Electronic Supplementary Material (ESI) for Dalton Transactions.

# Facile Synthesis of [(NHC)MCl(cod)] and [(NHC)MCl(CO)$_2$] (M= Rh, Ir) complexes

R. Savka and H. Plenio*

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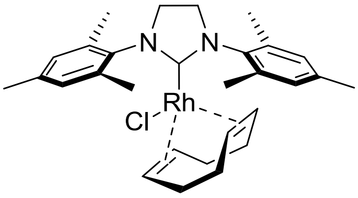
**General experimental:** Chloro(1,5-cycloctadiene)-rhodium(I) dimer (assay 98%) was purchased from Sigma-Aldrich and chloro(1,5-cycloctadiene)-iridium(I) dimer (assay >93%) was purchased from TCI Europe. All reactions were carried under air and technical grade solvents were used. Potassium carbonate was used as received without further purification. $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker AC300 or a DRX500 spectrometer. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to the residual peak of chloroform ($^{1}$H NMR=7.26, $^{13}$C NMR = 77.16 ppm). Abbreviations for NMR: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, hep = heptet, m = multiplet, br = broad signal.

All reaction leading to metal complexes were done under ambient atmosphere and in technical (non-dried) grade solvents.

**General procedure for the synthesis of [(NHC)RhCl(cod)] (X = Cl, I), [(IMes)IrCl(cod)] and [(IPr)IrCl(cod)] complexes:**

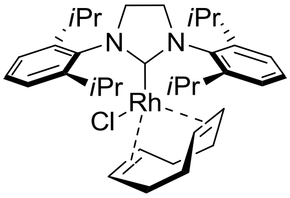
A vial was charged with the corresponding NHC·HX (1 equiv), [MCl(cod)]$_2$ (0.5 equiv) and $K_2CO_3$ (3 equiv). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until filtrate becomes colorless and the solvent was removed *in vacuo*.

**Preparation of [(SIMes)RhCl(cod)].**[1]



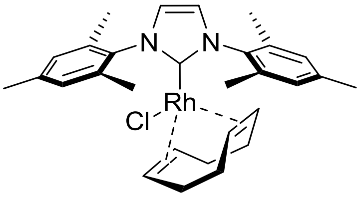
A vial was charged with SIMes·HCl (69.54 mg, 0.202 mmol), [RhCl(cod)]$_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo* to afford the desired complex as yellow microcrystalline solid (93.4 mg, 83% yield). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 2H, $H_{Ar}$), 6.97 (s, 2H, $H_{Ar}$), 4.47 (br, 2H, $H_{cod}$), 3.94 – 3.78 (m, 4H, $NCH_2$), 3.37 (br, 2H, $H_{cod}$), 2.60 (s, 6H, Me), 2.34 (s, 6H, Me), 2.32 (s, 6H, Me), 1.85 – 1.71 (m, 4H, $H_{cod}$), 1.56 – 1.47 (m, 4H, $H_{cod}$).

**Preparation of [(SIPr)RhCl(cod)].**



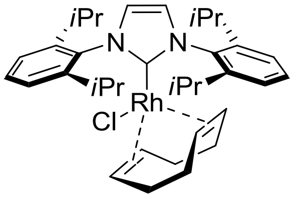
A vial was charged with SIPr·HCl (86.3 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo.* The residue was purified by column chromatography (cyclohexane/ethyl acetate, 4:1, v/v) to afford the desired complex as yellow microcrystalline solid (102 mg, 79% yield). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, $J$ = 7.6 Hz, 2H, $H_{Ar}$), 7.37 (d, $J$ = 6.8 Hz, 2H, $H_{Ar}$), 7.23 (d, $J$ = 7.2 Hz, 2H, $H_{Ar}$), 4.56 – 4.50 (m, 2H, $H_{cod}$), 4.08 – 3.96 (m, 4H, $NCH_2$), 3.92 – 3.85 (m, 2H, $CH(CH_3)_2$), 3.28 – 3.22 (m, 2H, $H_{cod}$), 3.10 (hep, $J$ = 6.5 Hz, 2H, $CH(CH_3)_2$), 1.78 – 1.68 (m, 2H, $H_{cod}$), 1.63 – 1.40 (m, 12H, {m, 6H, $H_{cod}$ + d, $J$ = 6.6 Hz, 6H, $CH(CH_3)_2$}), 1.37 (d, $J$ = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, $J$ = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.20 (d, $J$ = 6.9 Hz, 6H, $CH(CH_3)_2$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 215.91 (d, $J_{Rh\text{-}C}$ = 47.3 Hz, $C_{carbene}$), 149.86, 146.31, 136.87, 129.07, 125.21, 123.37, 96.76 (d, $J_{Rh\text{-}C}$ = 7.0 Hz, $C_{cod}$), 67.36 (d, $J_{Rh\text{-}C}$ = 14.3 Hz, $C_{cod}$), 53.85, 32.60, 29.07, 28.74, 28.20, 27.10, 24.43, 23.19. MS (EI), *m/z*: $[M]^+$ (33.7%), $[M\text{-}Cl]^+$ (100%).

**Preparation of [(IMes)RhCl(cod)].**[1]



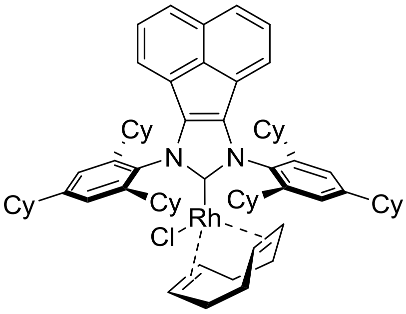
A vial was charged with IMes·HCl (68.9 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo*. Pentane (3 mL) was added, the formed solution was sonicated for 1 min to induce precipitation of the product and then kept in the fridge at -40°C for 1h. The precipitate was collected by filtration, washed with small amount of cold pentane and dried *in vacuo* to afford the desired complex as yellow microcrystalline solid (80 mg, 72% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.06 (s, 2H, $H_{Ar}$), 7.01 (s, 2H, $H_{Ar}$), 6.95 (s, 2H, NCH), 4.52 (br, 2H, $H_{cod}$), 3.29 (br, 2H, $H_{cod}$), 2.40 (s, 6H, Me), 2.39 (s, 6H, Me), 2.11 (s, 6H, Me), 1.93 – 1.76 (m, 4H, $H_{cod}$), 1.62 – 1.49 (m, 4H, $H_{cod}$).

**Preparation of [(IPr)RhCl(cod)].**[2]



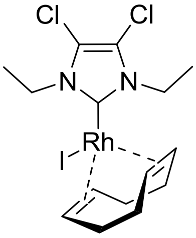
A vial was charged with IPr·HCl (85.9 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo*. Pentane (3mL) was added, the solution was sonicated for 1 min and kept in the fridge at -40°C for 1h. The precipitate (93.4 mg) was collected by filtration, washed with small amount of cold pentane. Concentration of the filtrate gave additional amount of product as yellow crystals (10.7 mg). After drying *in vacuo* the desired complex was obtained as yellow microcrystalline solid (104.1 mg, 81% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, $J$ = 7.7 Hz, 2H, $H_{Ar}$), 7.35 (br, 4H, $H_{Ar}$), 7.02 (s, 2H, NCH), 4.61 – 4.51 (m, 2H, $H_{cod}$), 3.58 (br, 2H, $CH(CH_3)_2$), 3.30 – 3.18 (m, 2H, $H_{cod}$), 2.53 (br, 2H, $CH(CH_3)_2$), 1.91 – 1.62 (m, 4H, $H_{cod}$), 1.61 – 1.20 (m, 16H, $H_{cod}$ + Me), 1.09 (d, $J$ = 6.8 Hz, 12H, $CH(CH_3)_2$). Elemental analysis calcd. for $C_{35}H_{49}ClN_2Rh$: C 66.19, H 7.62, N 4.41. Found: C 66.08, H 7.59, N 4.39.

**Preparation of [(NHC)RhCl(cod)].**[6]



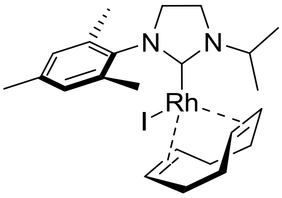
A vial was charged with NHC·HCl (177.2 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo*. Methanol (5 mL) was added and the precipitate was collected by filtration, washed with methanol and dried *in vacuo* to afford the desired complex as yellow microcrystalline solid (197.6 mg, 90% yield). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $J$ = 8.2 Hz, 2H, acenapht.), 7.29 – 7.21 (m, 6H {t, 2H, $J$ = 8.0 Hz, acenapht. + s, 4H, $H_{Ar}$}), 6.59 (d, $J$ = 7.0 Hz, 2H, acenapht.), 4.62 – 4.57 (m, 2H, $H_{cod}$), 3.57 – 3.51(m, 2H, $H_{cod}$), 3.05 (br, 2H, $H_{cod}$), 2.67 (tt, $J$ = 11.9, 3.3 Hz, 2H), 2.58 – 0.75 (m, 68H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 192.83 (d, $J_{Rh\text{-}C}$ = 53.4 Hz, $C_{carbene}$), 149.25, 140.30, 133.27, 129.97, 129.47, 127.37, 127.00, 126.85, 123.69 (br), 121.88, 96.32 (d, $J_{Rh\text{-}C}$ = 7.1 Hz, $C_{cod}$), 67.80 (d, $J_{Rh\text{-}C}$ = 13.9 Hz, $C_{cod}$), 45.04, 39.80 (br), 36.92, 34.79, 33.51, 32.83, 28.47, 27.18, 27.10, 26.44, 26.27.MS (ESI): *m/z* calcd for $C_{69}H_{88}N_2Rh$: 1047.6 $[M\text{-}Cl]^+$; found: 1047.7.

**Preparation of [(NHC)RhI(cod)]**.



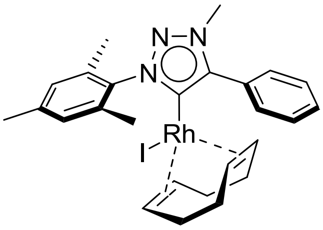
A vial was charged with NHC·HI (64.8 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo* to afford the desired complex as yellow solid (98.9 mg, 92% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.31 – 5.21 (m, 2H, $H_{cod}$), 4.70 (dq, $J$ = 14.5, 7.3 Hz, 2H, $CH_2CH_3$), 4.47 (dq, $J$ = 14.1, 7.1 Hz, 2H, $CH_2CH_3$), 3.46 – 3.37 (m, 2H, $H_{cod}$), 2.41 – 2.24 (m, 4H, $H_{cod}$), 2.05 – 1.90 (m, 2H, $H_{cod}$), 1.89 – 1.73 (m, 2H, $H_{cod}$), 1.54 (t, $J$ = 7.2 Hz, 6H, $CH_2CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 182.54 (d, $J_{Rh\text{-}C}$ = 50.5 Hz, $C_{carbene}$), 116.13, 97.19 (d, $J_{Rh\text{-}C}$ = 6.7 Hz, $C_{cod}$), 72.64 (d, $J_{Rh\text{-}C}$ = 13.8 Hz, $C_{cod}$), 45.69, 32.34, 29.65, 14.98. MS (EI), *m/z*: $[M]^+$ (95.2%), $[M\text{-}I]^+$ (68.5%).

**Preparation of [(NHC)RhI(cod)]**.



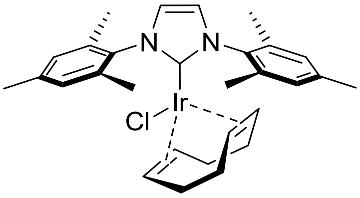
A vial was charged with NHC·HI (72.4 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo*. The residue was crystallized from $CH_2Cl_2$/pentane to afford the desired complex as yellow-orange microcrystalline solid (88.6 mg, 77% yield). $^1H$ NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H, $H_{Ar}$), 6.88 (s, 1H, $H_{Ar}$), 5.88 (hep, $J$ = 6.7 Hz, 1H, $CH(CH_3)_2$), 5.06 – 5.00 (m, 1H, $H_{cod}$), 4.95 (td, $J$ = 7.7, 3.1 Hz, 1H, $H_{cod}$), 3.81 – 3.76 (m, 1H, $H_{cod}$), 3.76 – 3.56 (m, 4H, $NCH_2CH_2N$), 3.29 – 3.23 (m, 1H, $H_{cod}$), 2.60 (s, 3H, Me), 2.39 – 2.33 (m, 1H, $H_{cod}$), 2.32 (s, 3H, Me), 2.07 (s, 3H, Me), 2.06 – 1.98 (m, 1H, $H_{cod}$), 1.92 – 1.74 (m, 3H, $H_{cod}$), 1.66 – 1.57 (m, 1H, $H_{cod}$), 1.43 – 1.33 (m, 8H {m, 2H, $H_{cod}$ + 1.41 (d, $J$ = 6.6 Hz, 3H, $CH(CH_3)_2$) + 1.36 (d, $J$ = 6.7 Hz, 3H, $CH(CH_3)_2$)}). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 210.28 (d, $J_{Rh\text{-}C}$ = 45.6 Hz, $C_{carbene}$), 138.19, 137.77, 136.56, 135.30, 130.03, 128.44, 95.74 (d, $J_{Rh\text{-}C}$ = 6.4 Hz, $C_{cod}$), 95.33 (d, $J_{Rh\text{-}C}$ = 7.0 Hz, $C_{cod}$), 70.67 (t, $J_{Rh\text{-}C}$ = 14.6 Hz, $C_{cod}$), 51.41, 51.24, 42.02, 34.36, 31.38, 30.63, 30.07, 27.74, 22.12, 21.12, 20.90, 20.07, 18.24. MS (EI), *m/z*: $[M]^+$ (24.5%), $[M\text{-}I]^+$ (100%). Elemental analysis: calcd. For $C_{23}H_{34}IN_2Rh$ C 48.61, H 6.03, N 4.93. Found: C 48.63, H 5.97, N 4.89.

