Electronic Supplementary Information for the article

Rhodium complexes with planar-chiral cyclopentadienyl ligands: synthesis from tert-butylacetylene and catalytic performance in C-H activation of arylhydroxamates

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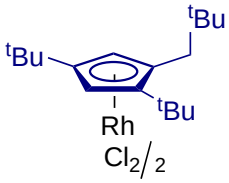
General considerations. Unless otherwise stated all reactions were carried out under argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was carried out in air. Complex $[(cod)RhCl]_2$ was synthesized according to the literature procedure.[1] All other reagents were obtained from commercial sources (Acros, Aldrich, J&K Scientific, Strem, or Vekton) and used as received. High resolution mass spectra were recorded using Bruker microTOF spectrometer with electrospray ionization (ESI). Enantiomeric excess values of the organic products were measured using Shimadzu HPLC equipped with Daicel Chiralpak IA-3 or IB-3 (4.6 × 150 mm) columns and diode array detector with flow rate 1 mL/min. ^1H and ^{13}C NMR spectra were measured using Bruker Avance 600MHz or Varian Inova 400MHz spectrometers at 20 °C. The chemical shifts are reported relative to residual signals of the solvent ($CHCl_3$: 7.26 for ^1H, 77.16 for ^{13}C; CD_3COCHD_2: 2.05 for ^1H, 29.84 for ^{13}C; $CD_3S(O)CHD_2$: ^1H: δ 2.50 ppm; ^{13}C: δ 39.52 ppm). The copies of NMR spectra of the new compounds are given at the end of this document.

Synthesis of non-functionalized complexes

An improved synthesis of $[(\eta^5\text{-}1,3\text{-}^t\mathrm{Bu}_2\text{-}4\text{-}^t\mathrm{BuCH}_2\text{-}\mathrm{C}_5\mathrm{H}_2)\mathrm{RhCl}_2]_2$ (2)



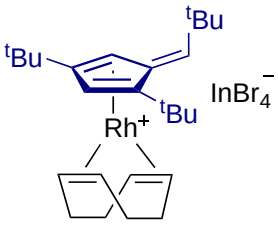
Granular $AlCl_3$ (162 mg, 0.6 mmol, threefold excess) was placed in the 10 ml Schlenk tube. Then Schlenk tube was evacuated and backfilled argon. Al_2Cl_6 was grinded with a spatula inside the Schlenk tube under argon atmosphere. Then 3 ml of CH_2Cl_2 was added followed by $[(cod)RhCl]_2$ (100 mg, 0.2 mmol). Resulting mixture was stirred for 10 min. Initial yellow color of the solution changed to green, then became yellow again. Then tert-butylacetylene (198 mg, 2.4 mmol, 300 µL, twofold excess) was added one portion, and the solution immediately became red. The solution was stirred overnight, then 1 ml of concentrated hydrochloric acid was added, and the mixture was stirred vigorously for additional 20 min. The solution opened to air and washed with water twice to remove $AlCl_3$. The red organic layer was dried with anhydrous Na_2SO_4, evaporated to dryness, and triturated with pentane (3x5 ml) to obtain the orange-red product, which was dried in vacuum. The product has sufficient purity for application in catalysis without additional purification.

Yield: 160 mg, 0.38 mmol, 95%.

^{1}H NMR (400 MHz, chloroform-d): δ = 5.54 (s, 1H), 5.32 (s, 1H), 2.75 (d, 1H, J = 14.9 Hz), 2.63 (d, 1H, J = 14.9 Hz), 1.43 (s, 9H), 1.34 (s, 9H), 1.00 (s, 9H) ppm.

^{1}H NMR data is in agreement with those reported previously.[2]

Synthesis of $[(\eta^5\text{-}1,3,6\text{-}^t\mathrm{Bu}_3\text{-fulvene})\mathrm{Rh}(1,5\text{-}\mathrm{C}_8\mathrm{H}_{12})]^+\mathrm{InBr}_4^-$ (4InBr4)



Complex $[(cod)RhCl]_2$ (100 mg, 0.2 mmol) and anhydrous $InBr_3$ (284 mg, 0.8 mmol) were placed in the Schlenk tube. Then CH_2Cl_2 (2 ml) was added and the yellow-green solution was stirred for 5 min. Then tert-butylacetylene (0.6 ml, 4.8 mmol) was added one portion. The yellow-green color of the solution slowly changes to red. After 6 hours, the red reaction mixture was filtered, the precipitate was washed with CH_2Cl_2 (3x3 ml), and the combined solutions were evaporated to dryness. The resulting residue was washed with Et_2O (3×5 ml) and dried in vacuum to give product as red solid. A single crystal suitable for X-ray diffraction was obtained by slow diffusion of Et_2O vapors into the solution of complex in CH_2Cl_2 at 4 °C.

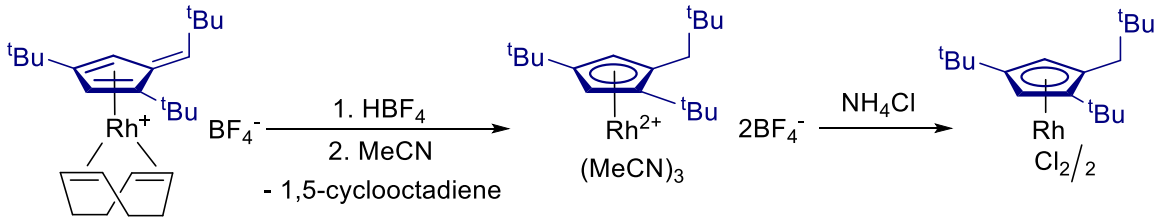
Yield: 250 mg, 0.28 mmol, 70%.

^{1}H NMR (400 MHz, acetone-d_6): δ = 7.52 (s, 1H), 7.01 (s, 1H) 5.76 (s, 1H), 5.72-5.66 (m, 1H), 5.58–5.48 (m, 1H), 5.48–5.39 (m, 1H), 5.37–5.31 (m, 1H), 2.83 (dd, *J* = 15.1, 7.7 Hz, 1H), 2.64–2.45 (m, 3H), 2.42–2.32 (m, 1H), 2.31–2.12 (m, 3H), 1.45 (s, 9H), 1.43 (s, 9H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, acetone-d_6): δ = 152.5, 139.3 (d, $J_{Rh\text{-}C}$ = 4.3 Hz), 119.8 (d, $J_{Rh\text{-}C}$ = 5.3 Hz), 114.4 (d, $J_{Rh\text{-}C}$ = 3.1 Hz), 104.8 (d, $J_{Rh\text{-}C}$ = 3.5 Hz), 90.6 (d, $J_{Rh\text{-}C}$ = 11.3 Hz), 88.4 (d, $J_{Rh\text{-}C}$ = 11.1 Hz), 87.6 (d, $J_{Rh\text{-}C}$ = 9.8 Hz), 86.7 (d, $J_{Rh\text{-}C}$ = 10.3 Hz), 79.7 (d, $J_{Rh\text{-}C}$ = 4.8 Hz), 39.7, 35.3, 35.1, 34.4, 33.0, 32.7 (CH_3), 30.64 (CH_3), 30.62 (CH_3), 30.0, 29.0 ppm.

Elemental analysis. Calculated for $C_{26}H_{42}Br_4InRh\times0.5Et_2O$: C, 36.20%; H, 5.10%. Found: C, 36.10%; H, 5.05%.

Protonation of the fulvene complex 4 in the presence of acetonitrile



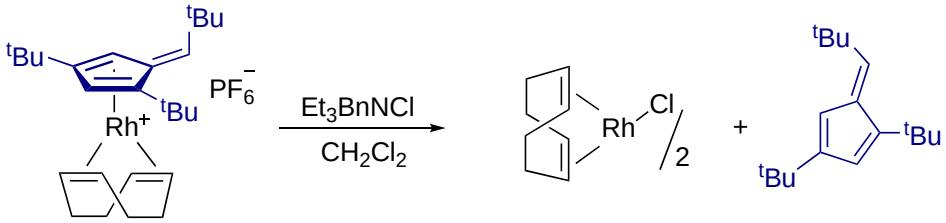
Under argon atmosphere complex[3] $[(\eta^5\text{-}1,3,6\text{-}^t\text{Bu}_3\text{-fulvene})\text{Rh}(1,5\text{-}C_8H_{12})]^+BF_4^-$ (108 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (1 ml). Then $HBF_4\times Et_2O$ (27 µL, 0.2 mmol) added and the mixture was stirred for 1 hour. Then MeCN (62 µL, 1.2 mmol, 6 equiv., twofold excess) was added and reaction keep stirred for additional 20 min. Red solution become orange, indicating the formation of the complex $[(\eta^5\text{-}1,3,6\text{-}^t\text{Bu}_3\text{-fulvene})\text{Rh}(\text{MeCN})_3](BF_4)_2$. The sample was taken out of solution and NMR spectrum was measured (free cyclooctadiene was also detected). Finally, the saturated aqueous solution of NH_4Cl was added and the mixture was variously stirred overnight. The mixture was opened to air and the orange organic phase was separated. Organic solution was dried with anhydrous Na_2SO_4, evaporated to dryness. The residue was triturated with pentane (3×5 ml) and dried in vacuum to give the complex **2** as orange-red precipitate.

Yield: 67 mg, 0.16 mmol, 80%.

^{1}H NMR data of complex **2** is in agreement with those reported previously.[2]

^{1}H NMR spectrum of the presumed intermediate acetonitrile complex $[(\eta^5\text{-}1,3,6\text{-}^t\text{Bu}_3\text{-fulvene})\text{Rh}(\text{MeCN})_3](BF_4)_2$ (acetone-d_6, 400 MHz): δ = 6.66 (s, 1H), 6.37 (s, 1H), 3.96–3.17 (m, 9H, $C\underline{H}_3CN$), 2.96 (d, 1H, *J* = 14.7 Hz), 2.36 (d, 1H, *J* = 14.3 Hz), 1.56 (s, 9H), 1.44 (s, 9H), 1.08 (s, 9H) ppm.

