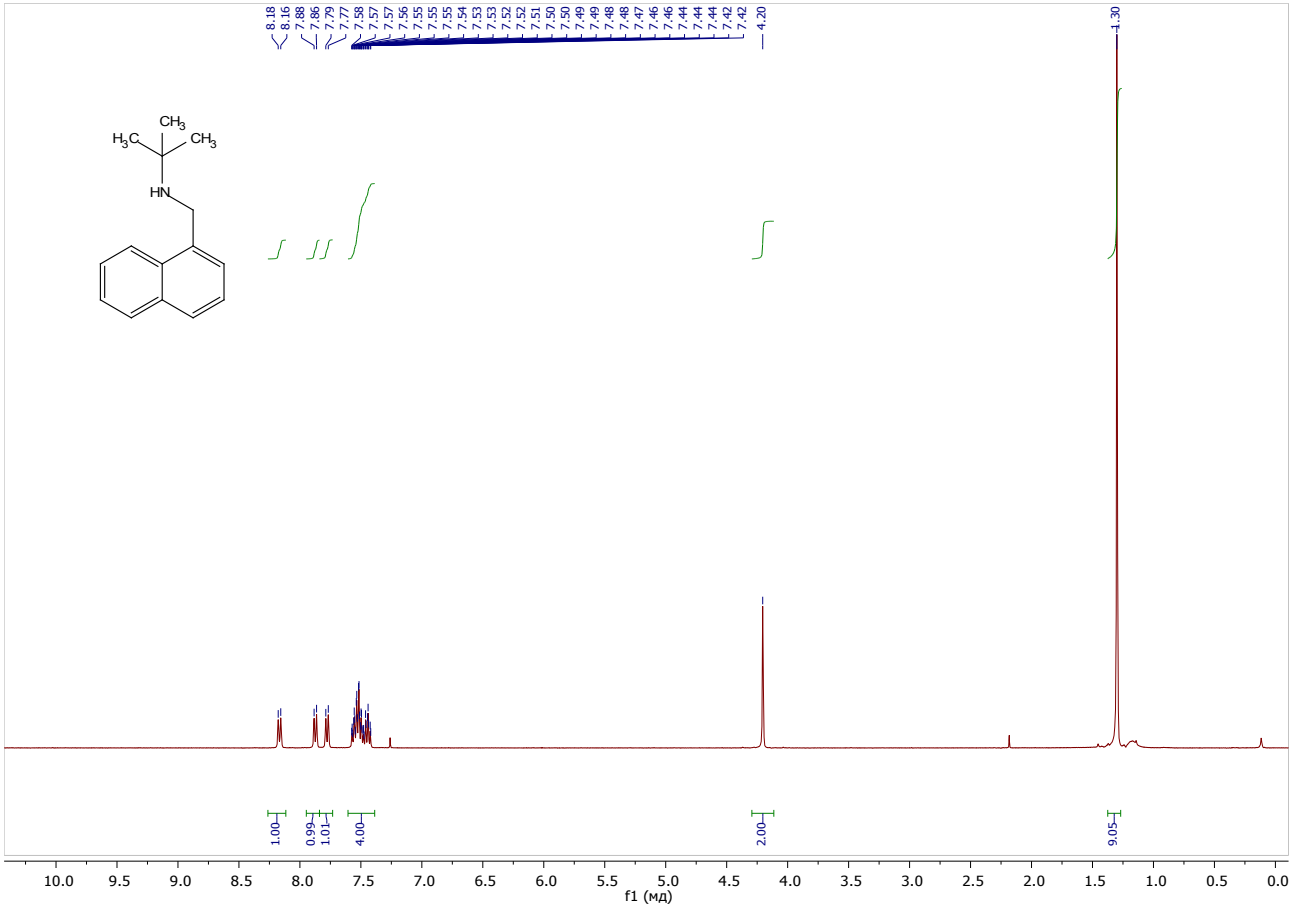
4-(4-methoxybenzyl)morpholine (14) ^{1}H NMR (400 MHz, $CDCl_3$)