**Preparation of [(*a*NHC)RhI(cod)]**.



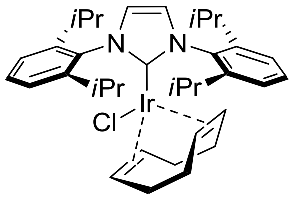
A vial was charged with *a*NHC·HI (81.9 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo*. Pentane (3 mL) was added, the precipitate collected by filtration, washed with pentane and dried *in vacuo* to afford the desired complex as yellow solid (106 mg, 85% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H, $H_{Ph}$), 7.62 – 7.49 (m, 3H, $H_{Ph}$), 7.07 (s, 1H, $H_{Ar}$), 6.97 (s, 1H, $H_{Ar}$), 5.02 – 4.91 (m, 1H, $H_{cod}$), 4.90 – 4.80 (m, 1H, $H_{cod}$), 4.07 (s, 3H, Me-triazol), 3.49 – 3.40 (m, 1H, $H_{cod}$), 3.33 – 3.24 (m, 1H, $H_{cod}$), 2.50 (s, 3H, Me), 2.39 (s, 3H, Me), 2.08 – 1.91 (m, 3H, $H_{cod}$), 1.89 (s, 3H, Me), 1.76 – 1.48 (m, 4H, $H_{cod}$), 1.47 – 1.33 (m, 1H, $H_{cod}$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.80 (d, $J_{Rh\text{-}C}$ = 46.3 Hz, $C_{carbene}$), 145.82, 139.96, 136.56, 136.33, 134.51, 130.89, 130.02, 129.70, 129.13, 128.36, 128.30, 93.61 (d, $J_{Rh\text{-}C}$ = 7.3 Hz, $C_{cod}$), 93.27 (d, $J_{Rh\text{-}C}$ = 7.0 Hz, $C_{cod}$), 72.07 (d, $J_{Rh\text{-}C}$ = 14.3 Hz, $C_{cod}$), 70.40 (d, $J_{Rh\text{-}C}$ = 14.2 Hz, $C_{cod}$), 37.44, 32.82, 31.67, 29.85, 29.18, 21.66, 21.32, 17.89. MS (EI), *m/z*: [M]$^+$ (26.5%), [M-I]$^+$ (84.8%).

**Preparation of [(IMes)IrCl(cod)].**[3]



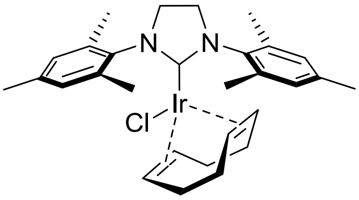
A vial was charged with IMes·HCl (60.9 mg, 0.178 mmol), $[IrCl(cod)]_2$ (60 mg, 0.089 mmol) and $K_2CO_3$ (74 mg, 0.534 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo*. Pentane (3mL) was added, the solution was sonicated for 1 min and kept in the fridge at -40°C for 1h. The precipitate was collected by filtration, washed with small amount of cold pentane and dried *in vacuo* to afford the desired complex as yellow-orange microcrystalline solid (76.8 mg, 67% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.01 (br, 2H, $H_{Ar}$), 6.98 (br, 2H, $H_{Ar}$), 6.95 (s, 2H, NCH), 4.20 – 411 (m, 2H, $H_{cod}$), 3.01 – 2.93 (m, 2H, $H_{cod}$), 2.36 (s, 6H, Me), 2.35 (s, 6H, Me), 2.16 (s, 6H, Me), 1.79 – 1.58 (m, 4H, $H_{cod}$), 1.41 – 1.19 (m, 4H, $H_{cod}$).

**Preparation of [(IPr)IrCl(cod)].**[3]



A vial was charged with IPr·HCl (63.3 mg, 0.148 mmol), $[IrCl(cod)]_2$ (50 mg, 0.074 mmol) and $K_2CO_3$ (61.3 mg, 0.444 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until the filtrate becomes colorless and the solvent was removed *in vacuo* to afford the desired complex as orange microcrystalline solid (103.5 mg, 96% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.7 Hz, 2H, $H_{Ar}$), 7.31 (br, 4H, $H_{Ar}$), 7.02 (s, 2H, NCH), 4.25 – 4.15 (m, 2H, $H_{cod}$), 3.43 (br, 2H, $CH(CH_3)_2$), 2.94 – 2.84 (m, 2H, $H_{cod}$), 2.72 (br, 2H, $CH(CH_3)_2$), 1.77 – 1.63 (m, 2H, $H_{cod}$), 1.61 – 1.13 (m, 18H, $H_{cod}$ + Me), 1.10 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$).

**Preparation of [(SIMes)IrCl(cod)].**[3]

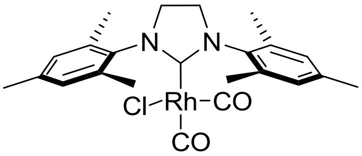


A vial was charged with SIMes·HCl (51 mg, 0.148 mmol), $[IrCl(cod)]_2$ (50 mg, 0.074 mmol) and $K_2CO_3$ (24.6 mg, 0.177 mmol). The resulting mixture was suspended in acetone (1.0 mL) and stirred for 20 h at 60 ºC. After this time the solvent was removed *in vacuo* and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until filtrate becomes colorless and the solvent was removed *in vacuo*. The residue was washed with cold pentane (2 mL) and dried *in vacuo* to afford the desired complex as yellow microcrystalline solid (65.2 mg, 68% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 2H, $H_{Ar}$), 6.94 (s, 2H, $H_{Ar}$), 4.14 – 4.06 (m, 2H, $H_{cod}$), 3.93 – 3.87 (m, 4H, $NCH_2$), 3.11 – 3.03 (m, 2H, $H_{cod}$), 2.55 (s, 6H, Me), 2.35 (s, 6H, Me), 2.32 (s, 6H, Me), 1.69 – 1.54 (m, 4H, $H_{cod}$), 1.37 – 1.18 (m, 4H, $H_{cod}$).

**General procedure for one-pot synthesis of $[(NHC)RhCl(CO)_2]$ complexes:**

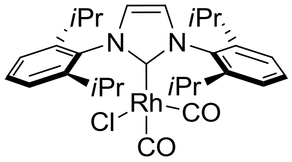
A vial was charged with the corresponding NHC·HCl (1 equiv), $[RhCl(cod)]_2$ (0.5 equiv) and $K_2CO_3$ (3 equiv). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. Next, the mixture was cooled to room temperature and carbon monoxide was bubbled through the mixture under vigorous stirring for 20 min. After that the volatiles were removed *in vacuo*, the residue dissolved in dichloromethane and filtered through Celite which was washed with dichloromethane until filtrate becomes colorless. The solvent was removed *in vacuo* and pentane (5 mL) was added. The pale yellow precipitate was collected by filtration, washed with pentane and dried *in vacuo*.

### Preparation of $[(SIMes)RhCl(CO)_2]$.[4]



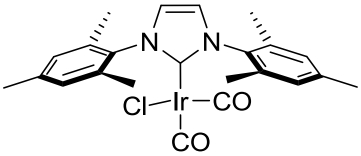
A vial was charged with SIMes·HCl (69.54 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. Next, the mixture was cooled to room temperature and carbon monoxide was bubbled through the mixture under vigorous stirring for 20 min. After that the volatiles were removed *in vacuo*, the residue dissolved in dichloromethane and filtered through Celite which was washed with dichloromethane until filtrate becomes colorless. The solvent was removed *in vacuo* and pentane (5 mL) was added. The pale yellow precipitate was collected by filtration, washed with pentane and dried *in vacuo* to afford the desired complex as pale yellow solid (95.5 mg, 94% yield). $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 4H, $H_{Ar}$), 4.00 (s, 4H, $NCH_2$), 2.43 (s, 12H, Me), 2.32 (s, 6H, Me).

### Preparation of $[(IPr)RhCl(CO)_2]$.[5]



A vial was charged with IPr·HCl (85.9 mg, 0.202 mmol), $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) and $K_2CO_3$ (83.6 mg, 0.606 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. Next, the mixture was cooled to room temperature and carbon monoxide was bubbled through the mixture under vigorous stirring for 20 min. After that the volatiles were removed *in vacuo*, the residue dissolved in dichloromethane and filtered through Celite which was washed with dichloromethane until filtrate becomes colorless. The solvent was removed *in vacuo* and pentane (5 mL) was added. The pale yellow precipitate was collected by filtration, washed with pentane and dried *in vacuo* to afford the desired complex as pale yellow solid (76 mg, 64% yield). $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.50 (t, $J$ = 7.8 Hz, 2H, $H_{Ar}$), 7.32 (d, $J$ = 7.8 Hz, 4H, $H_{Ar}$), 7.18 (s, 2H, NCH), 2.90 (hep, $J$ = 6.8 Hz, 4H, $C\mathit{H}(CH_3)_2$), 1.39 (d, $J$ = 6.7 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.13 (d, $J$ = 6.8 Hz, 12H, $CH(C\mathit{H}_3)_2$).

**Preparation of [(IMes)IrCl(CO)$_2$].**[3]



A vial was charged with IMes·HCl (50.72 mg, 0.148 mmol), [IrCl(cod)]$_2$ (50 mg, 0.074 mmol) and $K_2CO_3$ (61.6 mg, 0.444 mmol). The resulting mixture was suspended in acetone (3.0 mL) and stirred for 20 h at 60 ºC. Next, the mixture was cooled to room temperature and carbon monoxide was bubbled through the mixture under vigorous stirring for 20 min. After that the volatiles were removed *in vacuo*, the residue dissolved in dichloromethane and filtered through Celite which was washed with dichloromethane until filtrate becomes colorless. The solvent was removed *in vacuo* and pentane (5 mL) was added. The precipitate was collected by filtration, washed with pentane and dried *in vacuo* to afford the desired complex as pale yellow solid (71 mg, 81% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2H, NCH), 7.01 (s, 4H, $H_{Ar}$), 2.36 (s, 6H, Me), 2.21 (s, 12H, Me). Elemental analysis: calcd. For $C_{23}H_{24}ClIrN_2O_2$: C 46.97, H 4.76, N 4.76. Found: C 46.71, H 4.07, N 4.72.

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[2] M. Kim, J. Kwak, S. Chang, *Angew. Chem. Int. Ed.* **2009**, *48*, 8935–8939.

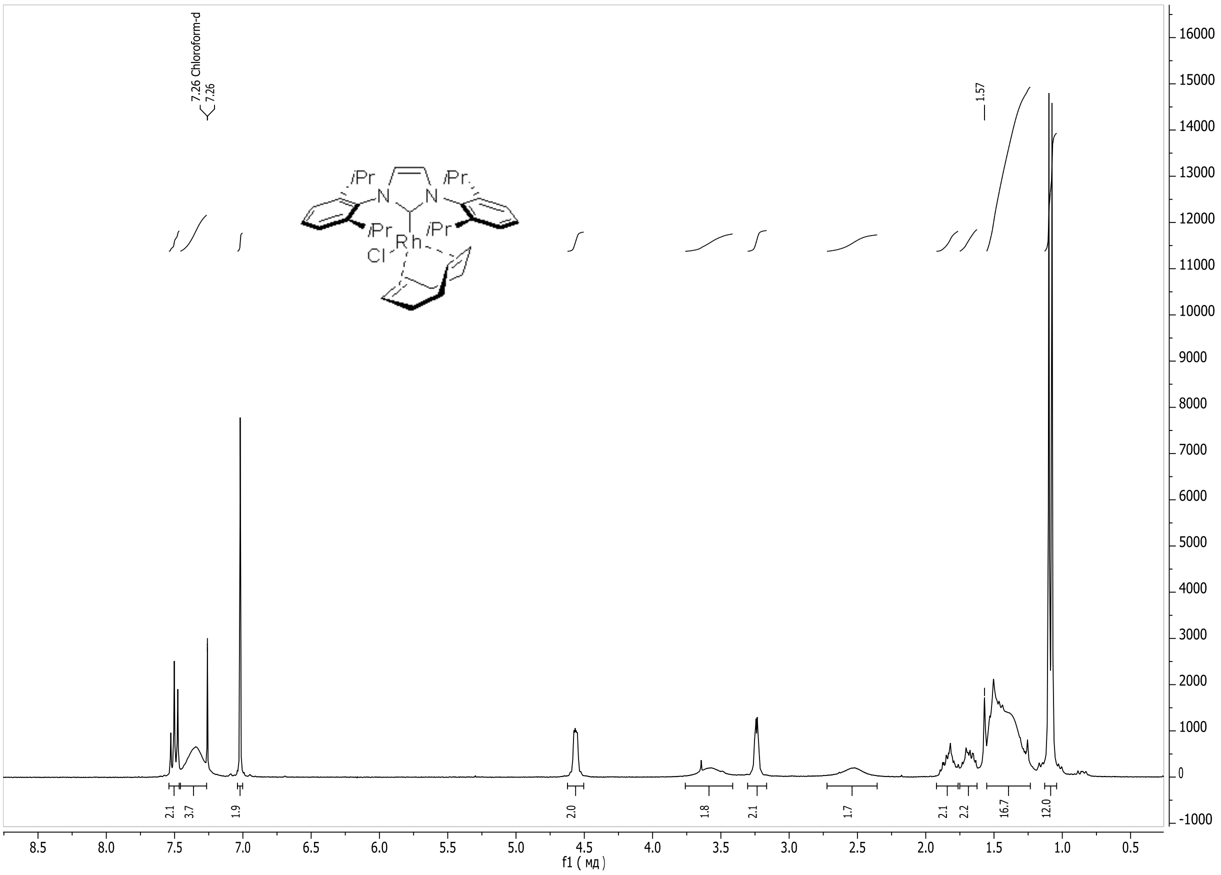
[3] R. A. Kelly, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202-210.