Reaction of the fulvene complex 4 in the presence of chloride anion

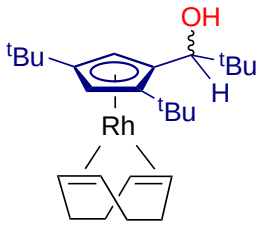


Under argon atmosphere complex[3] $[(\eta^5\text{-}1,3,6\text{-}^t\text{Bu}_3\text{-fulvene})\text{Rh}(1,5\text{-}C_8H_{12})]^+PF_6^-$ (60 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (1 ml) and $[Et_3BnN]Cl$ (23 mg, 0.1 mmol) was added. The red solution became yellow and the reaction mixture was stirred for 6 hours. The solution was open to air and evaporated to dryness. The residue was triturated with pentane (3×5 ml), the combined pentane solutions were passed through a short pad of SiO_2 and evaporated to give free 1,3,6-^{t}Bu$_3$-fulvene (established by ^{1}H NMR,[4] the yield was not measured). The solid residue was dissolved in benzene and filtered through a short pad of SiO_2. The resulting yellow solution evaporated to dryness to give $[(\text{cod})\text{RhCl}]_2$ as yellow powder.

Yield: 20 mg, 0.04 mmol, 80%.

Synthesis of hydroxy-substituted complexes

Synthesis of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(OH)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5OH)



Under argon atmosphere complex[3] [(η^5-1,3,6-^{t}Bu$_3$-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^+$PF$_6^-$ (120 mg, 0.2 mmol; BF_4^- or $InBr_4^-$ salts can be used as well) and K_2CO_3 (56 mg, 0.4 mmol) were suspended in THF (1 ml) and H_2O (36 mg, 2 mmol, 36 µL) was added. The color of the reaction mixture changes from red to brown. The mixture was stirred for 1 hour, then opened to air, and the solvent was evaporated. The residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated and dried in vacuum to give the product **5**OH as yellow oil.

Yield: 73 mg, 0.154 mmol, 77%.

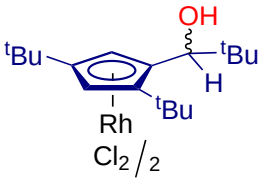
Since there are two diastereomeric Cp ligands, two sets of signals are observed in the spectrum. Tentative assignment to isomers is marked as A and B.

^{1}H NMR (Chloroform-*d*, 400 MHz): δ = 4.91 (s, 1H, Cp^A), 4.80 (s, 1H, Cp^B), 4.66 (s, 1H, Cp^A), 4.54 (s, 1H, Cp^B), 4.45 (s, 1H, CpC$\underline{H}^B$), 4.44 (s, 1H, CpC$\underline{H}^A$) 4.04 – 3.90 (m, 6H, COD$^{\underline{CH}}$), 3.89 – 3.80 (m, 2H, COD$^{\underline{CH}}$), 2.48 (s, 1H, O$\underline{H}^A$), 2.35 – 2.11 (m, 8H, COD$^{\underline{CH2}}$), 2.10 – 2.01 (m, 2H, COD$^{\underline{CH2}}$), 1.94 – 1.75 (m, 6H, COD$^{\underline{CH2}}$), 1.37 (s, 1H, O$\underline{H}^B$), 1.24 (s, 18H, ^{t}Bu^{A+B}), 1.22 (s, 18H, ^{t}Bu^{A+B}), 1.17 (s, 9H, ^{t}Bu^B), 1.01 (s, 9H, ^{t}Bu^A).

^{13}C NMR (Chloroform-*d*, 101 MHz): δ = 117.76 (d, J_{Rh-C} = 5.0 Hz), 116.57 (d, J_{Rh-C} = 3.4 Hz), 105.68 (d, J_{Rh-C} = 4.4 Hz), 83.31 (d, J_{Rh-C} = 3.8 Hz), 82.83 (d, J_{Rh-C} = 3.6 Hz), 82.49 (d, J_{Rh-C} = 3.8 Hz), 79.06 (d, J_{Rh-C} = 4.2 Hz), 76.52, 65.88 (d, J_{Rh-C} = 13.8 Hz), 65.10 (d, J_{Rh-C} = 13.5 Hz), 65.06 (d, J_{Rh-C} = 13.9 Hz), 63.80 (d, J_{Rh-C} = 13.6 Hz), 36.17, 35.66, 34.03, 32.49, 32.46, 32.37, 32.23, 32.21, 32.19, 31.73, 31.55, 31.25, 29.84 ppm.

HRMS (ESI). Calculated for C$_{26}$H$_{43}$ORh [M]$^+$ = 474.2363, found 474.2352.

Synthesis of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(OH)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (2OH-Cl).



Under argon atmosphere complex **2OH-I** (20 mg, 0.032 mmol) was placed in a Schlenk tube (protected from light by aluminum foil) and dissolved in CH_2Cl_2 (2ml). Then $AgBF_4$ (13 mg, 0.066 mmol) was added, the violet solution became bright orange, and the precipitate of AgI was formed. The precipitated was filtered off and the solution was transferred to another Schlenk tube which contained Et_3BnNCl (15 mg, 0.064 mmol, 2 equiv.) dissolved in CH_2Cl_2 (1ml). The resulting mixture was stirred for 10 min, then opened to the air and evaporated to dryness. Orange residue was extracted with benzene and filtered through a short pad of SiO_2 to remove [Et_3BnN][BF_4]. The filtrate was evaporated to dryness to give the product **2OH-Cl** as orange powder.

Yield: 11mg, 0.25 mmol, 79%.

Single crystals of the complex suitable for X-ray diffraction were obtained by slow diffusion of pentane vapors into the solution of complex in $CDCl_3$.

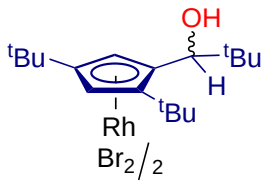
Since there are two diastereomeric Cp ligands, two sets of signals are observed in the spectrum. Tentative assignment to isomers is marked as A and B.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.33 (s, 1H, Cp^A), 6.12 (s, 1H, Cp^B), 5.81 (s, 1H, Cp^B), 5.70 (s, 1H), 5.16 (d, 1H, *J* = 6.1 Hz), 4.53 (d, 1H, *J* = 3.9 Hz), 4.48 (d, 1H, *J* = 3.7 Hz), 4.16 (d, 1H, *J* = 6.1 Hz), 1.44 (s, 18H), 1.28 (s, 9H), 1.27 (s, 9H), 1.03 (s, 9H), 0.95 (s, 9H) ppm.

^{13}C NMR (DMSO-d_6, 101 MHz): δ = 132.53, 129.06, 110.51 (d, J_{Rh-C} = 6.8 Hz), 110.25 (d, J_{Rh-C} = 5.9 Hz), 107.41 (d, J_{Rh-C} =7.4 Hz), 106.47 (d, J_{Rh-C} =7.3 Hz), 106.32 (d, J_{Rh-C} =7.8 Hz), 101.21 (d, J_{Rh-C} = 7.5 Hz), 92.38, 90.13 (d, J_{Rh-C} = 6.3 Hz), 87.96 (d, J_{Rh-C} = 6.0 Hz), 83.86 (d, J_{Rh-C} = 7.7 Hz), 74.32, 70.27, 51.95, 35.76, 35.42, 33.79, 33.73, 31.41, 30.90, 30.72, 30.59, 29.54, 29.48, 27.38, 26.78 ppm.

HRMS (ESI). Calculated for $C_{18}H_{31}ClORh$ $[M_{monomer}-Cl]^+$= 401.1117. Found 401.1118.

Synthesis of $[(\eta^5\text{-}1,3\text{-}^tBu_2\text{-}4\text{-}^tBu(OH)CH\text{-}C_5H_2)RhBr_2]_2$ (2OH-Br).



Under argon atmosphere complex **2OH-I** (20 mg, 0.032 mmol) was placed in a Schlenk tube (protected from light by aluminum foil) and dissolved in CH_2Cl_2 (2ml). Then $AgBF_4$ (13 mg, 0.066 mmol) was added, the violet solution became bright orange, and the precipitate of AgI was formed. The precipitated was filtered off and the solution was transferred to another Schlenk tube which contained Et_4NBr (21 mg, 0.064 mg, 2 equiv.) in CH_2Cl_2 (1ml) in another Schlenk tube. Reaction mixture immediately became dark orange. The mixture was stirred for 10 min, then opened to air and evaporated to dryness. The residue was extracted with benzene and filtered through a short pad of SiO_2 to remove $[Et_4N][BF_4]$. The filtrate was evaporated to dryness to give the product **2OH-Br** as orange powder.

Yield: 14 mg, 0.26 mmol, 83%.

Single crystals of the complex suitable for X-ray diffraction were obtained by slow diffusion of pentane vapors into the solution of complex in $CDCl_3$.

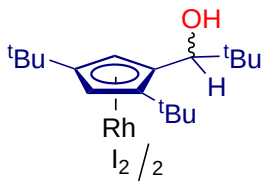
Since there are two diastereomeric Cp ligands, two sets of signals are observed in the spectrum. Tentative assignment to isomers is marked as A and B.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.42 (s, 1H, Cp^A), 6.16 (s, 1H, Cp^B), 5.80 (s, 1H, Cp^B), 5.70 (s, 1H, Cp^A), 4.57 (s, 1H, Cp^A), 4.23 (s, 1H, Cp^B), 1.46 (s, 18H, Cp^{A+B}), 1.30 (s, 9H, Cp^B), 1.28 (s, 9H, Cp^A), 1.05 (s, 9H, Cp^B), 0.96 (s, 9H, Cp^A) ppm.

^{13}C NMR (DMSO-d_6, 101 MHz): δ = 111.78 (d, *J* = 6.9 Hz), 111.35 (d, *J* = 5.0 Hz), 108.21 (d, *J* = 10.0 Hz), 107.64 (d, *J* = 8.1 Hz), 102.09 (d, *J* = 7.3 Hz), 91.79 (d, *J* = 7.3 Hz), 89.26 (d, *J* = 6.8 Hz), 87.72 (d, *J* = 6.8 Hz), 84.22 (d, *J* = 8.3 Hz), 74.18, 70.18, 35.78, 35.66, 33.95, 31.83, 31.16, 30.92, 30.82, 29.89, 29.79, 27.58, 26.91 ppm

HRMS (ESI). Calculated for $C_{18}H_{31}BrORh$ $[M_{monomer}-Br]^+$= 445.0613. Found 445.0607.