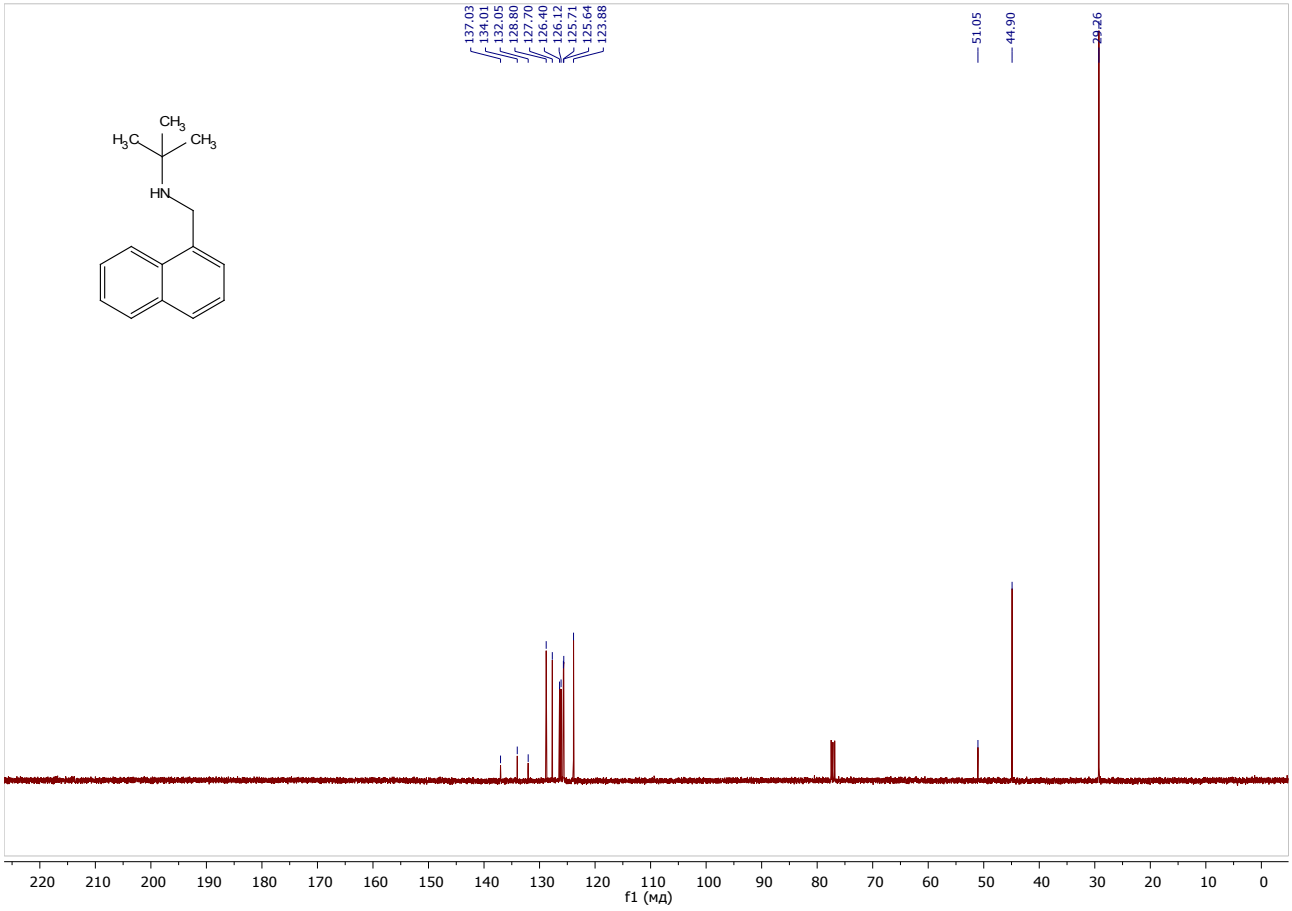
4-(4-methoxybenzyl)morpholine (14) ^{13}C NMR (101 MHz, $CDCl_3$)



2-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine (15) ^{1}H NMR (400 MHz, $CDCl_3$)



2-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine (15) ^{13}C NMR (101 MHz, $CDCl_3$)



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