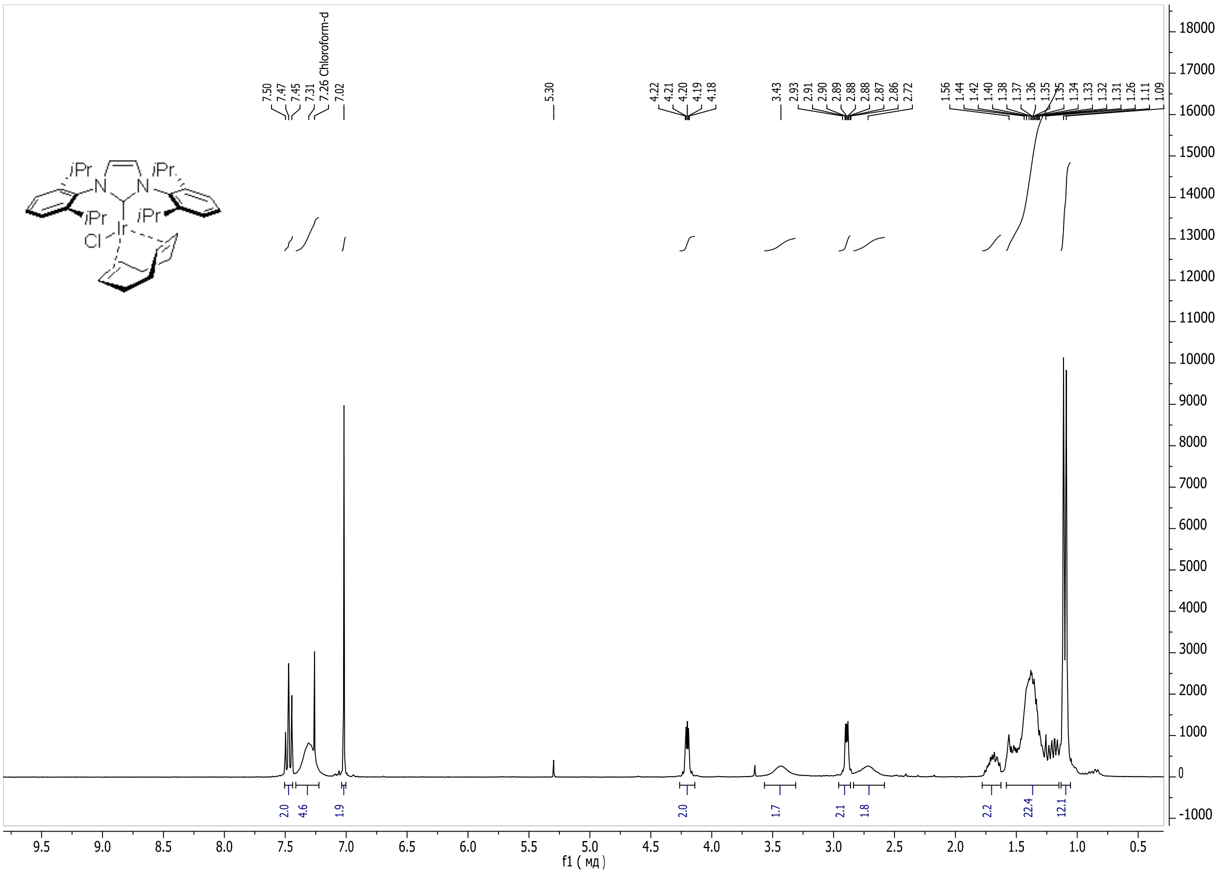
[4] M. Iglesias, D. J. Beetstra, B. Kariuki, K. J. Cavell, A. Dervisi, I. A. Fallis, *Eur. J. Inorg. Chem.* **2009**, *2009*, 1913–1919.

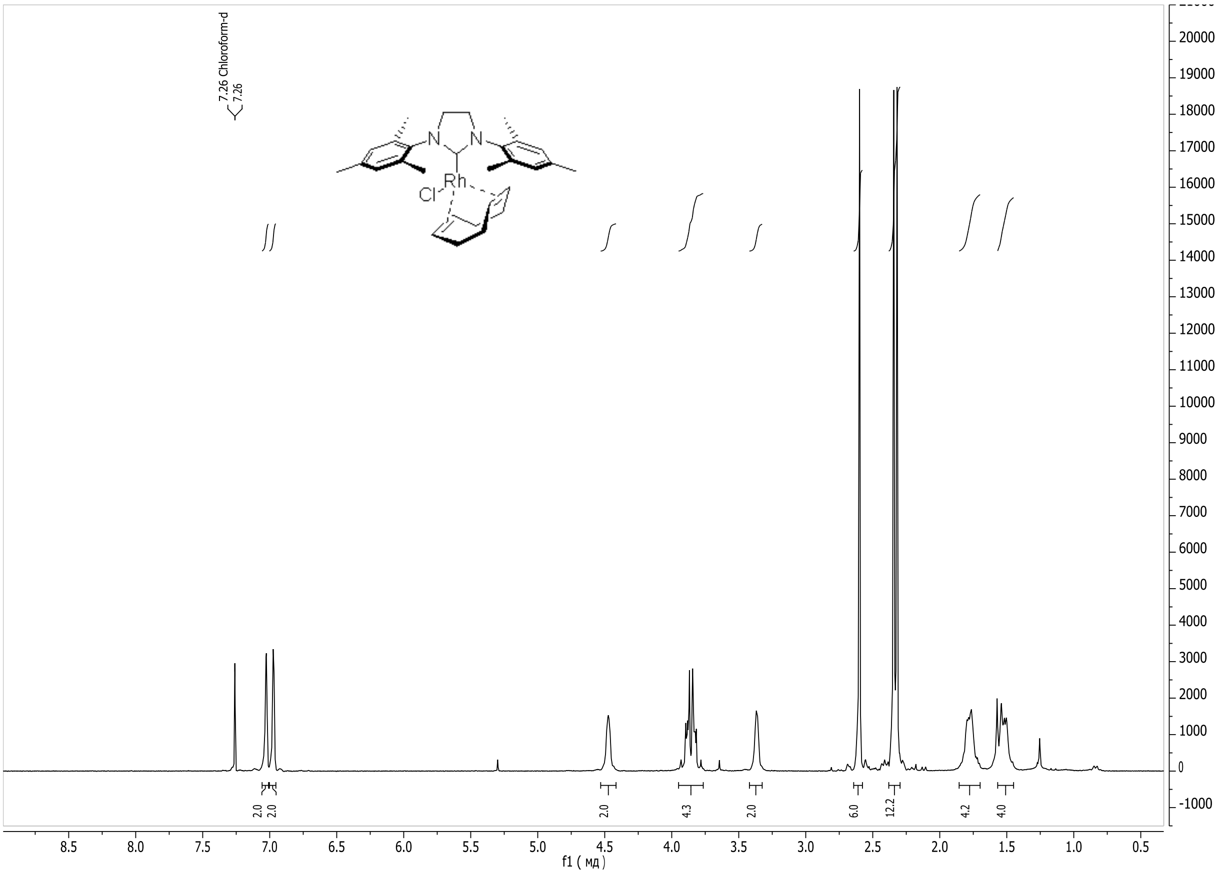
[5] T. Sato, Y. Hirose, D. Yoshioka, S. Oi, *Organometallics* **2012**, *31*, 6995–7003.

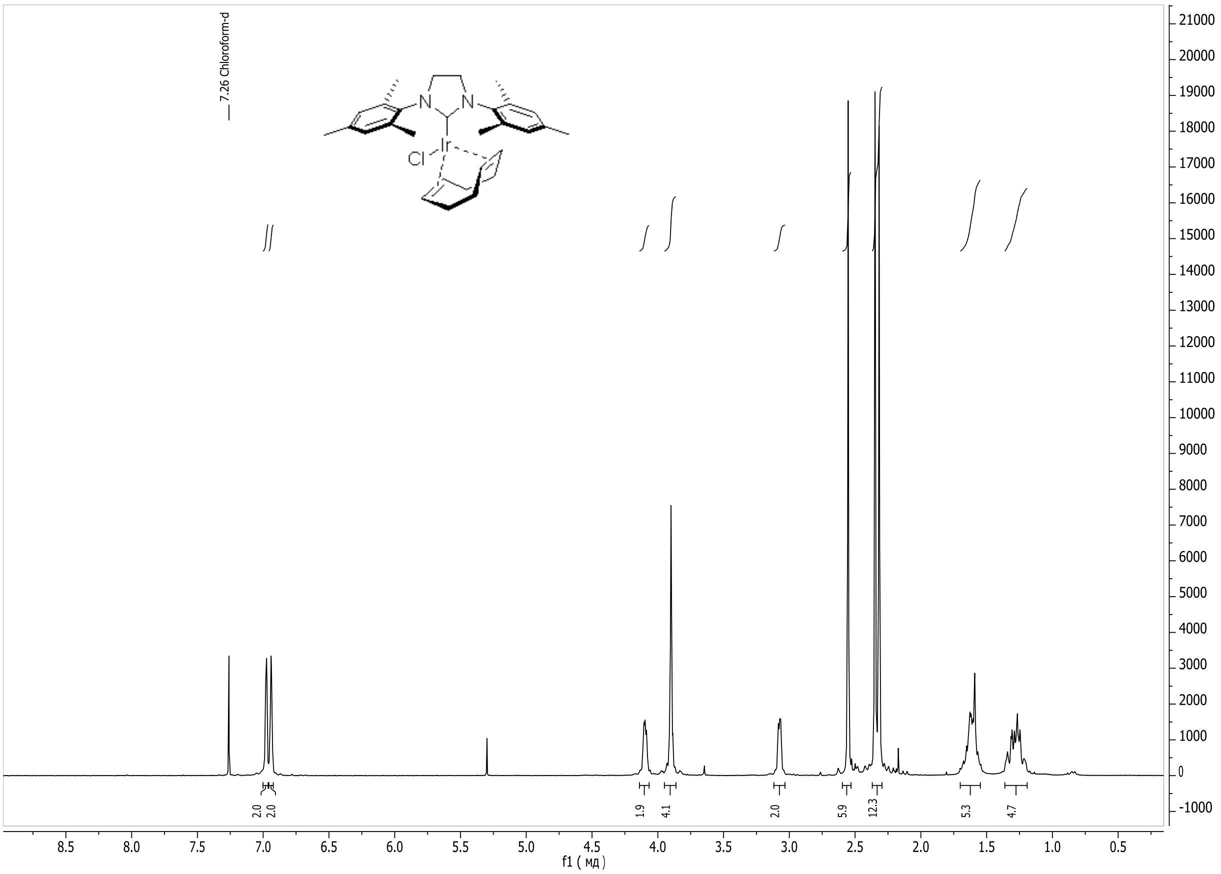
[6] R. Savka, H. Plenio, Metal complexes of very bulky *N*,*N*'-diaryl-imidazolylidene NHC ligands with 2,4,6-cycloalkyl substituents, *Eur. J. Inorg. Chem.* submitted, Sept. 2, 2014.