Synthesis of $[(\eta^5\text{-}1,3\text{-}^tBu_2\text{-}4\text{-}^tBu(OH)CH\text{-}C_5H_2)RhI_2]_2$ (2OH-I)



In air a solution of I_2 (45 mg, 0.18 mmol) in hexane (7 ml) was added dropwise to a stirred yellow solution of the complex **5OH** (84 mg, 0.18 mmol) in hexane (5 ml). The dark violet precipitate was formed immediately. After 5 minutes of stirring the solid residue was separated by

centrifugation, washed with pentane (4×5 ml) to remove residual cyclooctadiene and dried in vacuum to give the product **2OH-I** as a dark purple powder.

Yield: 103 mg, 0.083 mmol, 94%.

Since there are two diastereomeric Cp ligands, NMR spectra of **2OH-I** in non-coordinating solvents (for example, chloroform) are extremely complex due to the formation of homo- and hetero-chiral dimers. The NMR spectra in DMSO are simpler, because DMSO destroys the dimeric structures and form monomeric adducts. Still, two sets of signals are observed in the spectrum (marked as A and B).

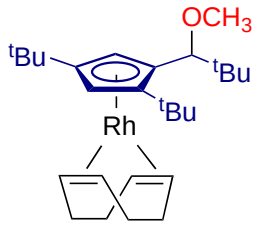
^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.52 (s, 1H, Cp^{A}), 6.23 (s, 1H, Cp^{B}), 5.83 (s, 1H, Cp^{B}), 5.69 (s, 1H, Cp^{A}), 5.01 (d, 1H, *J*=6.9 Hz, Cp^{B}), 4.64 (d, 1H, *J*=4.2 Hz, Cp^{A}), 4.34 (d, 1H, *J*=6.5 Hz, Cp^{A+B}), 1.47 (s, 18H, Cp^{A+B}), 1.32 (s, 9H, Cp^{B}), 1.30 (s, 9H, Cp^{A}), 1.06 (s, 9H, Cp^{B}), 0.98 (s, 9H, Cp^{A}) ppm.

^{13}C NMR (DMSO-d_6, 101 MHz): δ = 122.22 (d, *J* = 5.0 Hz), 115.40 (d, *J* = 2.7 Hz), 114.38 (d, *J* = 5.4 Hz), 111.61 (d), 110.20 (d, *J* = 7.2 Hz), 103.96 (d, *J* = 3.8 Hz), 89.22 (d, *J* = 6.3 Hz), 87.96 (d, *J*=7.3 Hz), 87.34 (d, *J* = 7.6 Hz), 85.34 (d), 74.37, 70.30, 36.17, 35.88, 34.17, 33.96, 32.53, 31.71, 31.22, 30.56, 30.45, 27.93, 27.15 ppm.

HRMS (ESI). Calculated for $C_{36}H_{62}I_3O_2Rh_2$ $[M\text{-}I]^+$= 1112.9994. Found 1112.9972.

Synthesis of alkoxy-substituted complexes

Synthesis of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CH$_3$O)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5OMe**).**



Under argon atmosphere complex [(η^5-1,3,6-^{t}Bu$_3$-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^+$PF$_6^-$ (101 mg, 0.17 mmol, BF_4^- or $InBr_4^-$ salts can be used as well) and ^{t}BuOK (19 mg, 0.17 mmol) were dissolved in MeOH (2 ml). The reaction mixture was stirred for 1 hour, then opened to air and the solvent was evaporated. The solid residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated and dried in vacuum to give the complex **5**OMe as yellow oil. It should be noted that the product is not stable on silica gel columns.

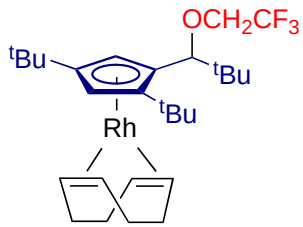
Yield: 79 mg, 0.16 mmol, 96%.

A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a pentane solution of the complex.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.68 (d, J = 2.3 Hz, 1H, CH^{Cp}), 4.47 (d, J = 2.2 Hz, 1H, CH^{Cp}), 4.07 (s, 1H, C<u>H</u>OCH$_3$), 3.98–3.95 (m, 2H, CH^{C8H12}), 3.91–3.88 (m, 2H, CH^{C8H12}), 2.98 (s, 3H, OCH_3), 2.31–2.23 (m, 2H, CH_2^{C8H12}), 2.20–2.13 (m, 2H, CH_2^{C8H12}), 2.01–1.98 (m, 2H, CH_2^{C8H12}), 1.81–1.75 (m, 2H, CH_2^{C8H12}), 1.29 (s, 9H, CH_3), 1.20 (s, 9H, CH_3), 1.18 (s, 9H, CH_3).

^{13}C NMR (151 MHz, $CDCl_3$) δ 119.3 (d, J_{Rh-C} = 3.1 Hz), 118.2 (d, J_{Rh-C} = 4.8 Hz), 105.7 (d, J_{Rh-C} = 4.1 Hz), 83.9 (s), 83.7 (d, J_{Rh-C} = 3.6 Hz), 80.8 (d, J_{Rh-C} = 4.2 Hz), 66.3 (d, J_{Rh-C} = 13.9 Hz), 65.0 (d, J_{Rh-C} = 13.8 Hz), 56.3, 36.1, 33.1, 32.7, 32.3, 32.2, 31.8, 31.2, 27.5.

Synthesis of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF$_3$CH$_2$O)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5**OCH$_2$CF$_3$).**



Under argon atmosphere [(η^5-1,3,6-^{t}Bu$_3$-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^+$PF$_6^-$ (120 mg, 0.2 mmol, BF_4^- or $InBr_4^-$ salts can be used as well) and anhydrous K_2CO_3 (28 mg, 0.2 mmol) were suspended in THF (1 ml) and TFE (200 mg, 20 mmol, 144 µL) was added. The reaction mixture changes from red to pale yellow. The mixture was stirred for 1 hour, then opened to air and the solvent was evaporated. The solid residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated to give the product as yellow crystals.

It should be noted that complex is not stable at silica gel columns. Unlike most (cyclopentadienyl)Rh(cod) complexes, the compounds containing perfluorinated alcohols **5**OCH(CF$_3$)$_2$ and **5**OCH$_2$CF$_3$ form crystals very easily. A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a hexane solution of the complex.

Yield: 89 mg, 0.160 mmol, 80%.

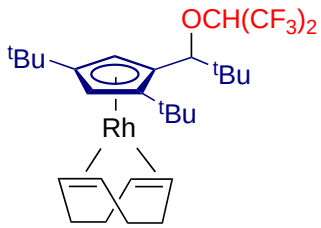
^{1}H NMR (chloroform-*d*, 400 MHz): δ = 4.73 (d, 1H, *J*=2.4 Hz, Cp), 4.50 (d, 1H, *J*=2.5 Hz, Cp), 4.35 (s, 1H, Cp), 4.03 – 3.86 (m, 4H, CH^{cod}), 3.54 – 3.37 (m, 1H, OC<u>H</u>$_2$CF$_3$), 3.30 – 3.14 (m, 1H, OC<u>H</u>$_2$CF$_3$), 2.34 – 2.09 (m, 4H, CH$_2$-cod), 2.04 – 1.92 (m, 2H, CH$_2$-cod), 1.85 – 1.71 (m, 2H, CH$_2$-cod), 1.28 (s, 9H, tBu), 1.20 (s, 9H, tBu), 1.19 (s, 9H, tBu) ppm.

^{13}C NMR (chloroform-*d*, 101 MHz): δ = 83.7 (d, *J* =3.7 Hz), 83.3, 81.3 (d, *J*=3.1 Hz), 66.7 (d, *J*=13.9 Hz), 65.5 (d, *J*=13.8 Hz), 65.21 – 64.35 (m, C-F), 36.3, 33.0, 32.6, 32.3, 32.2, 31.2, 29.8 27.3 ppm.

^{19}F NMR (chloroform-*d*, 376 MHz): δ = -74.25 (t, *J*=8.5 Hz) ppm.

HRMS (ESI). Calculated for C$_{28}$H$_{44}$F$_3$ORh [M]$^+$ = 556.2399. Found 556.2391.

Synthesis of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5**OCH(CF$_3$)$_2$).**



Under argon atmosphere [(η^5-1,3,6-^{t}Bu$_3$-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^+$PF$_6^-$ (120 mg, 0.2 mmol, BF_4^- or $InBr_4^-$ salts can be used as well) and anhydrous K_2CO_3 (28 mg, 0.2 mmol) were suspended in THF (1 ml) and HFIP (336 mg, 20 mmol, 210 µL) was added one portion. The color of the reaction mixture changes from red to pale yellow. The reaction mixture was stirred for 1 hour, then opened to air and the solvent was evaporated. The solid residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated to give the product as yellow crystals. A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a hexane solution of the complex. Yield: 121 mg, 0.194 mmol, 97%.

^{1}H NMR (chloroform-d, 400 MHz): δ = 4.86 (s, 1H, Cp), 4.79 (s, 1H, Cp), 4.58 (s, 1H, Cp), 4.05 – 3.90 (m, 4H, CH-cod), 3.89 – 3.78 (m, 1H, OC<u>H</u>(CF$_3$)$_2$), 2.34 – 2.12 (m, 4H, CH$_2$-cod), 2.02 – 1.92 (m, 2H, CH$_2$-cod), 1.84 – 1.73 (m, 2H, CH$_2$-cod), 1.27 (s, 18H, ^{t}Bu), 1.18 (s, 9H, ^{t}Bu) ppm.