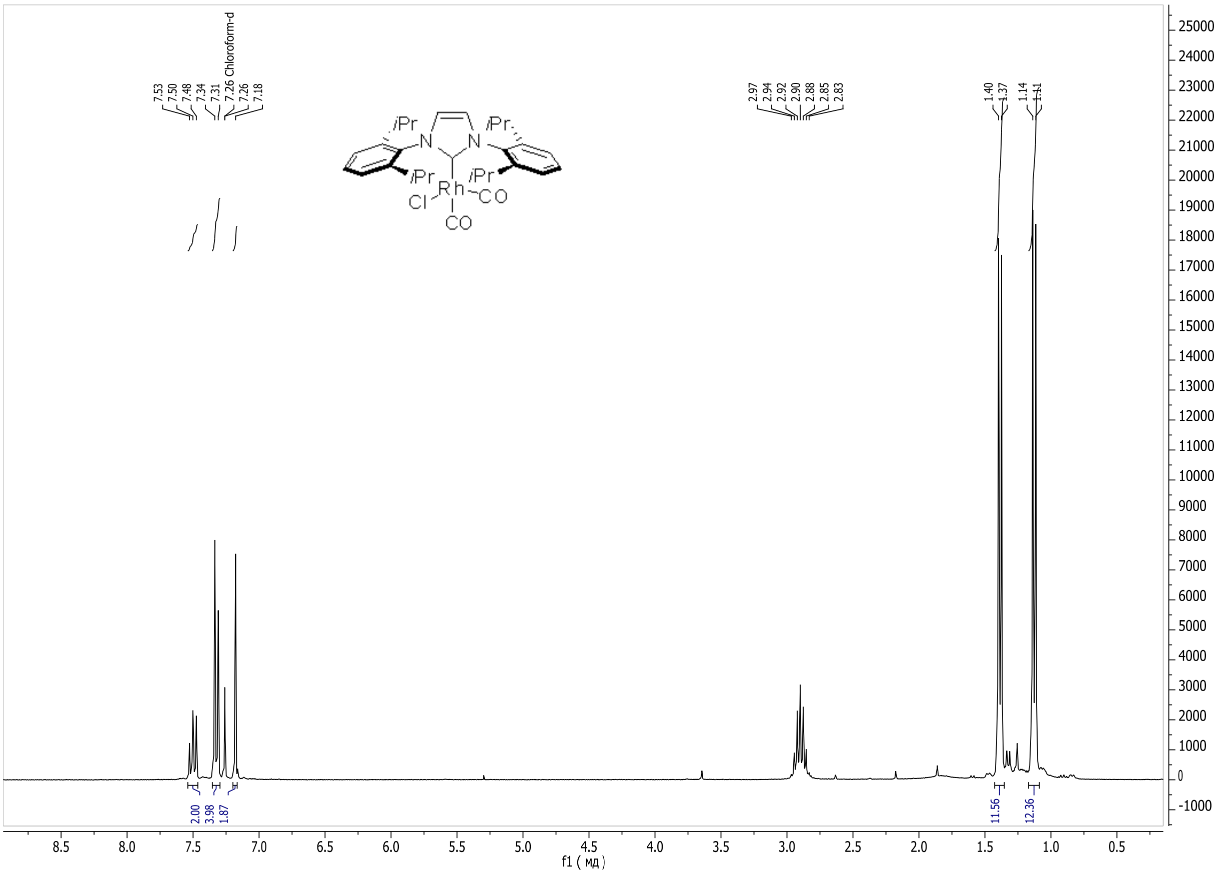
# NMR spectra of synthesized compounds

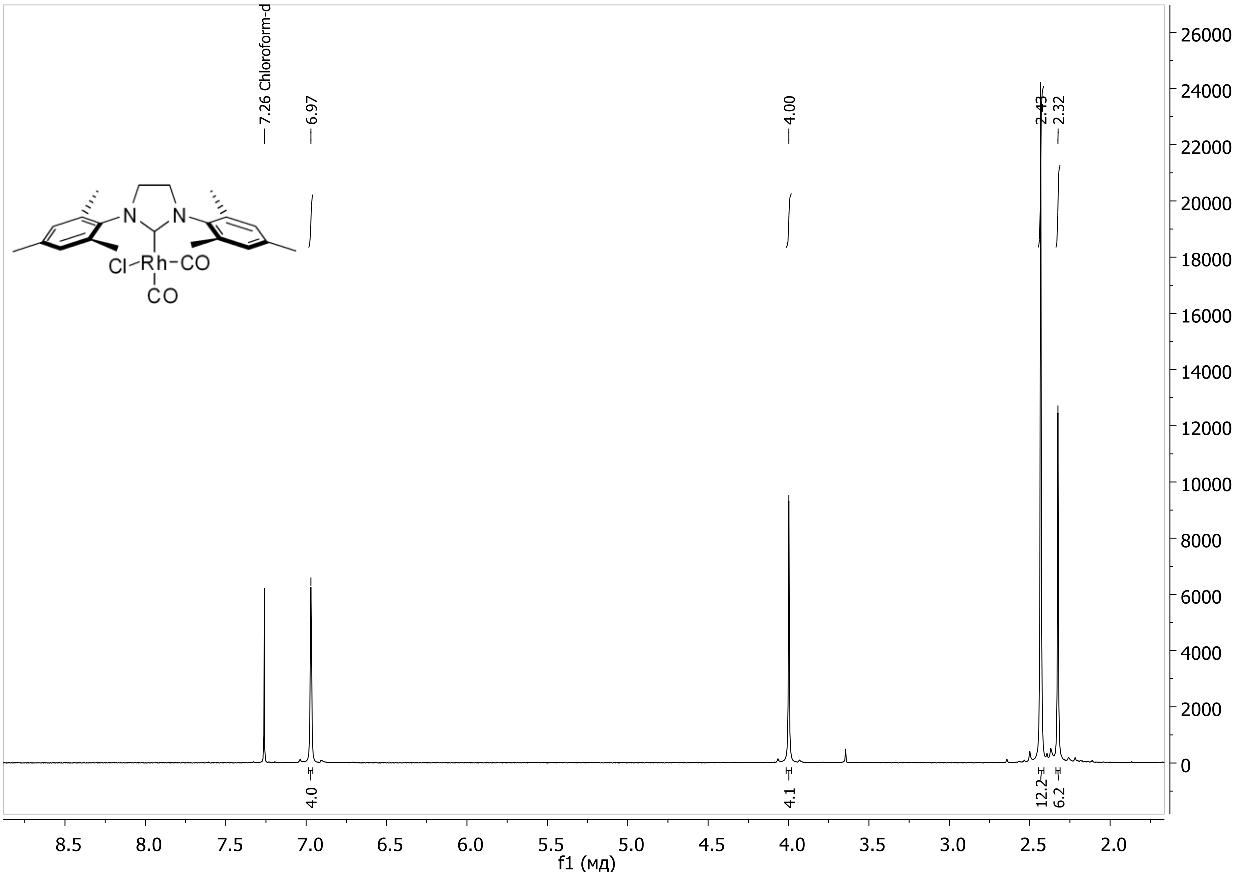





7.26 Chloroform-d
7.26
N
N
Rh
Cl
2.0
2.0
2.0
4.3
2.0
6.0
12.2
4.2
4.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 ( мд )
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


7.26 Chloroform-d
N
N
Ir
Cl
2.0
2.0
1.9
4.1
2.0
5.9
12.3
5.3
4.7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 ( мд )
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


7.53
7.50
7.48
7.34
7.31
7.26 Chloroform-d
7.26
7.18
2.97
2.94
2.92
2.90
2.88
2.85
2.83
1.40
1.37
1.14
1.11
*i*Pr
N
N
*i*Pr
*i*Pr
*i*Pr
Rh
Cl
CO
CO
2.00
3.98
1.87
11.56
12.36
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (мд)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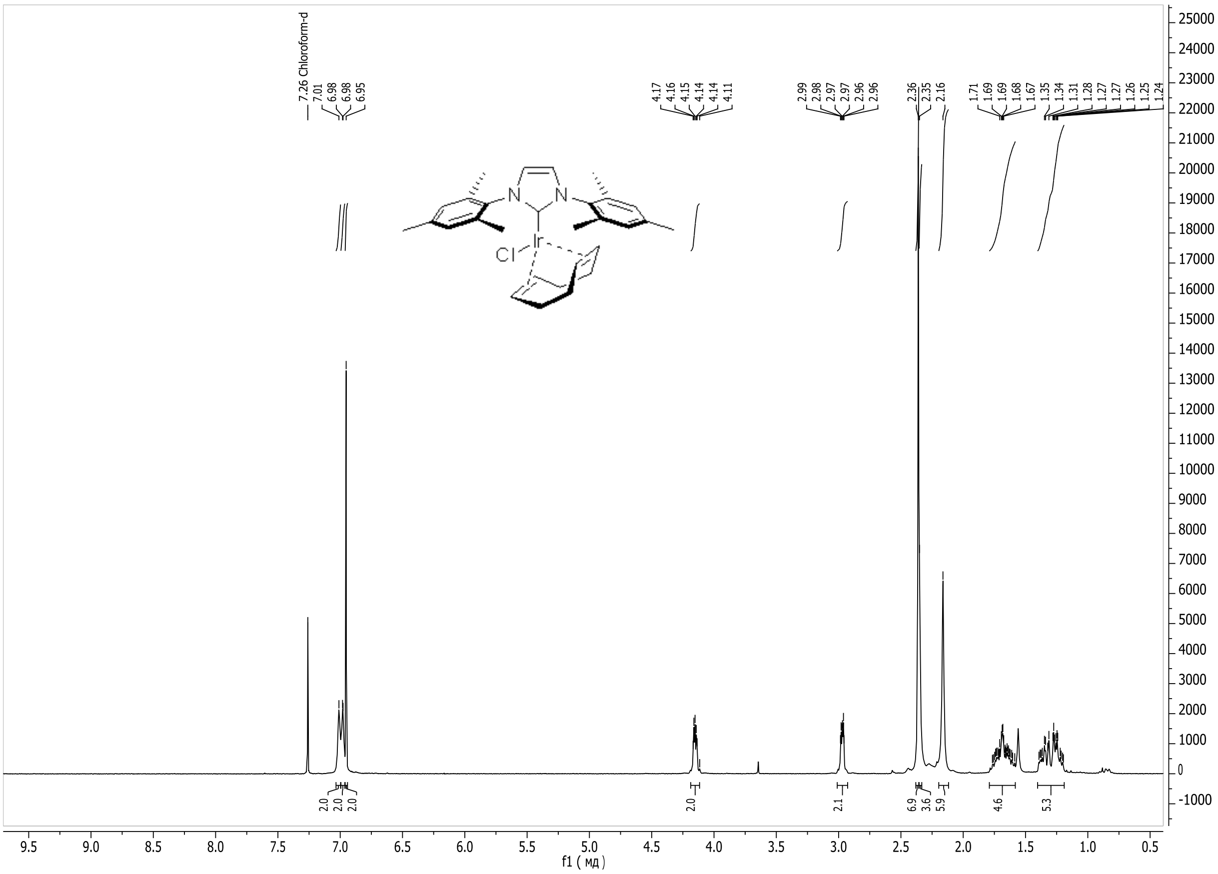
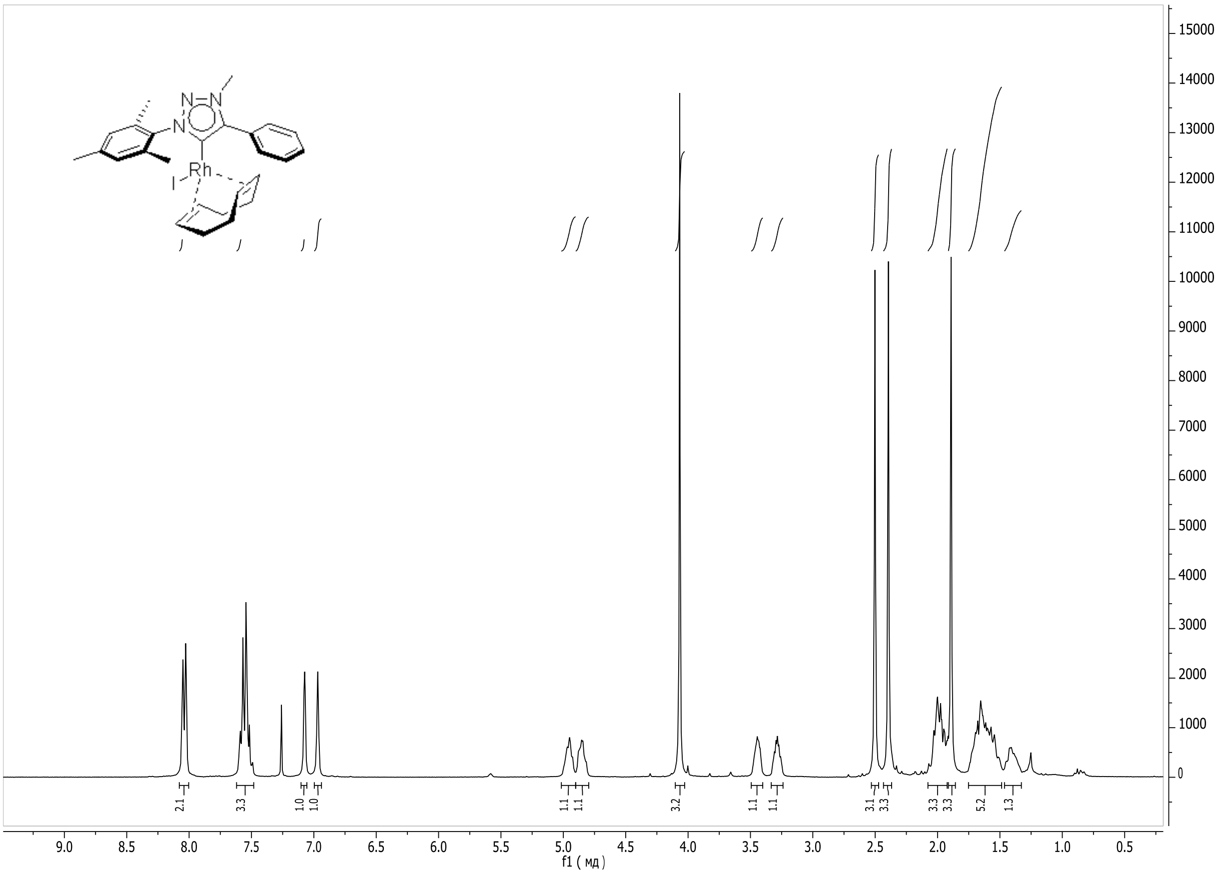
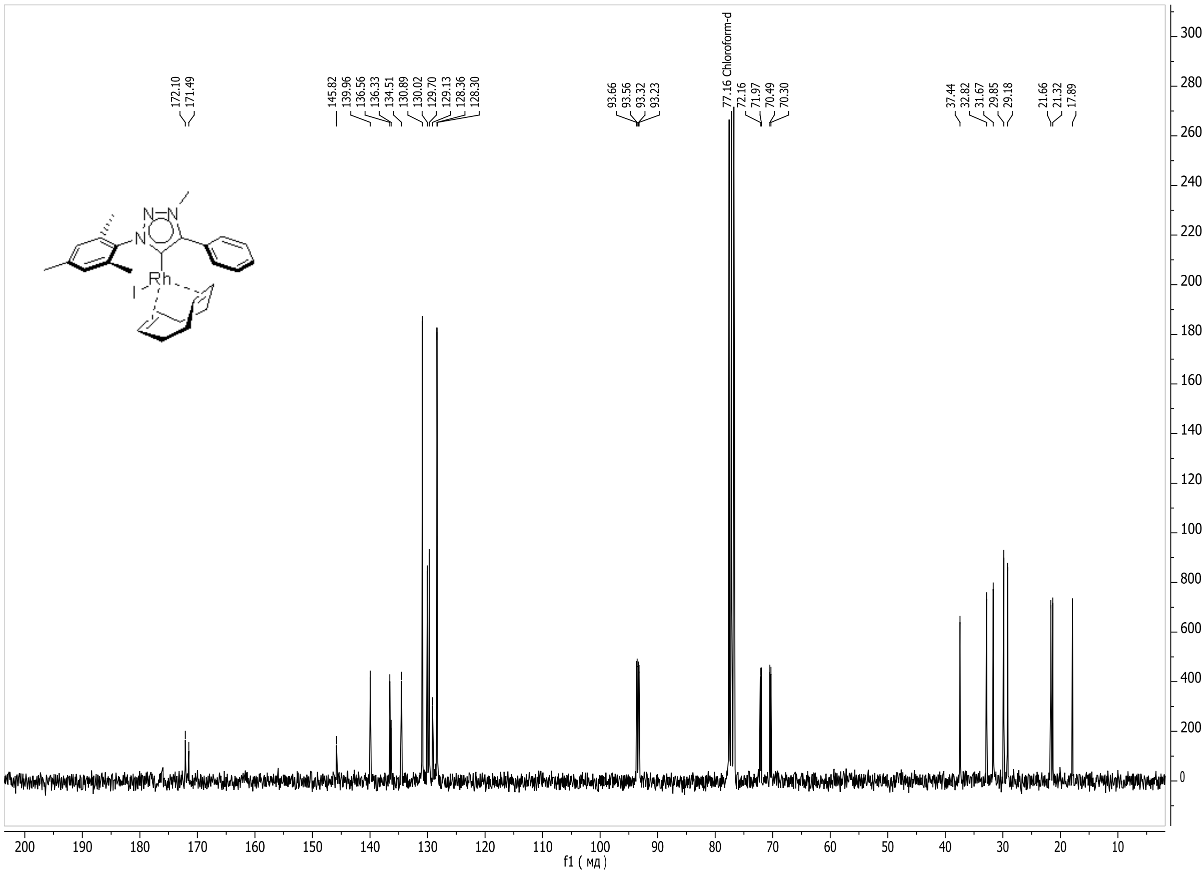
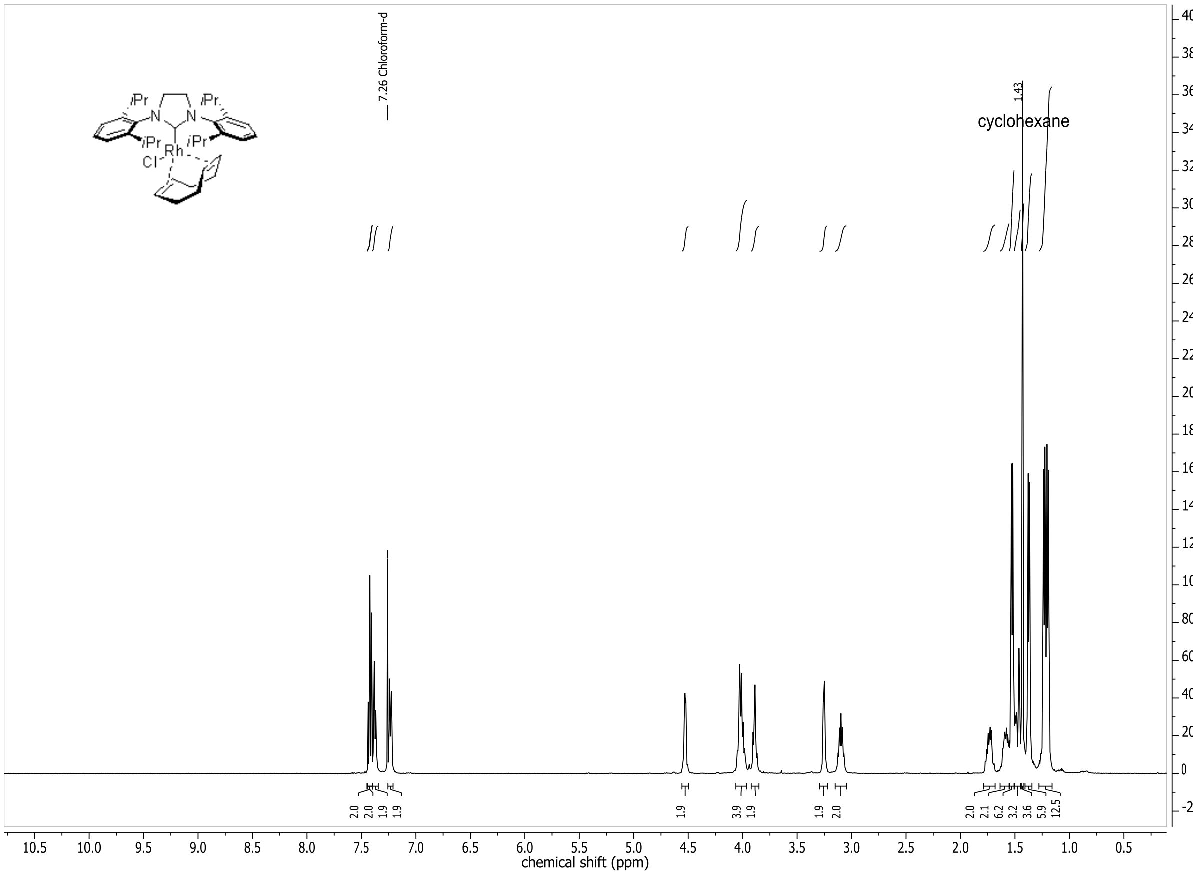
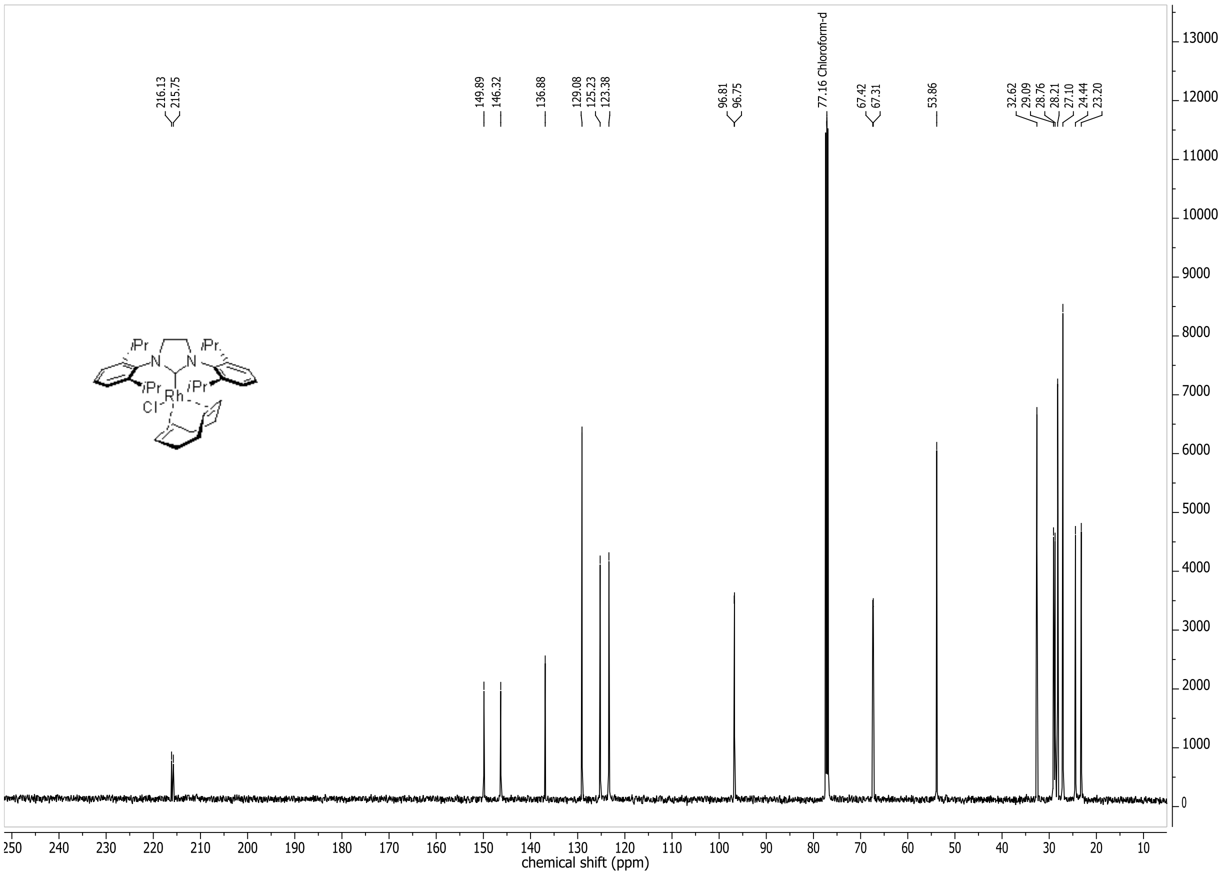
2.43
2.32
N
N
Cl
Rh
CO
CO
4.0
4.1
12.2
6.2
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (мд)

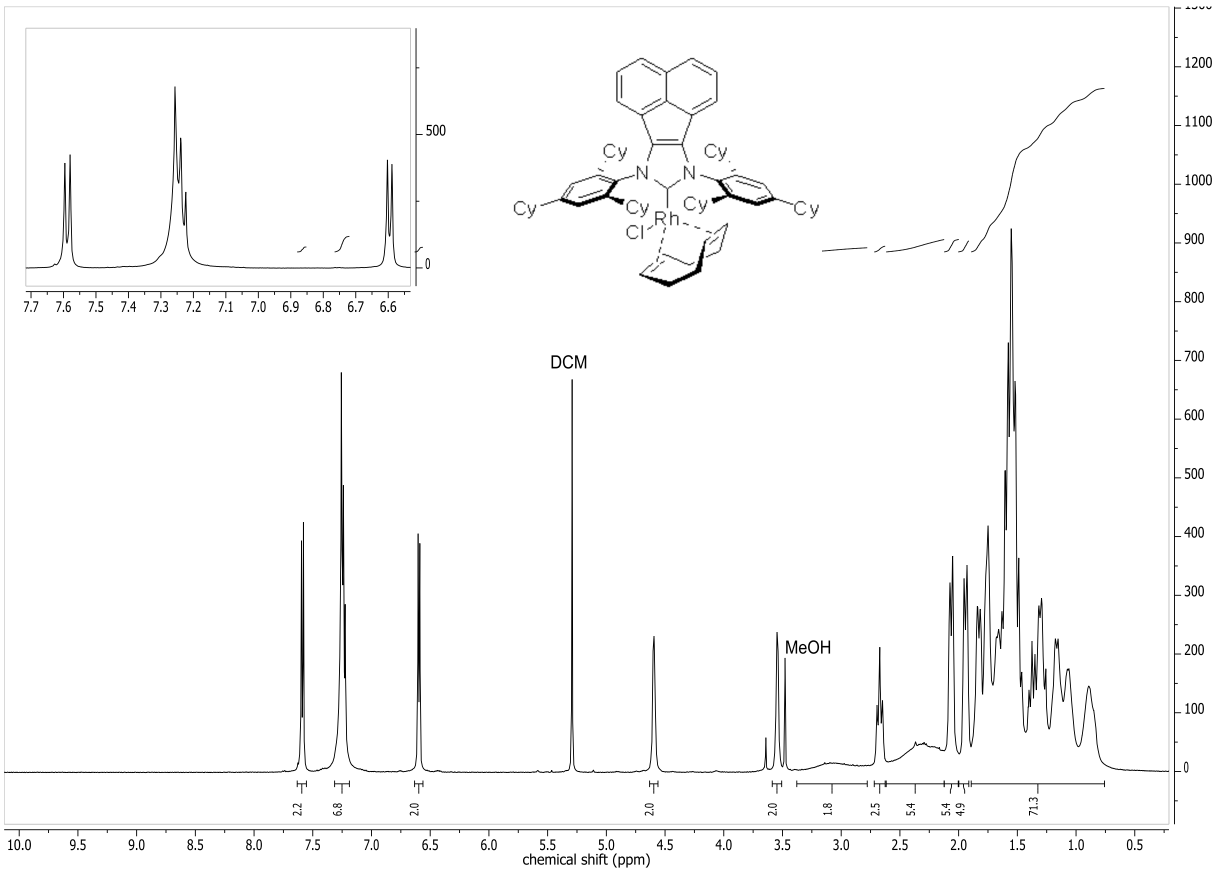

7.26 Chloroform-d
7.01
6.98
6.98
6.95
4.17
4.16
4.15
4.14
4.14
4.11
2.99
2.98
2.97
2.97
2.96
2.96
2.36
2.35
2.16
1.71
1.69
1.69
1.68
1.67
1.35
1.34
1.31
1.28
1.27
1.27
1.26
1.25
1.24
N
N
Ir
Cl
2.0
2.0
2.0
2.0
2.1
6.9
3.6
5.9
4.6
5.3
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 ( мд )

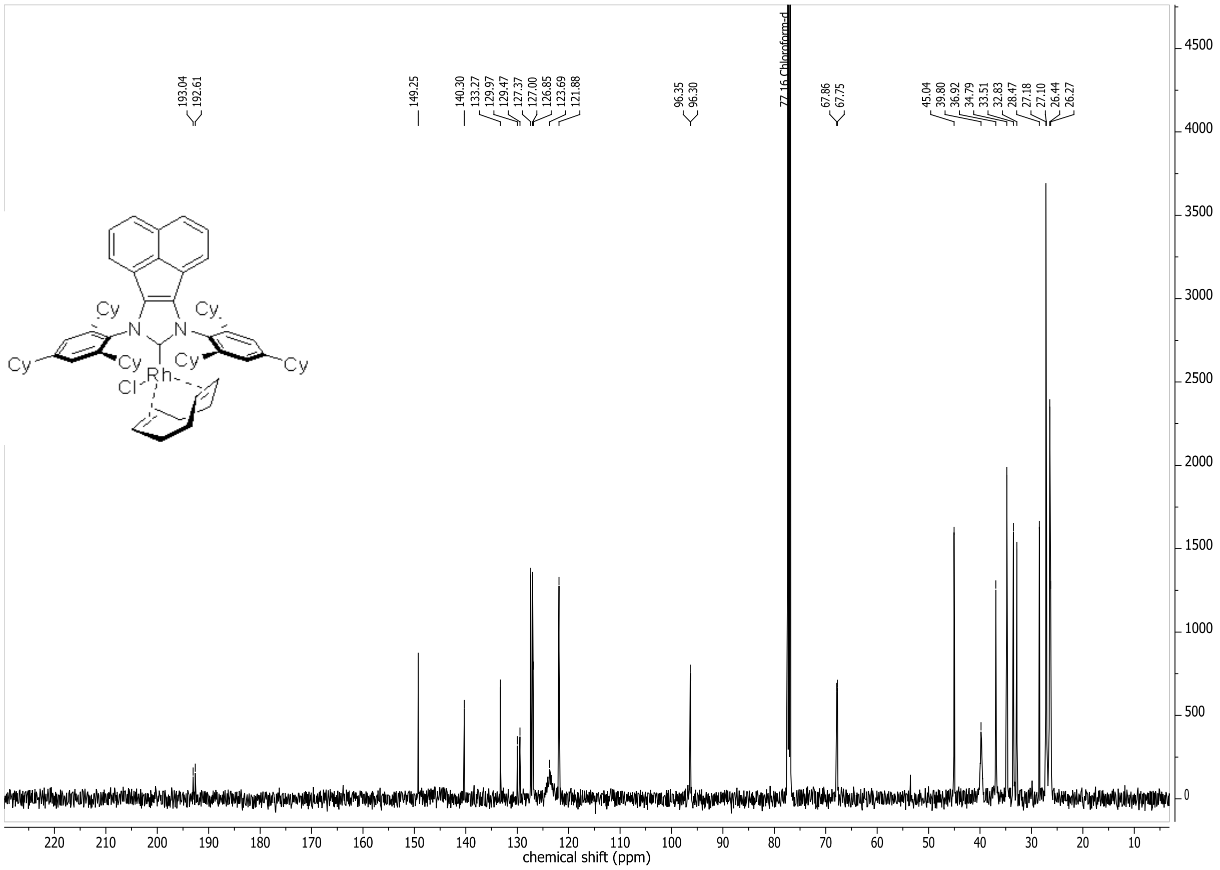

N
N
N
Rh
I
2.1
3.3
1.0
1.0
1.1
1.1
3.2
1.1
1.1
3.1
3.3
3.3
3.3
5.2
1.3
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 ( мд )