^{13}C NMR (chloroform-d, 101 MHz) : δ = 120.54 (d, $J_{Rh\text{-}C}$ =3.1 Hz, C$_{Cp}$), 119.09 (d, $J_{Rh\text{-}C}$=4.8 Hz, C^{Cp}), 100.36 (d, $J_{Rh\text{-}C}$=4.1 Hz, C^{Cp}), 85.24(C^{Cp}<u>C</u>H^{t}Bu), 84.72 (d, $J_{Rh\text{-}C}$=3.1 Hz, C^{C8H12}), 82.52 (d, $J_{Rh\text{-}C}$=4.0 Hz, C^{C8H12}), 71.80 (dt, $J_{F\text{-}C}$=62.8, 31.3 Hz, C^{CF3}), 67.22 (d, $J_{Rh\text{-}C}$=13.9 Hz, C^{C8H12}), 66.01 (d, $J_{Rh\text{-}C}$=13.9 Hz, C^{C8H12}), 36.65, 32.78 (CH$_3$), 32.35, 32.06 (CH$_3$), 31.14 (CH$_3$), 27.29 ppm.

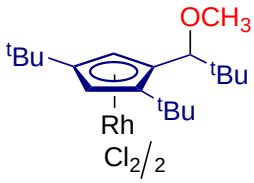
^{19}F NMR (chloroform-d, 376 MHz) δ = -71.75 (m), -72.57 (m) ppm.

HRMS (ESI). Calculated for C$_{29}$H$_{43}$F$_6$ORh [M]$^+$ = 624.2373. Found 624.2355.

Synthesis of halide complexes

General procedure for the chloride complexes. An excess of gaseous Cl_2 was bubbled through a solution of the yellow complex **5**OR (0.2 mmol) in hexane (10ml) in the dark. Protection from light is important to avoid side reactions of radical chlorination. The red precipitate was formed immediately. Chlorine was bubbled until the spot of the starting complex disappeared on TLC. Then the solid residue was separated by centrifugation, washed with pentane (4×5ml) and dried in vacuo to give product **2**OR-Cl as a red or orange powder.

Synthesis of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CH$_3$O)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (**2**OMe-Cl).



Yield: 65 mg, 0.072 mmol, 72%.

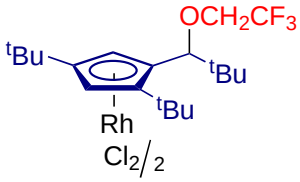
A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of petroleum ether vapors into the solution of complex in DCE.

^{1}H NMR (chloroform-*d*, 400 MHz): δ = 5.54 (s, 1H, Cp), 5.49 (s, 1H, Cp), 4.19 (s, 1H, -C<u>H</u>OCH$_3$), 3.54 (s, 3H, CHOC<u>H</u>$_3$), 1.48 (s, 9H, ^{t}Bu), 1.34 (s, 9H, ^{t}Bu), 1.08 (s, 9H, ^{t}Bu) ppm

^{13}C NMR (chloroform-*d*, 101 MHz): δ = 85.67, 81.74 (d, *J*=4.7 Hz), 60.90, 33.02, 31.51, 30.86, 29.78, 27.97 ppm

HRMS (ESI). Calculated for $C_{38}H_{66}Cl_3O_2Rh_2$ $[M-Cl]^+$= 865.2238. Found 865.2214.

Synthesis of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF$_3$CH$_2$O)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (**2**OCH$_2$CF$_3$-Cl).



Yield: 83 mg, 0.08 mmol, 80%.

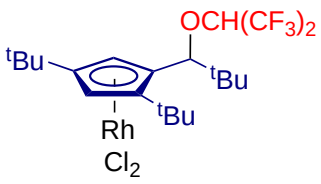
^{1}H NMR (chloroform-*d*, 300 MHz): δ = 5.49 (s, 2H, Cp), 5.02 – 4.75 (m, 1H,O<u>CH$_2$</u>CF$_3$), 4.39 (s, 1H, Cp), 4.08 – 3.83 (m, 1H,O<u>CH$_2$</u>CF$_3$), 1.44 (s, 9H, tBu), 1.32 (s, 9H, tBu), 1.03 (s, 9H, tBu) ppm.

^{13}C NMR (chloroform-*d*, 101 MHz): δ = 128.03, 125.26, 122.50, 106.47 (d, J_{Rh-C} = 9.1 Hz, Cp), 85.54 (O<u>C</u>H$_2$CF$_3$), 83.50 (d, J_{Rh-C} = 9.6 Hz), 82.91 (d, J_{Rh-C} = 7.8 Hz), 70.32 (q, J_{F-C} = 34.0 Hz, CF$_3$), 38.39, 33.16, 31.78 (CH$_3$), 30.93, 29.85 (CH$_3$), 27.89 (CH$_3$) ppm.

^{19}F NMR (chloroform-*d*, 282 MHz): δ = −73.17 ppm.

HRMS (ESI). Calculated for $C_{20}H_{32}ClF_3ORh$ $[M_{monomer}-Cl]^+$ = 483.1143. Found 483.1138.

Synthesis of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$ (**2**OCH(CF$_3$)$_2$-Cl).



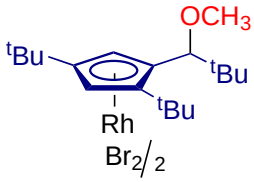
Yield: 100 mg, 0.17 mmol, 85%.

A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of pentane vapors into the solution of complex in DCM.

^{1}H NMR (chloroform-*d*, 400 MHz): δ = 5.83 (s, 1H, Cp), 5.58 (s, 1H, Cp), 4.54 (s, 1H, Cp), 4.08–3.91 (m, 1H, OCH(CF$_3$)$_2$), 1.58 (s, 9H, tBu), 1.41 (s, 9H, tBu), 1.37 (s, 9H, tBu) ppm.
^{13}C NMR (chloroform-*d*, 101 MHz): δ = 85.26 (d, J_{Rh-C} = 3.9 Hz), 84.88, 79.03 (d, J_{Rh-C} = 8.6 Hz), 74.40–72.79 (m), 37.52, 32.59, 31.47, 30.66, 28.92, 27.21 ppm.
^{19}F NMR (chloroform-*d*, 376 MHz): δ = -72.13 (bs), -72.63 (bs) ppm.
HRMS (ESI). Calculated for $C_{21}H_{31}Cl_2F_6ORh$ [M-Cl]$^+$ = 551.1022. Found 551.1007.

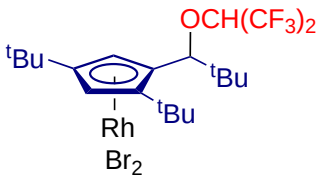
General procedure for the bromide complexes. In air a solution of Br_2 (31 µL, 0.6 mmol, 3 equiv.) in hexane (5 ml) was added dropwise to a stirred solution of the complex **5**OR (0.2 mmol) in hexane (5 ml). The dark orange precipitate was formed immediately. After 5 minutes of stirring the solid residue was separated by centrifugation, washed with pentane (4×5ml) and dried in vacuo to give product **2**OR-Br as a dark orange powder.

Synthesis of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CH$_3$O)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (2OMe-Br).



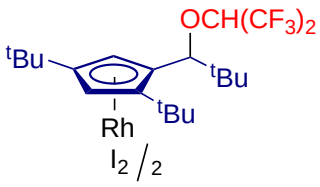
Yield: 100 mg, 0.093 mmol, 93%.
^{1}H NMR (chloroform-*d*, 400 MHz): δ = 5.56 (s, 1H, Cp), 5.51 (s, 1H, Cp), 4.28 (s, 1H, -CHOCH$_3$), 3.60 (s, 3H, CHOCH$_3$), 1.47 (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu), 1.05 (s, 9H, ^{t}Bu) ppm.
^{13}C NMR (chloroform-*d*, 101 MHz): δ = 108.52 (d, J_{Rh-C} = 4.0 Hz), 107.28 (d, J_{Rh-C} = 4.4 Hz), 105.18 (d, J_{Rh-C} = 4.6 Hz), 86.10, 82.23 (d, J_{Rh-C} = 6.1 Hz), 81.81 (d, J_{Rh-C} = 7.4 Hz), 61.42, 38.70, 33.29, 31.87, 30.91, 30.20, 28.21 ppm.
HRMS (ESI). Calculated for $C_{38}H_{66}Br_3O_2Rh_2$ [M−Br]$^+$= 997.0722. Found 997.0703.

Synthesis of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (2OCH(CF$_3$)$_2$-Br).



Yield: 113 mg, 0.166 mmol, 83%.
A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of hexane vapors into the solution of complex in DCE.
^{1}H NMR (chloroform-*d*, 400 MHz): δ = 5.88 (s, 1H), 5.72 (s, 1H), 4.48 (s, 1H), 4.17 – 3.84 (m, 1H, OCH(CF$_3$)$_2$), 1.61 (s, 9H, tBu), 1.40 (s, 9H, tBu), 1.31 (s, 9H, tBu) ppm.
^{13}C NMR (chloroform-*d*, 101 MHz): δ = 86.09 (d, *J*=5.1 Hz), 84.96, 79.02 (d, *J* = 7.2 Hz), 74.40–73.09 (m), 37.35, 32.62, 30.83, 30.46, 28.90, 27.26 ppm.
^{19}F NMR (chloroform-*d*, 376 MHz): δ = -71.98 – -72.21 (m), -72.34 – -72.55 (m) ppm.
HRMS (ESI). Calculated for $C_{21}H_{31}BrF_6ORh$ [$M_{monomer}$−Br]$^+$ = 595.0512. Found 595.0500.

Synthesis of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhI$_2$]$_2$ (**2**-OCH(CF$_3$)$_2$-I).



In air a solution of I_2 (25 mg, 0.1 mmol) in hexane (5 ml) was added dropwise to a yellow stirred solution of complex **5**OCH(CF$_3$)$_2$ (62 mg, 0.1 mmol) in hexane (2 ml). The dark precipitate was formed immediately. After 5 minutes of stirring the solid was separated by centrifugation, washed with pentane (4×5ml) to remove residual cyclooctadiene and dried in vacuo to give product **2**OCH(CF$_3$)$_2$-I as a dark purple solid. It should be noted that diluted solutions of this complex are green presumably due to the formation of an ionic isomer [^{R}CpRh(μ-I$_3$)Rh^{R}Cp]I.