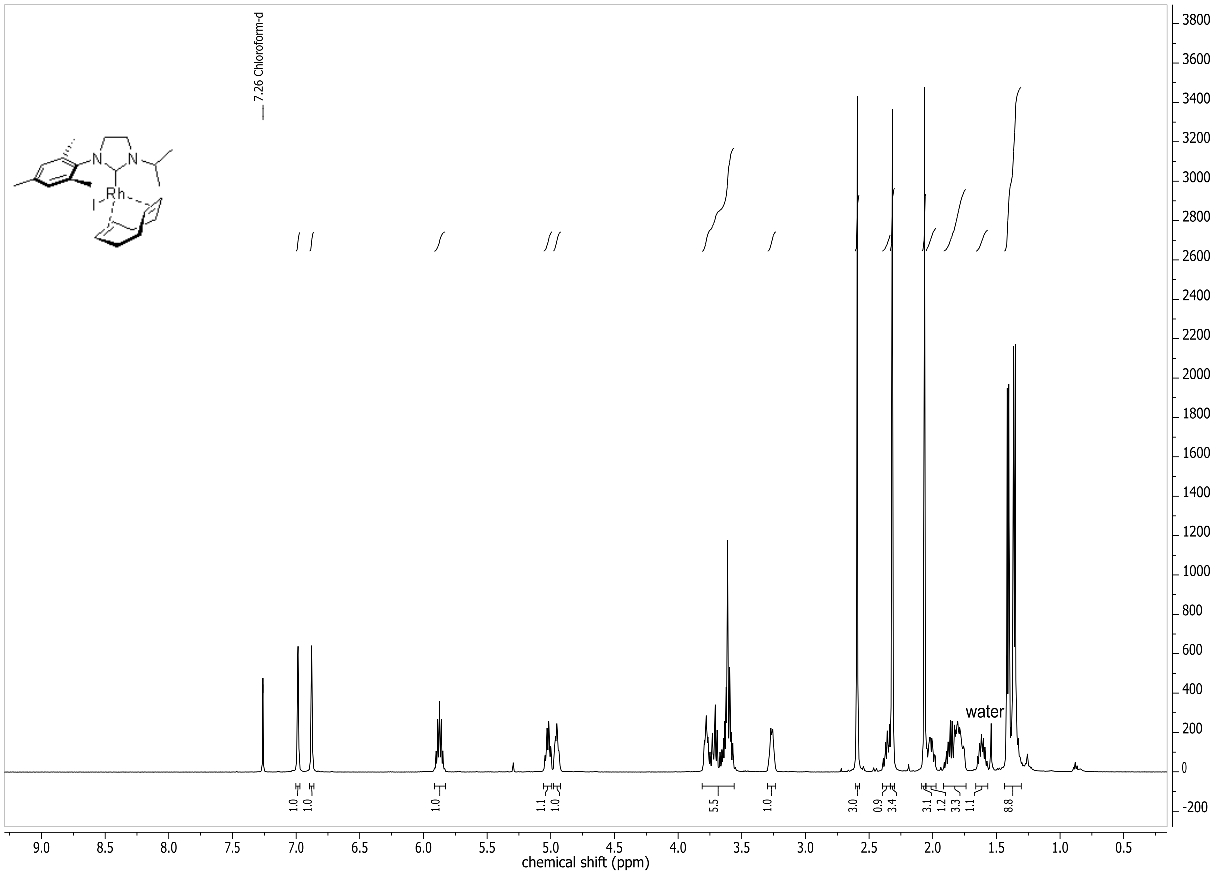

172.10
171.49
145.82
139.96
136.56
136.33
134.51
130.89
130.02
129.70
129.13
128.36
128.30
93.66
93.56
93.32
93.23
77.16 Chloroform-d
72.16
71.97
70.49
70.30
37.44
32.82
31.67
29.85
29.18
21.66
21.32
17.89
N
N
N
Rh
I
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 ( мд )

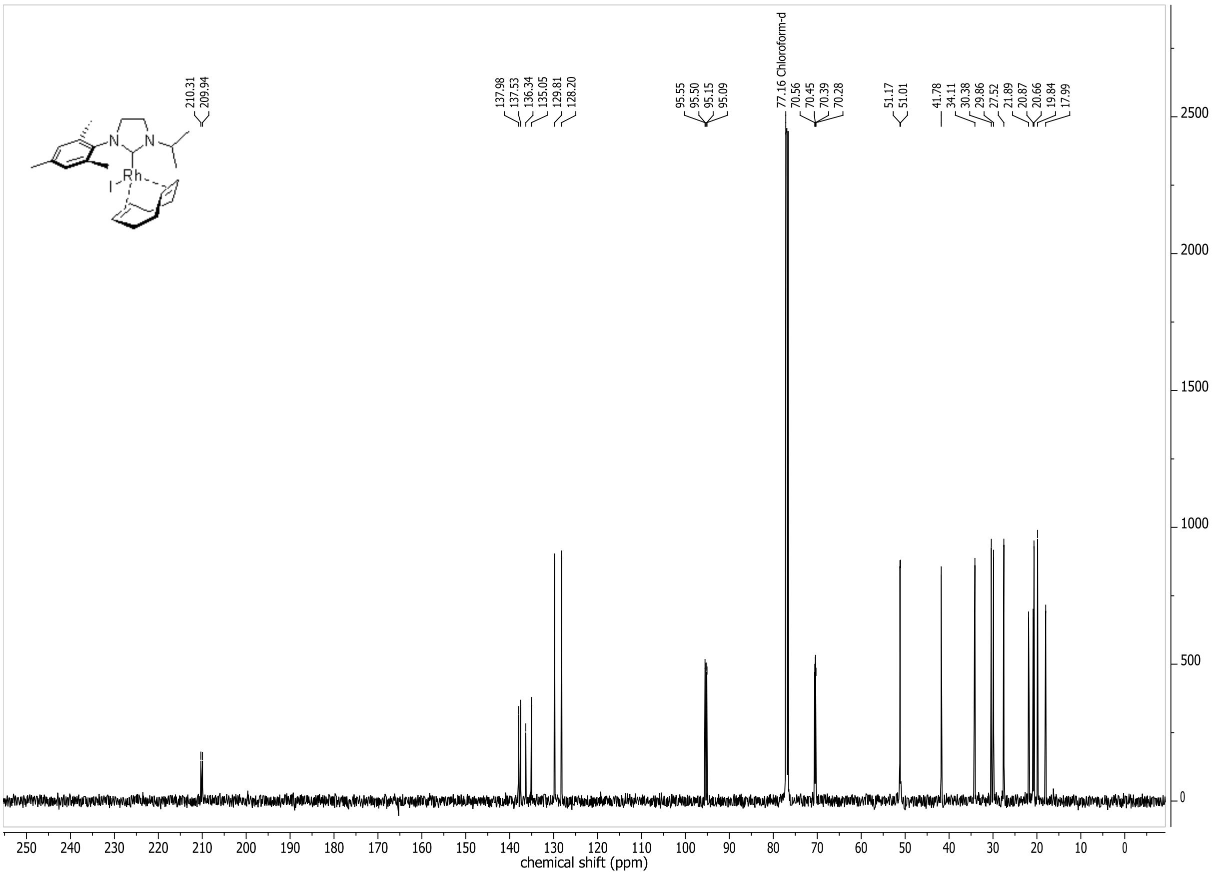

7.26 Chloroform-d
1.43
cyclohexane
iPr
iPr
iPr
iPr
N
N
Rh
Cl
2.0
2.0
1.9
1.9
1.9
3.9
1.9
1.9
2.0
2.0
2.1
6.2
3.2
3.6
5.9
12.5
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
chemical shift (ppm)

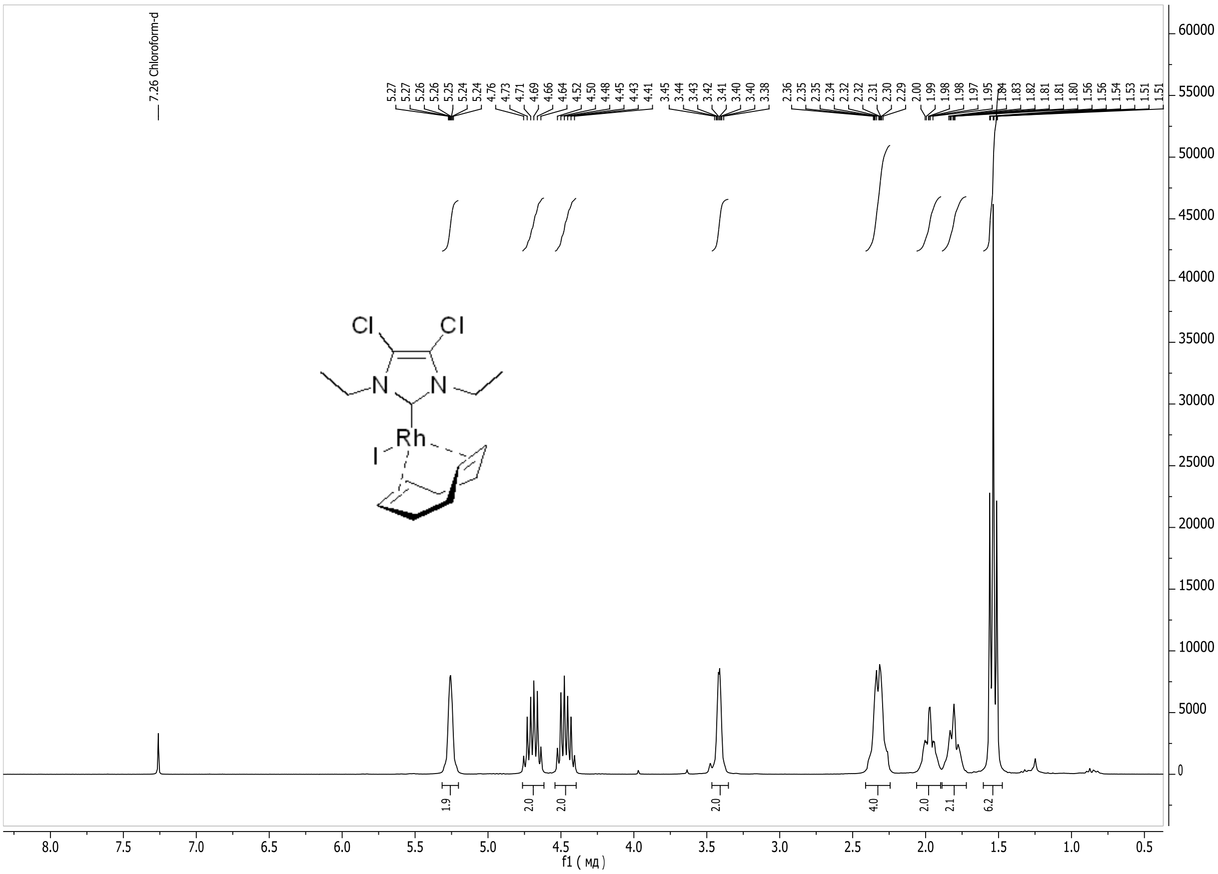

216.13
215.75
149.89
146.32
136.88
129.08
125.23
123.38
96.81
96.75
77.16 Chloroform-d
67.42
67.31
53.86
32.62
29.09
28.76
28.21
27.10
24.44
23.20
iPr
iPr
N
N
iPr
iPr
Rh
Cl
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
chemical shift (ppm)


7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
500
0
Cy
Cy
N
N
Cy
Cy
Cy
Cy
Rh
Cl
DCM
MeOH
2.2
6.8
2.0
2.0
2.0
1.8
2.5
5.4
5.4
4.9
71.3
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


193.04
192.61
149.25
140.30
133.27
129.97
129.47
127.37
127.00
126.85
123.69
121.88
96.35
96.30
77.16 Chloroform-d
67.86
67.75
45.04
39.80
36.92
34.79
33.51
32.83
28.47
27.18
27.10
26.44
26.27
Cy
Cy
Cy
Cy
Cy
Cy
N
N
Rh
Cl
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
chemical shift (ppm)


7.26 Chloroform-d
N
N
Rh
I
water
1.0
1.0
1.0
1.1
1.0
5.5
1.0
3.0
0.9
3.4
3.1
1.2
3.3
1.1
8.8
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


210.31
209.94
137.98
137.53
136.34
135.05
129.81
128.20
95.55
95.50
95.15
95.09
77.16 Chloroform-d
70.56
70.45
70.39
70.28
51.17
51.01
41.78
34.11
30.38
29.86
27.52
21.89
20.87
20.66
19.84
17.99
N
N
Rh
I
2500
2000
1500
1000
500
0
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