Yield: 38 mg, 0.049 mmol, 98%.

A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of petroleum ether vapors into the solution of complex in DCE.

^{1}H NMR (chloroform-*d*, 400 MHz): δ = 5.89 (s, 1H, Cp), 5.88 (s, 1H, Cp), 4.39 (s, 1H, Cp), 4.20 – 3.96 (m, 1H, OCH(CF$_3$)$_2$), 1.63 (s, 9H, tBu), 1.36 (s, 9H, tBu), 1.17 (s, 9H, tBu) ppm.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.12 (s, 1H, Cp), 5.65 (s, 1H, Cp), 5.14 (s, br, 1H, OCH(CF$_3$)$_2$), 4.83 (s, 1H), 1.42 (s, 9H, tBu), 1.30 (s, 9H, tBu), 1.22 (s, 9H, tBu) ppm.

^{13}C NMR (DMSO-d_6, 101 MHz): δ = 110.58, 102.28 (d, *J* = 6.8 Hz), 86.37, 86.04 (d, *J* = 7.7 Hz), 80.89 (d, *J* = 8.0 Hz), 74.41 – 72.75 (m), 38.31, 33.06, 31.03, 30.41, 29.77, 27.26 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz): δ = -70.82 (bs), -71.17 (bs) ppm.

HRMS (ESI). Calculated for $C_{21}H_{31}F_6IORh$ $[M_{monomer}–I]^+$= 643.0378. Found 643.0656.

Separation of enantiomers of the racemic complexes

Separation of the racemic mixture 2OCH_2CF_3-Cl

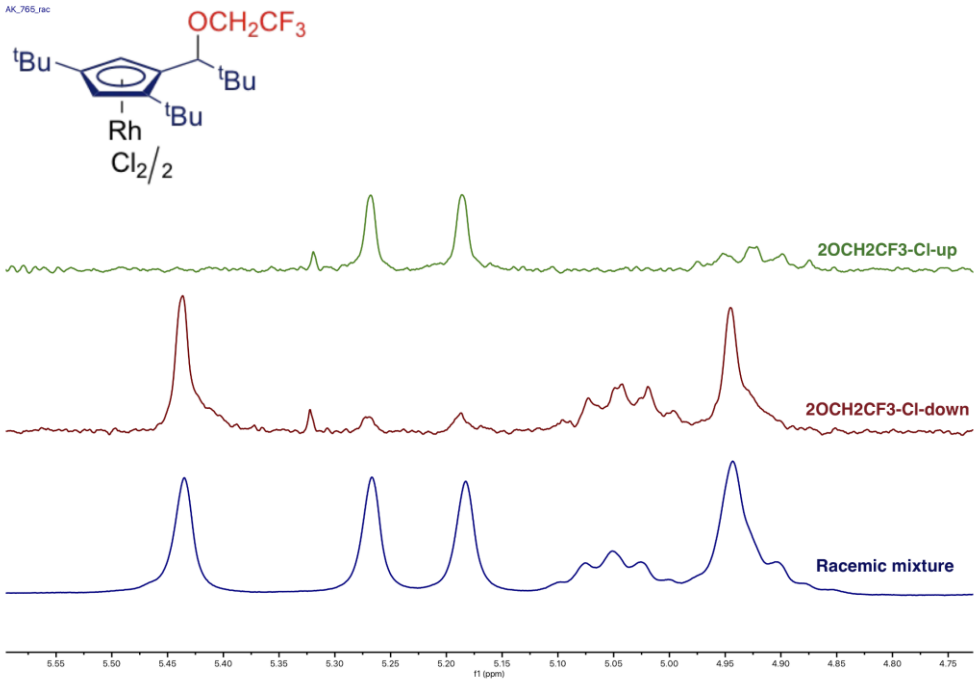
In a 5 ml flask a mixture of the racemic chloride complex **2**OCH_2CF_3-Cl (35 mg, 0.067 mmol, 1 equiv.) and R-phenylglycinol (32 mg, 0.168 mmol, 2.5 equiv.) was dissolved in acetone (0.4 ml). This orange-yellow mixture was placed on a preparative TLC plate and eluted with hexane/acetone (3:1) mixture. Then, two orange silica gel bands were collected from the plate and placed separately on two Shott glass filters. The products were washed off the silica with a mixture of acetone and a few drops of HCl. The resulting red solutions were evaporated to dryness and extracted with 5 ml of CH_2Cl_2. The red solutions were washed twice with 10% aqueous HCl, dried over anhydrous Na_2SO_4, evaporated to dryness. The resulting oily residues were triturated with pentane to obtain an orange powders of enantiomerically pure complexes **2**OCH_2CF_3-Cl-up and **2**OCH_2CF_3-Cl-down.

To assess the quality of separation, the enantiomerically pure complex was dissolved in $CDCl_3$ and 1 equivalent of S-1-phenylethylamine (5.2 µL, 0.04 mmol) was added. The color of the solutions changed from red to orange indicating the formation of diastereomeric adducts. After recording of the spectra, the complex can be regenerated by diluting $CDCl_3$ from the NMR tube with 5 ml of CH_2Cl_2 and washing the resulting solution twice with 10% aqueous HCl. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The resulting oil was triturated with pentane to obtain orange powder of **2**OCH_2CF_3-Cl.

Yield of the isomer **2**OCH_2CF_3-Cl-up collected from the top band on silica plate: 13 mg, 37% (50% is theoretical maximum), ee > 95%.

Yield of the isomer **2**OCH_2CF_3-Cl-down collected from the bottom band on silica plate: 11 mg 31% (50% is theoretical maximum), ee ≈ 80%. The purify can be improved by collecting more narrow bands from TLC plate.

^{1}H NMR spectra of the individual enantiomers **2**OCH_2CF_3-Cl-up and **2**OCH_2CF_3-Cl-down completely coincide with the spectrum of the racemic **2**OCH_2CF_3-Cl.



Separation of the racemic mixture 2OCH$(CF_3)_2$-Cl

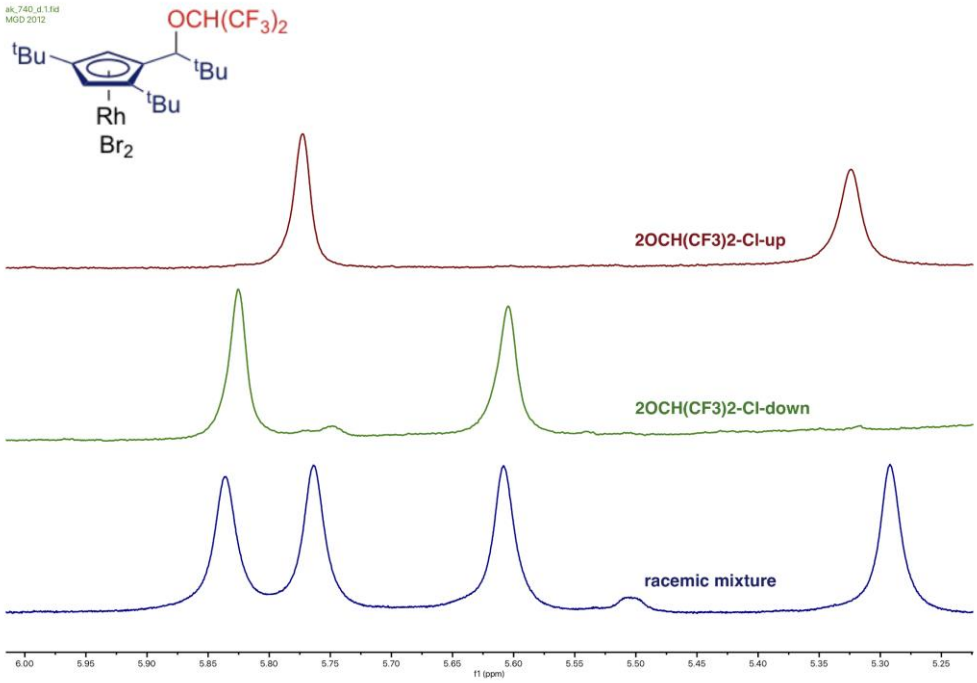
In a 5 ml flask, a mixture of the bromide complex **2**OCH$(CF_3)_2$-Cl (29 mg, 0.05 mmol, 1 equiv.) and R-phenylglycinol (32 mg, 0.2 mmol, 4 equiv.) was dissolved in acetone (0.4 ml). The orange-yellow mixture was spotted on a preparative TLC plate and eluted with hexane/EtOAc (3:1). Then, two orange silica gel bands were collected from the plate and placed separately on two Shott glass filters. The products were washed off the silica with a mixture of acetone and a few drops of HCl. The resulting red solutions was evaporated to dryness, extracted with 5 ml of CH_2Cl_2. The red solution is washed twice with 10% aqueous HCl. Dried over anhydrous Na_2SO_4, evaporated to dryness. The resulting oils were triturated with pentane to obtain an orange powders of **2**OCH$(CF_3)_2$-Cl-up and **2**OCH$(CF_3)_2$-Cl-down.

To assess the quality of separation, 1 equivalent of S-1-phenylethylamine (5.2 µL, 0.04 mmol) was added to the red solutions of the complexes in $CDCl_3$. The color of the solutions changed to orange indicating the formation of diastereomeric adducts. After recording the spectra, the solutions were diluted with 5 ml CH_2Cl_2 was washed twice with 10% aqueous HCl. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The resulting oils were triturated with pentane to obtain an orange powders of **2**OCH$(CF_3)_2$-Cl-up and **2**OCH$(CF_3)_2$-Cl-down.

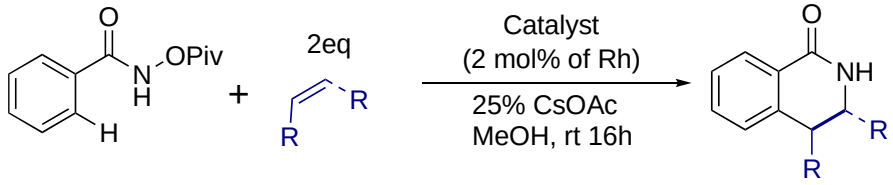
Yield of the isomer **2**OCH$(CF_3)_2$-Cl-up collected from the top band on silica plate: 11 mg, 38% (50% is theoretical maximum), ee > 95%.

Yield of the isomer **2**OCH$(CF_3)_2$-Cl-down collected from the bottom band on silica plate: 14 mg, 48% (50% is theoretical maximum), ee ≈ 80%. The purify can be improved by collecting more narrow bands from TLC plate.

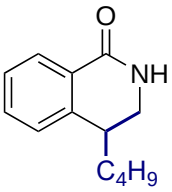
^{1}H NMR spectra of individual enantiomers **2**OCH$(CF_3)_2$-Cl-up and **2**OCH$(CF_3)_2$-Cl-down completely coincides with the spectrum of the racemic complex **2**OCH$(CF_3)_2$-Cl.



Catalytic Reactions



General procedure: O-pivaloyl hydroxamate **8** (22 mg, 0.10 mmol), rhodium catalyst (2 µmol, 2 mol-% of Rh), and CsOAc (5 mg, 0.025 mmol, 25 mol-%) were placed in a reaction vial and dissolved in MeOH (0.5 mL). Then corresponding alkene (0.20 mmol, 2.0 equiv.) was added to the stirred solution. The resulting mixture was stirred for 16 hours and then the solvent was evaporated in vacuo. The residue was subjected to column chromatography on silica (eluent: CH_2Cl_2:EtOAc 5:1), which gave target dihydroisoquinolones.



4-butyl-3,4-dihydroisoquinolin-1(2H)-one (9)

Catalyst **2**OCH_2CF_3-Cl: Yield 19 mg (0.093 mmol, 93%) colorless solid, ee = 34%

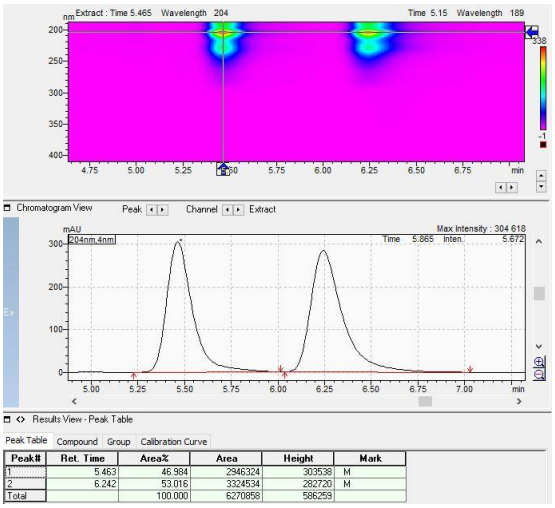
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 19 mg (0.093 mmol, 93%) colorless solid, ee = 54%

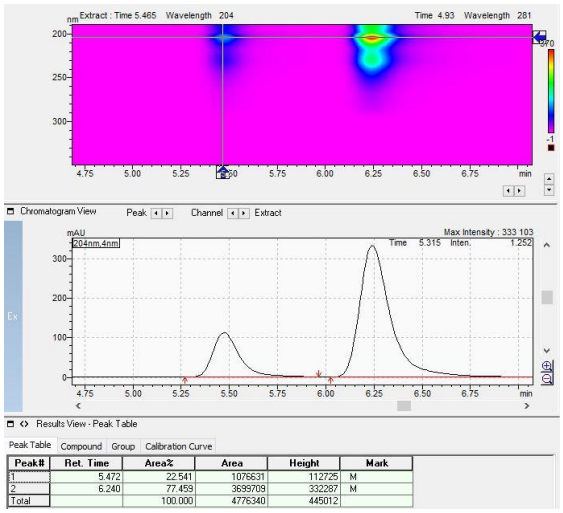
^{1}H NMR (chloroform-*d*, 400 MHz): δ = 8.05 (dd, 1H, *J*=7.8, 1.4 Hz), 7.45 (td, 1H, *J*=7.5, 1.4 Hz), 7.34 (td, 1H, *J*=7.6, 1.2 Hz), 7.20 (d, 1H, *J*=7.5 Hz), 6.75 (s, 1H), 3.71 (dd, 1H, *J*=12.5, 4.4 Hz), 3.39 (dt, 1H, *J*=12.5, 3.9 Hz), 2.82 (tt, 1H, *J*=7.6, 3.8 Hz), 1.68 (q, 2H, *J*=7.2 Hz), 1.40 – 1.23 (m, 4H), 0.88 (t, 3H, *J*=7.0 Hz) ppm.

^{13}C NMR (chloroform-*d*, 101 MHz): δ = 166.41, 143.40, 132.20, 128.19, 127.11, 44.21, 38.00, 33.16, 29.66, 22.80, 14.11.

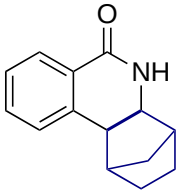
The NMR spectra of the product are similar to those previously reported.[5]

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 ml/min; tr = 5.5 min, tr = 6.2 min.





1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6(2H)-one (10)



Catalyst **2**OCH_2CF_3-Cl: Yield 17 mg (0.080 mmol, 80%) colorless solid, ee = 42%

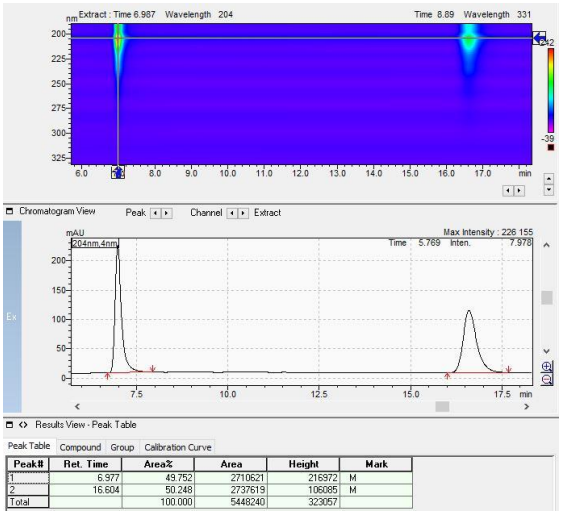
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 18 mg (0.085 mmol, 85%) colorless solid, ee = 76%

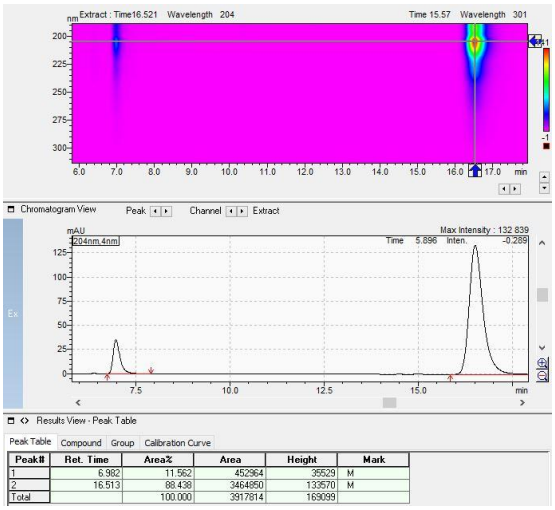
^{1}H NMR (chloroform-*d*, 400 MHz): δ = 8.09 (d, 1H, *J*=7.8 Hz), 7.45 (t, 1H, *J*=7.5 Hz), 7.22 (d, 1H, *J*=7.7 Hz), 6.45 (s, 1H), 3.81 (d, 1H, *J*=8.9 Hz), 3.12 (d, 1H, *J*=8.9 Hz),

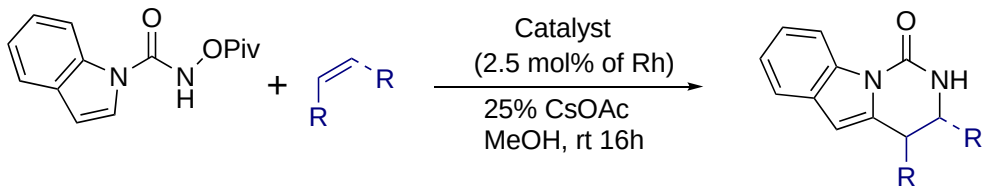
2.32 (s, 1H), 2.25 (d, 1H, *J*=3.9 Hz), 1.70 – 1.62 (m, 3H), 1.52 (t, 1H, *J*=8.8 Hz), 1.25 (d, 1H, *J*=3.0 Hz), 1.18 (d, 1H, *J*=10.6 Hz) ppm.

The NMR spectra of the product are similar to those previously reported.[3]

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 ml/min; tr = 7.0 min, tr = 16.6 min.

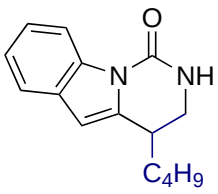






General procedure:

N-(pivaloyloxy)-1H-indole-1-carboxamide **11** (26 mg, 0.10 mmol), rhodium catalyst (2.5 µmol, 2.5 mol-% of Rh), and CsOAc (5 mg, 0.025 mmol, 25 mol-%) were placed in a reaction vial and dissolved in MeOH (0.5 mL). Then corresponding alkene (0.20 mmol, 2.0 equiv.) was added and the mixture was stirred for 16 hours. The resulting solutioon was diluted with CH_2Cl_2 and transferred to a round-bottom flask. Silica was added to the flask and volatiles were evaporated under a vacuum. The purification was performed by flash column chromatography on silica gel (eluent indicated for each case) to give 3,4-dihydropyrimido[1,6-a]indol-1(2H)-ones.