7.26 Chloroform-d
5.27
5.27
5.26
5.26
5.25
5.24
5.24
4.76
4.73
4.71
4.69
4.66
4.64
4.52
4.50
4.48
4.45
4.43
4.41
3.45
3.44
3.43
3.42
3.41
3.40
3.40
3.38
2.36
2.35
2.35
2.34
2.32
2.32
2.31
2.30
2.29
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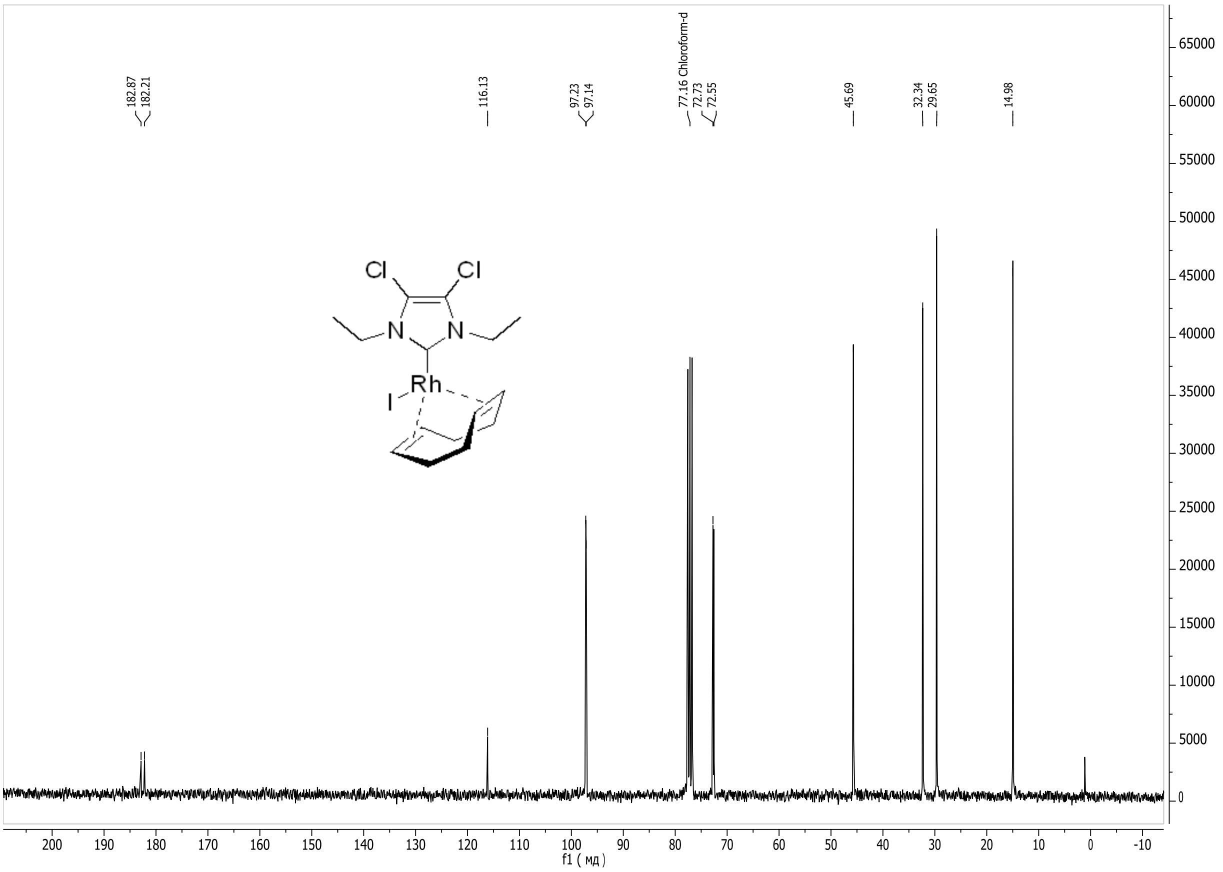
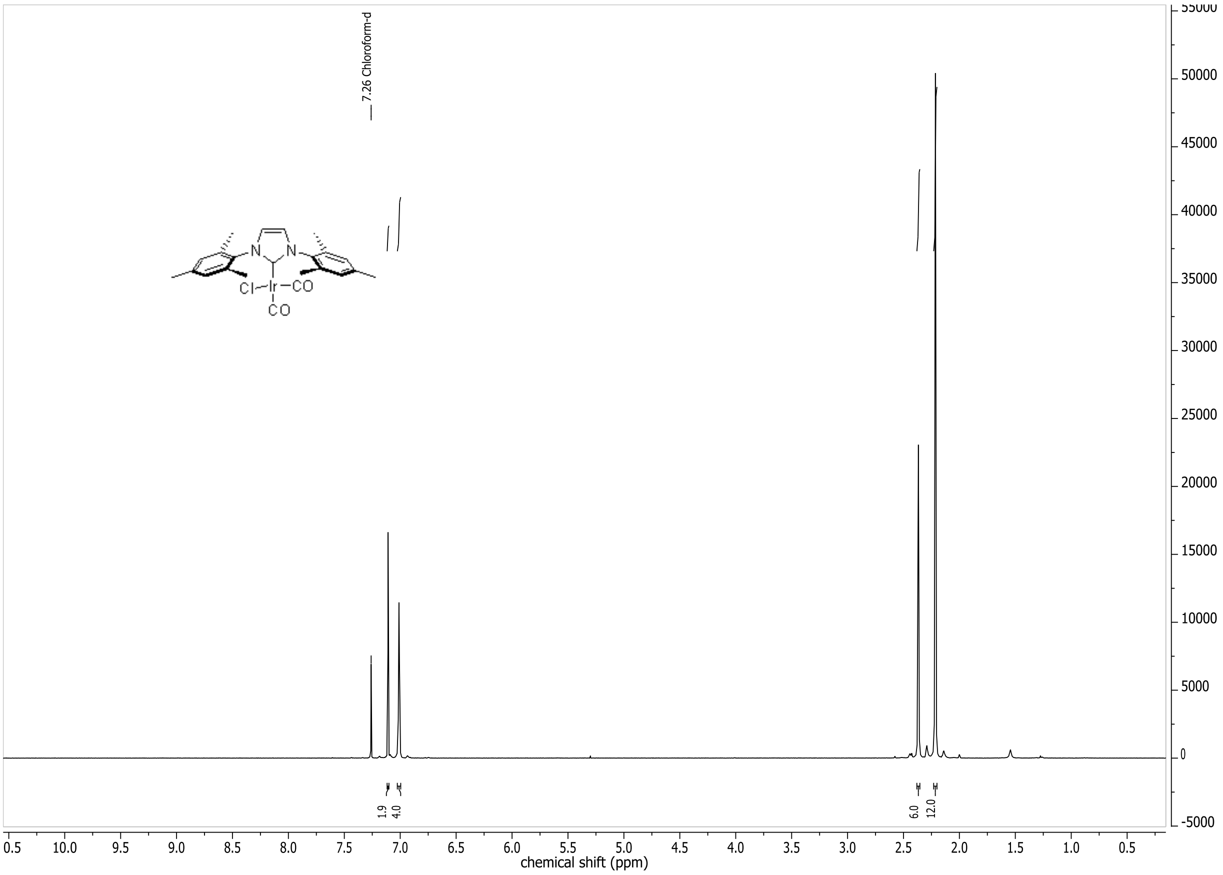
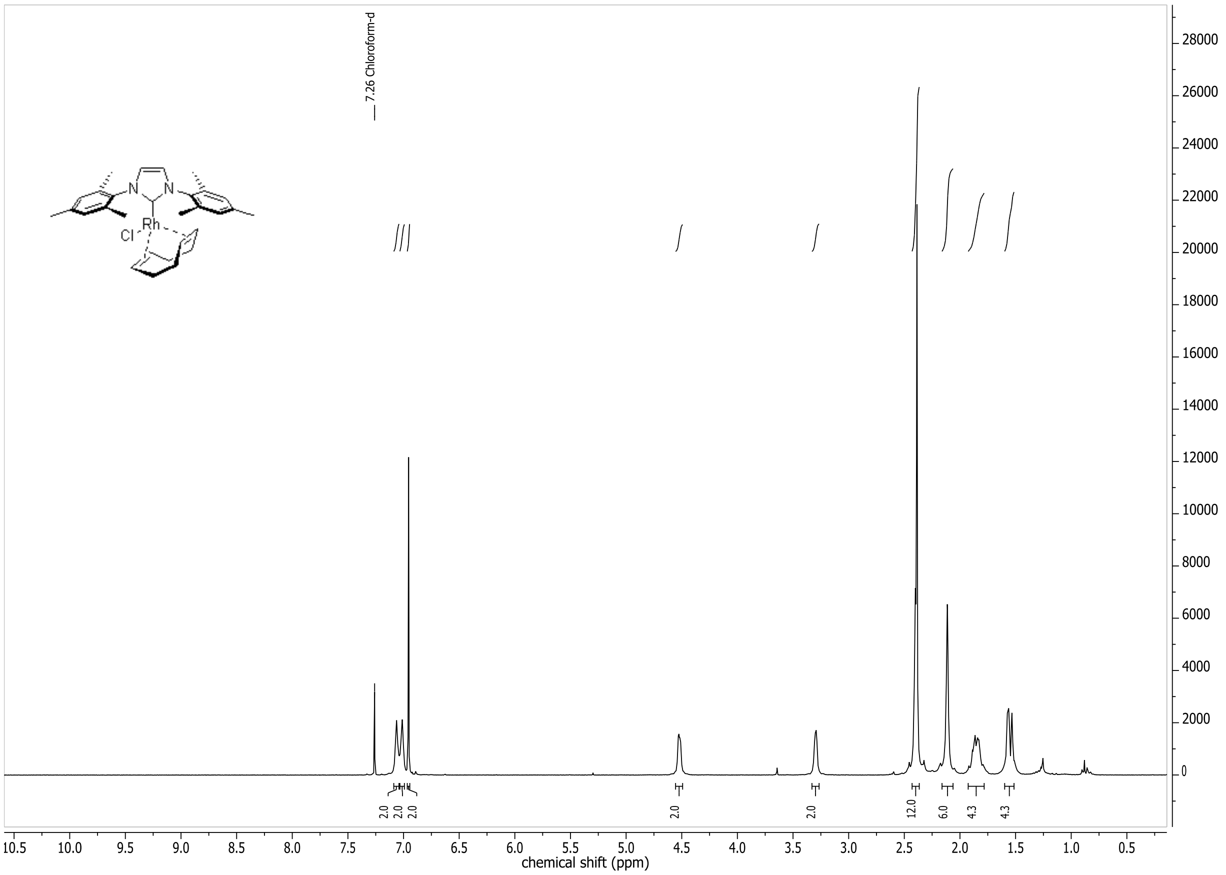
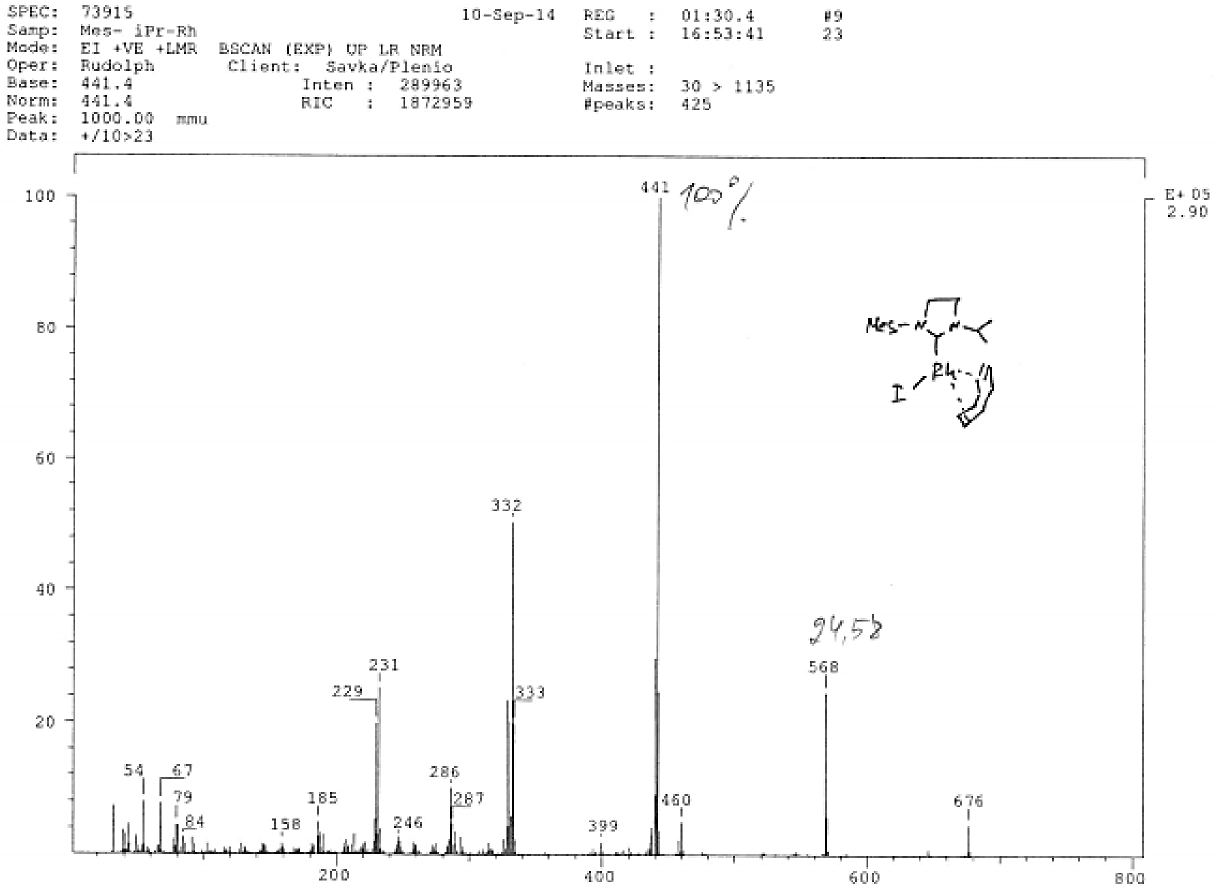
1.99
1.98
1.97
1.95
1.84
1.83
1.82
1.81
1.81
1.80
1.56
1.56
1.54
1.53
1.51
1.51
Cl
Cl
N
N
Rh
I
1.9
2.0
2.0
2.0
4.0
2.0
2.1
6.2
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 ( мд )


182.87
182.21
116.13
97.23
97.14
77.16 Chloroform-d
72.73
72.55
45.69
32.34
29.65
14.98
Cl
Cl
N
N
Rh
I
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 ( мд)

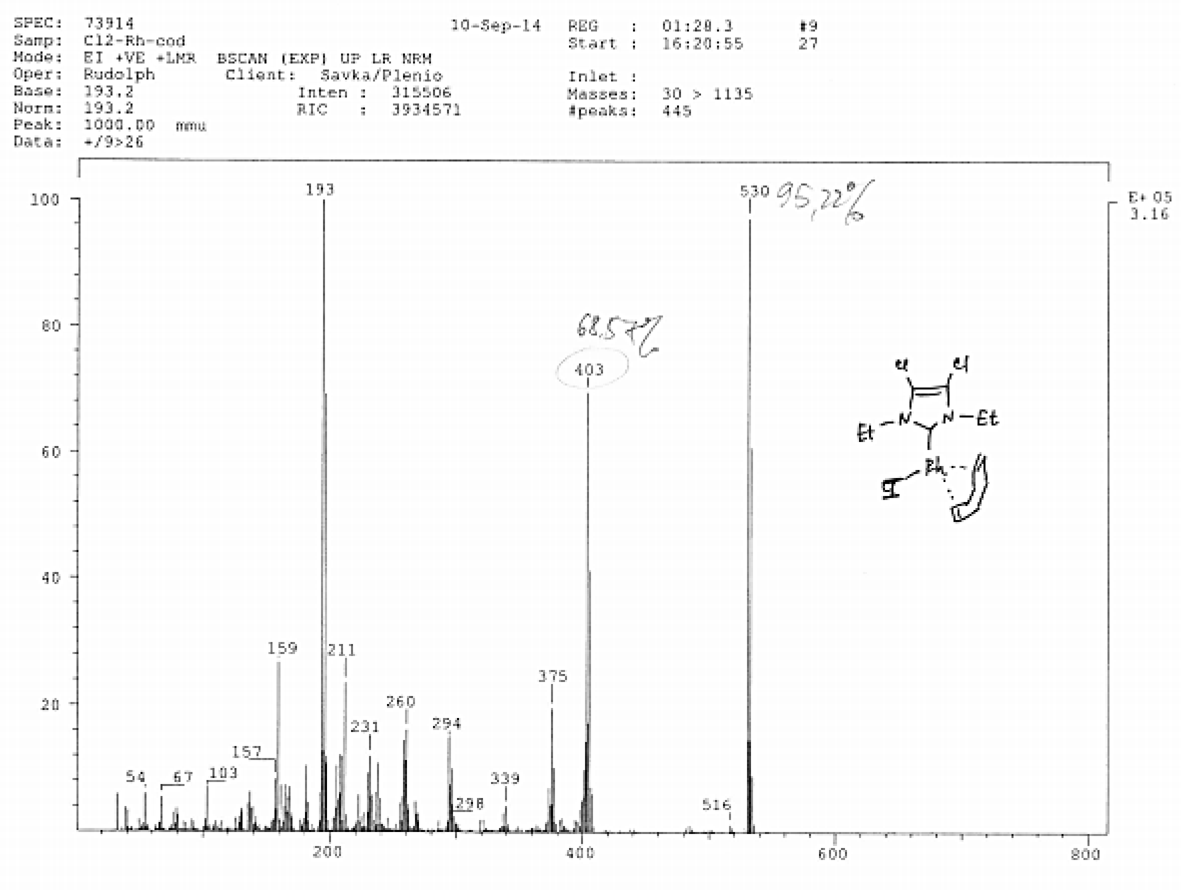

7.26 Chloroform-d
N
N
Cl
Ir
CO
CO
1.9
4.0
6.0
12.0
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
chemical shift (ppm)


7.26 Chloroform-d
N
N
Rh
Cl
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
2.0
2.0
2.0
2.0
2.0
12.0
6.0
4.3
4.3
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)

# Mass spectra of synthesized compounds

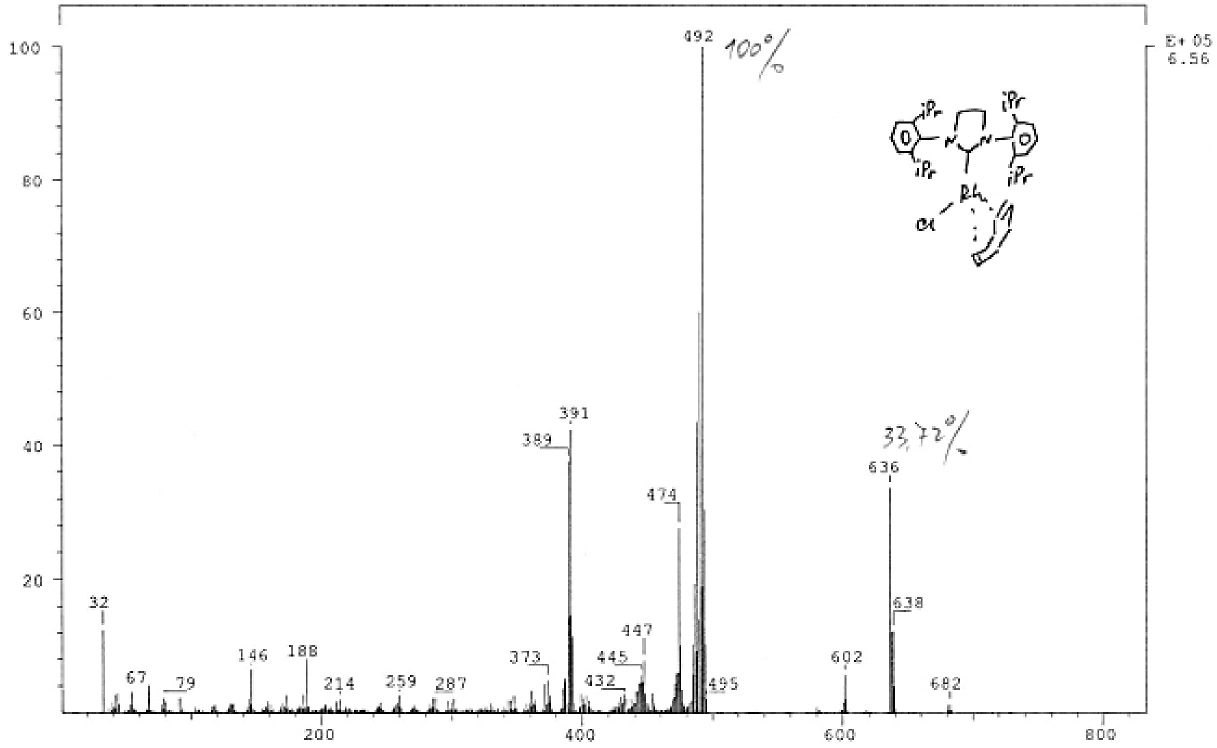


```
SPEC:  73915                            10-Sep-14   REG   :  01:30.4     #9
Samp:  Mes- iPr-Rh                                  Start :  16:53:41    23
Mode:  EI +VE +LMR  BSCAN (EXP) UP LR NRM
Oper:  Rudolph       Client:   Savka/Plenio         Inlet :
Base:  441.4                Inten :   289963        Masses:  30 > 1135
Norm:  441.4                RIC   :  1872959        #peaks:  425
Peak:  1000.00  mmu
Data:  +/10>23
```

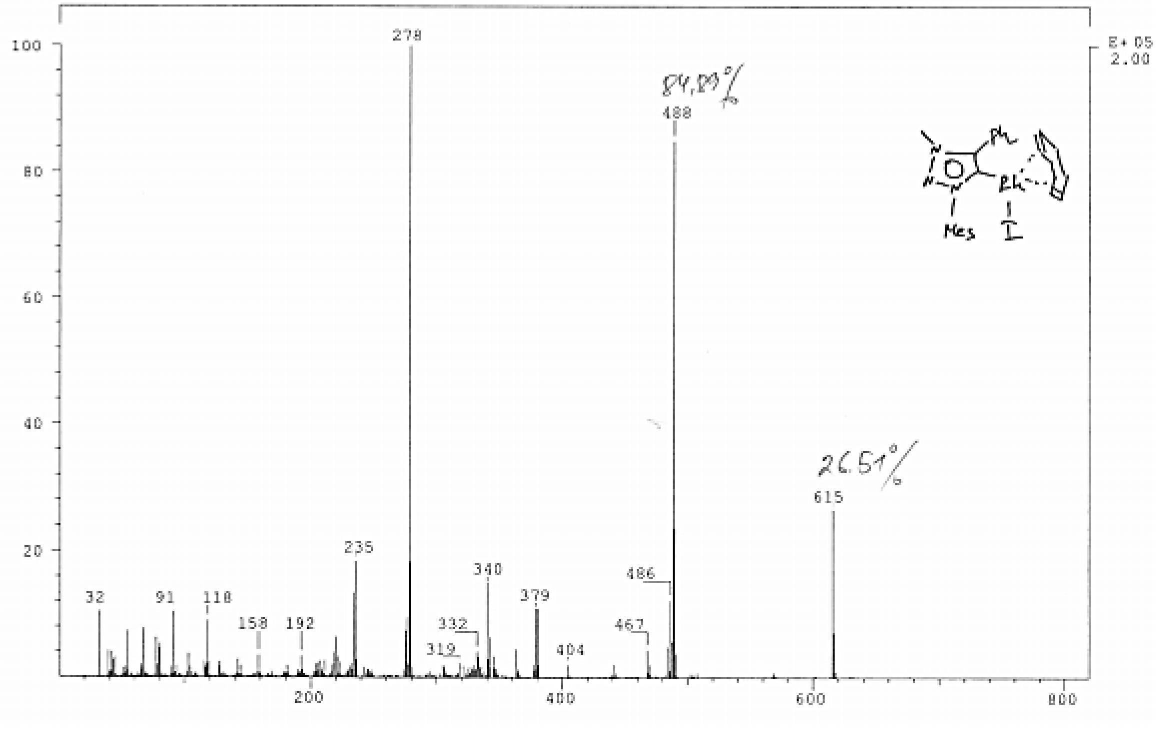


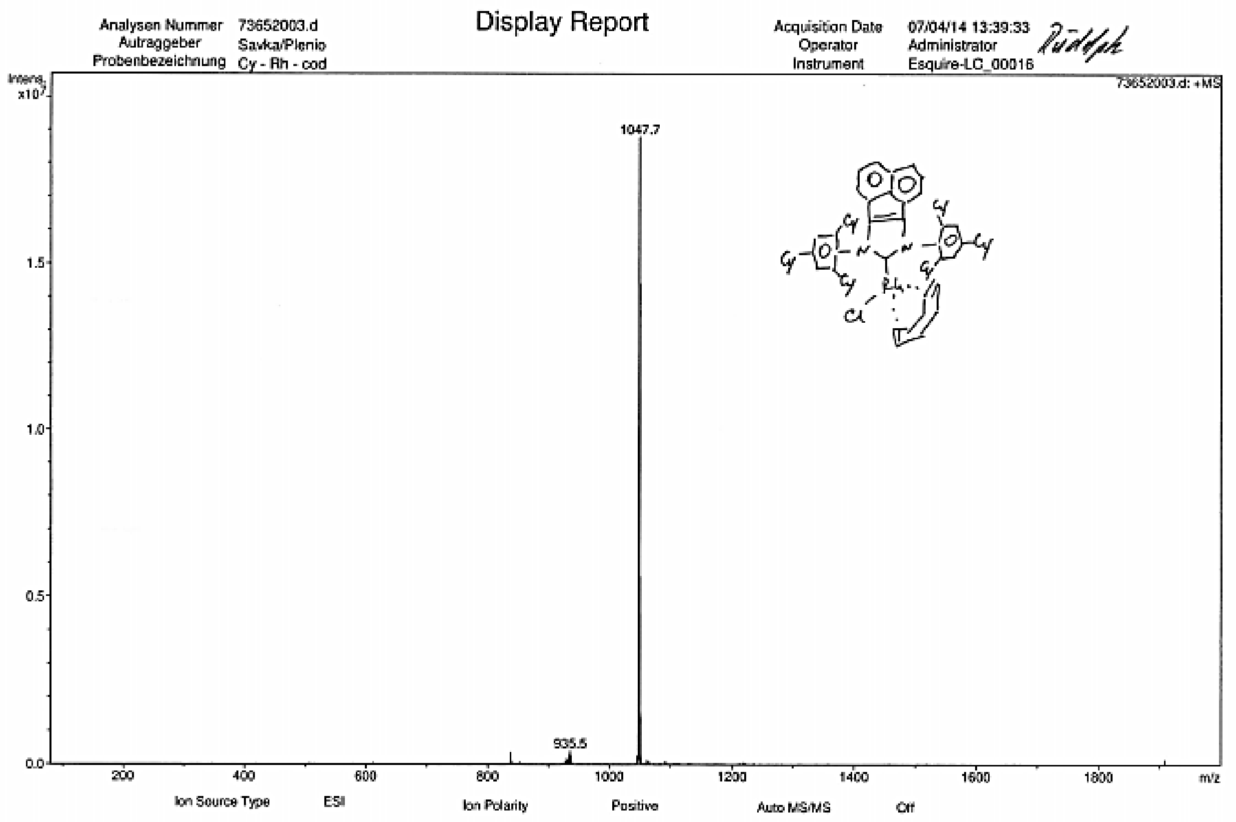
```
SPEC:  73914                          10-Sep-14   REG   :  01:28.3     #9
Samp:  Cl2-Rh-cod                                 Start :  16:20:55    27
Mode:  EI +VE +LMR  BSCAN (EXP) UP LR NRM
Oper:  Rudolph       Client:   Savka/Plenio       Inlet :
Base:  193.2               Inten :   315506       Masses:  30 > 1135
Norm:  193.2               RIC   :  3934571       #peaks:  445
Peak:  1000.00  mmu
Data:  +/9>26
```

```
SPEC:  73917                              10-Sep-14   REG    :  01:16.7      #9
Samp:  SIPr-Rh-cod                                    Start  :  17:20:22     27
Mode:  EI +VE +LMR  BSCAN (EXP) UP LR NRM
Oper:  Rudolph        Client:  Savka/Plenio           Inlet  :
Base:  492.3                Inten :  655750           Masses:   30 > 1135
Norm:  492.3                RIC   :  6144020          #peaks:   583
Peak:  1000.00  mmu
Data:  +/8>27
```



```
SPEC:  73916                              10-Sep-14   REG    :  01:34.4      #9
Samp:  Triazol-Rh                                     Start  :  17:03:28     25
Mode:  EI +VE +LMR  BSCAN (EXP) UP LR NRM
Oper:  Rudolph        Client:  Savka/Plenio           Inlet  :
Base:  278.4                Inten :  199670           Masses:   30 > 1135
Norm:  278.4                RIC   :  1385878          #peaks:   445
Peak:  1000.00  mmu
Data:  +/10>23
```





Analysen Nummer 73652003.d
Autraggeber Savka/Plenio
Probenbezeichnung Cy - Rh - cod

Display Report

Acquisition Date 07/04/14 13:39:33
Operator Administrator
Instrument Esquire-LC_00016

Ion Source Type ESI
Ion Polarity Positive
Auto MS/MS Off

## Mikroanalytisches Laboratorium **KOLBE**

Höhenweg 17
D-45470 Mülheim an der Ruhr

Telefon : +49 - (0)208 - 32502
Telefax : +49 - (0)208 - 382314
www.mirko-lab.de

Prof. Dr. Herbert Plenio
Technische Universität Darmstadt
Organometallchemie
Eduard Zintl-Institut für Anorganische und Physikalische Chemie
Alarich-Weiss-Str. 23
D-64287 Darmstadt

Datum : 10.11.2014

| Probenbezeichnung | % C | % H | % N | | | | | V2O5 |
|---|---|---|---|---|---|---|---|---|
| IMES - Ir - Co | 46,71 | 4,07 | 4,72 | | | | | x |
| IPr - Rh - cod | 66,08 | 7,59 | 4,39 | | | | | x |
| Mes - iPr - Rh | 48,63 | 5,97 | 4,89 | | | | | x |

Mit freundlichen Grüssen

Inge Springer

H. KOLBE
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Höhenweg 17
D-45470 Mülheim a. d. Ruhr