12. Eluent: Hexane/EtOAc 3/1. Colorless solid

Cp*$RhCl_2/_2$ Yield 12 mg (0.05 mmol, 50%)

Catalyst **2**: Yield 20 mg (0.083 mmol, 83%), ee = 26%

Catalyst **2**OCH_2CF_3-Cl: Yield 21 mg (0.086 mmol, 87%), ee = 2%

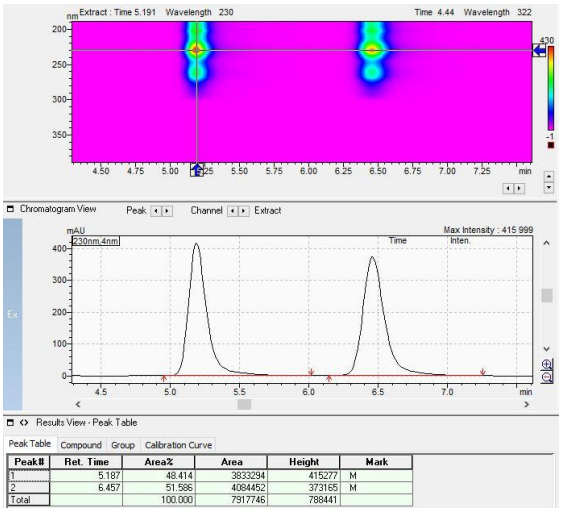
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 19 mg (0.079 mmol, 79%), ee = 2%

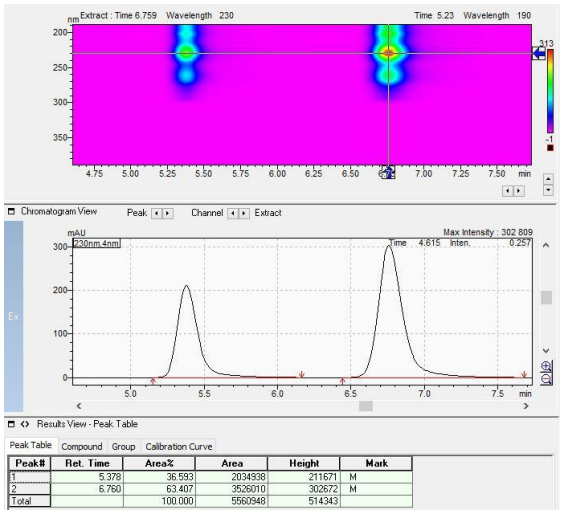
^{1}H NMR (chloroform-d, 400 MHz): δ = 8.33 (d, 1H, J=8.2 Hz), 7.50 (d, 1H, J=7.7 Hz), 7.32 – 7.11 (m, 2 H), 6.35 (s, 1H), 6.30 (s, 1H), 3.72 – 3.40 (m, 1H), 3.26 (t, 1H, J=10.1 Hz), 3.10 (s, 1H), 2.03 – 1.88 (m, 1H), 1.74 – 1.57 (m, 1H), 1.53 – 1.33 (m, 4H), 0.94 (t, 3H, J=6.9 Hz) ppm.

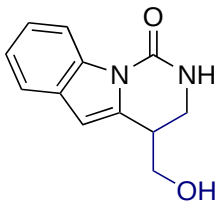
^{13}C NMR (chloroform-*d*, 101 MHz): δ = 152.57, 139.27, 135.46, 129.29, 123.72, 122.76, 120.07, 115.30, 102.74, 44.34, 33.65, 30.96, 29.16, 22.79, 14.07 ppm.

HRMS (APCI): Exact mass calculated for $C_{15}H_{19}N_2O$ $[M+H]^+$ = 243.1491, found 243.1489.

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 5.2 min, tr = 6.5 min.







13. Eluent: EtOAc/Hexane 5/1. Beige solid

Catalyst $[Cp^*RhCl_2]_2$: Yield 18 mg (0.081 mmol, 83%)

Catalyst **2**: Yield 18 mg (0.083 mmol, 83%), ee = 32%

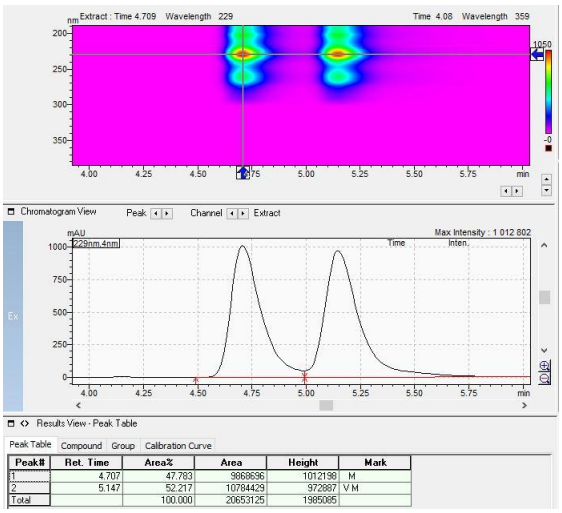
Catalyst **2**OCH_2CF_3-Cl: Yield 17 mg (0.08 mmol, 80%), ee = 22%

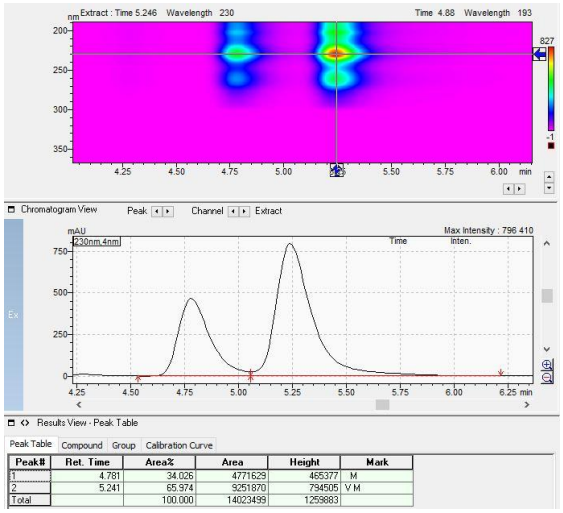
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 17 mg (0.08 mmol, 80%), ee = 20%

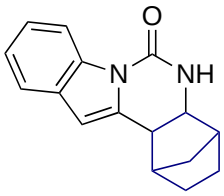
1H NMR (acetone-d6, 400 MHz): δ = 8.29 (d, 1H, J=8.1 Hz, CH^{Ar}), 7.49 (d, 1H, J=7.6 Hz, CH^{Ar}), 7.26 – 7.08 (m, 2H, CH^{Ar}), 6.90 (s, br, 1H, NH), 6.46 (s, 1H, CH^{ind}), 3.94 (dd, 1H, J=10.7, 5.4 Hz), 3.80 (dt, 1H, J=10.7, 7.5 Hz), 3.72 – 3.62 (m, 1H), 3.57 – 3.47 (m, 1H), 3.33 (p, 1H, J=5.8 Hz), 2.99 (s, 1H, OH) ppm.

^{1}H NMR data is in agreement with those reported previously.[6]

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 4.7 min, tr = 5.1 min.







14. Eluent: Hexane/EtOAc 3/1.

Catalyst $[Cp^*RhCl_2]_2$: Yield 23 mg (0.091 mmol, 91%)

Catalyst **2**: Yield 21 mg (0.083 mmol, 83%), ee = 74%

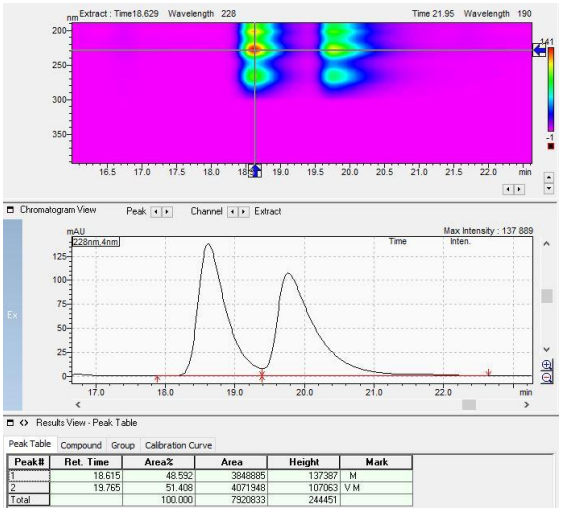
Catalyst **2**OCH_2CF_3-Cl: Yield 22 mg (0.087 mmol, 87%), ee = 4%

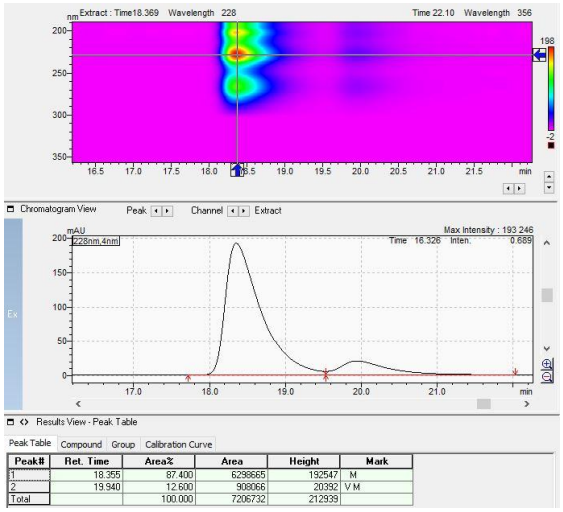
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 23 mg (0.091 mmol, 91%), ee = 46%

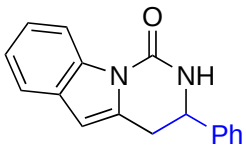
^{1}H NMR (chloroform-d, 400 MHz): δ = 8.39 (d, 1H, J=8.1 Hz), 7.49 (d, 1H, J=7.6 Hz), 7.31 – 7.15 (m, 2H), 6.36 (s, 1H), 6.12 (s, 1H), 3.73 (d, 1H, J=8.6 Hz), 3.27 (d, 1H, J=8.7 Hz), 2.47 (s, 1H), 2.32 (s, 1H), 1.69 – 1.59 (m, 3H), 1.52 – 1.45 (m, 1H), 1.32 – 1.21 (m, 2H) ppm

^{1}H NMR data is in agreement with those reported previously.[6]

HPLC: Chiralpak IB-3 column (4.6 × 150 mm), heptane/i-PrOH 98:2, 1.0 ml/min; tr = 18.3 min, tr = 19.9 min.







15a. Eluent: Hexane/EtOAc 3/1

Catalyst $[Cp^*RhCl_2]_2$: Yield 7 mg (0.027 mmol, 27%)

Catalyst **2**: Yield 10 mg (0.039 mmol, 39%), ee = 32%

Catalyst **2**OCH_2CF_3-Cl: Yield 5 mg (0.019 mmol, 19%), ee = 10%

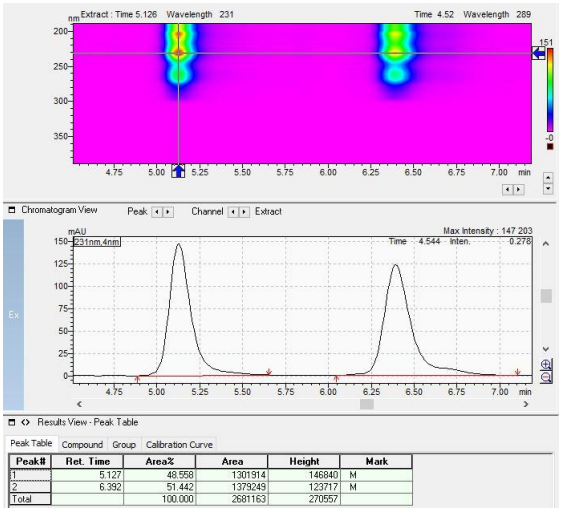
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 2 mg (0.007 mmol, 7%), ee = 30%

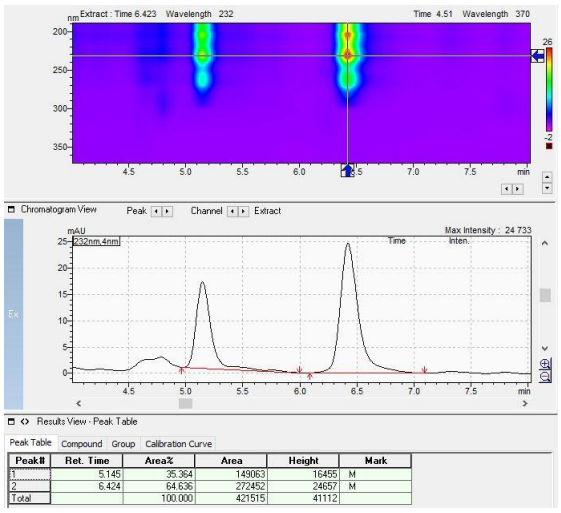
^{1}H NMR (chloroform-d, 400 MHz): δ = 8.36 (d, 1H, J=8.1 Hz, C-H^{ind}), 7.50 (d, 1H, J=7.7 Hz, C-H^{ind}), 7.40 (s, 5H, C-H^{Ar}), 7.33 – 7.15 (m, 2H, C-H^{ind}), 6.34 (s, 1H), 5.56 (s, 1H), 4.83 (dd, 1H, J=10.6, 4.3 Hz), 3.43 – 3.29 (m, 1H), 3.27 – 3.11 (m, 1H) ppm

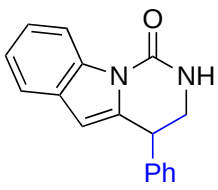
^{13}C NMR (chloroform-*d*, 101 MHz): δ = 152.30, 139.99, 135.37, 133.58, 129.46, 129.21, 128.73, 126.36, 123.92, 123.00, 120.16, 115.41, 104.02, 55.31, 31.99 ppm

HRMS (APCI): Exact mass calculated for $C_{15}H_{19}N_2O$ $[M+H]^+$ = 263.1179, found 263.1181.

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 5.1 min, tr = 6.4 min.







15b. Eluent: Hexane/EtOAc 3/1

Catalyst $[Cp^*RhCl_2]_2$: product was not observed

Catalyst **2**: Yield 7 mg (0.026 mmol, 26%), ee = 38%

Catalyst **2**OCH_2CF_3-Cl: Yield 15 mg (0.057 mmol, 57%), ee = 10%

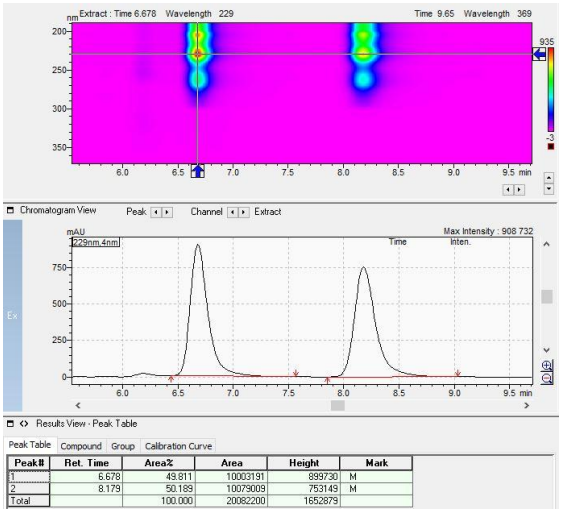
Catalyst **2**$OCH(CF_3)_2$-Cl: Yield 19 mg (0.073 mmol, 73%), ee = 56%

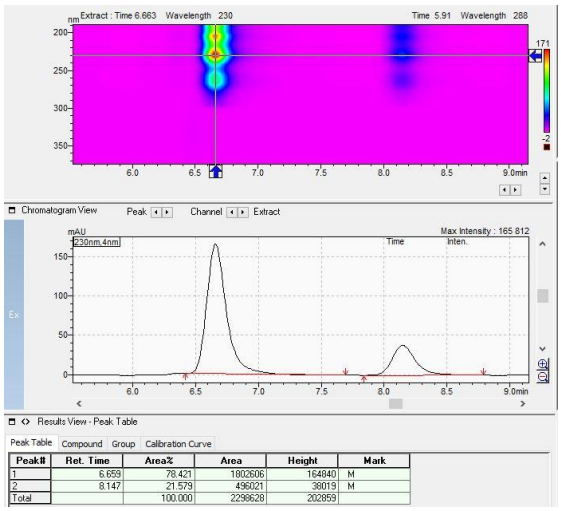
^{1}H NMR (chloroform-*d*, 400 MHz): δ = 8.38 (d, 1H, *J*=8.3 Hz), 7.46 (d, 1H, *J*=7.7 Hz), 7.34 (m, 6H), 7.22 (t, 1H, *J*=7.6 Hz), 6.38 (s, 1H), 6.09 (s, 1H), 4.42 (t, 1H, *J*=7.8 Hz), 3.66 (d, 2H, *J*=8.0 Hz) ppm.

HRMS (APCI): Exact mass calculated for $C_{15}H_{19}N_2O$ $[M+H]^+$ = 263.1179, found 263.1181.

^{1}H NMR data is in agreement with those reported previously.[7]

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 6.7 min, tr = 8.2 min.





X-ray diffraction data

X-ray diffraction data for **2**OMe-Cl, **2**OCH$(CF_3)_2$-I, and **5**OMe were collected at 120 K with a Bruker APEXII DUO CCD diffractometer; data for other compounds were collected at 100 K with a Bruker Quest D8 CMOS diffractometer, both using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Structures were solved using Intrinsic Phasing with the ShelXT[8] structure solution program in Olex2[9] and then refined with the XL[10] refinement package using Least-Squares minimization against F^2 in the anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Tables S1 and S2. CCDC 2288541 (**2**OCH$(CF_3)_2$-Br), 2288542 (**2**OCH$(CF_3)_2$-Cl), 2288540 (**5**OCH$(CF_3)_2$), 2288538 (**2**OCH$(CF_3)_2$-I), 2288545 (**5**OCH$_2CF_3$), 2288539 (**2**OH-Br), 2288536 (**2**OH-Cl), 2288543 (**2**OMe-Cl), 2288535 (**5**OMe), and 2288537 (**4**InBr_4) contain the supplementary crystallographic data for this paper. The Flack parameters for **2**OMe-Cl and **5**OMe, which crystallize in the chiral space groups, are 0.46(4) and 0.48(10), respectively.

Table S1. Crystal data and structure refinement parameters.

	2OCH$(CF_3)_2$-Br	**2**OCH$(CF_3)_2$-Cl	**5**OCH$(CF_3)_2$	**2**OCH$(CF_3)_2$-I	**5**OCH$_2CF_3$
Empirical formula	$C_{21}H_{31}Br_2F_6ORh$	$C_{43}H_{64}Cl_6F_{12}O_2Rh_2$	$C_{29}H_{43}F_6ORh$	$C_{42}H_{62}F_{12}I_4O_2Rh_2$	$C_{28}H_{44}F_3ORh$
Formula weight	676.19	1259.46	624.54	1540.33	556.54
T, K	100	100	100	120	100
Crystal size, mm	0.02×0.03×0.3	0.1×0.1×0.3	0.05×0.15×0.25	0.01×0.1×0.15	0.15×0.2×0.25
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	Pbca	$P2_1/c$	Pn	P-1	Pbca
Z	8	4	4	1	16
a, Å	11.4548(7)	17.0112(4)	14.6789(6)	8.6707(2)	18.4463(3)
b, Å	15.3010(10)	21.2381(5)	13.2778(6)	11.7677(2)	22.9213(4)
c, Å	28.4594(17)	14.5656(4)	14.8188(6)	12.3696(2)	25.6566(4)
α, °	90	90	90	97.3570(10)	90
β, °	90	99.9180(10)	103.6160(10)	95.4620(10)	90
γ, °	90	90	90	92.0970(10)	90
V, Å^3	4988.1(5)	5183.7(2)	2807.1(2)	1244.53(4)	10847.9(3)
D_{calc} (g cm^{-1})	1.801	1.614	1.478	2.055	1.363
Linear absorption, μ (cm^{-1})	39.44	10.24	6.69	32.22	6.68
F(000)	2672	2552	1296	740	4672
$2\theta_{max}$, °	50	56	52	58	50
Reflections measured	37534	63687	24206	43948	100324
Independent reflections	4385	12503	10650	6614	9544

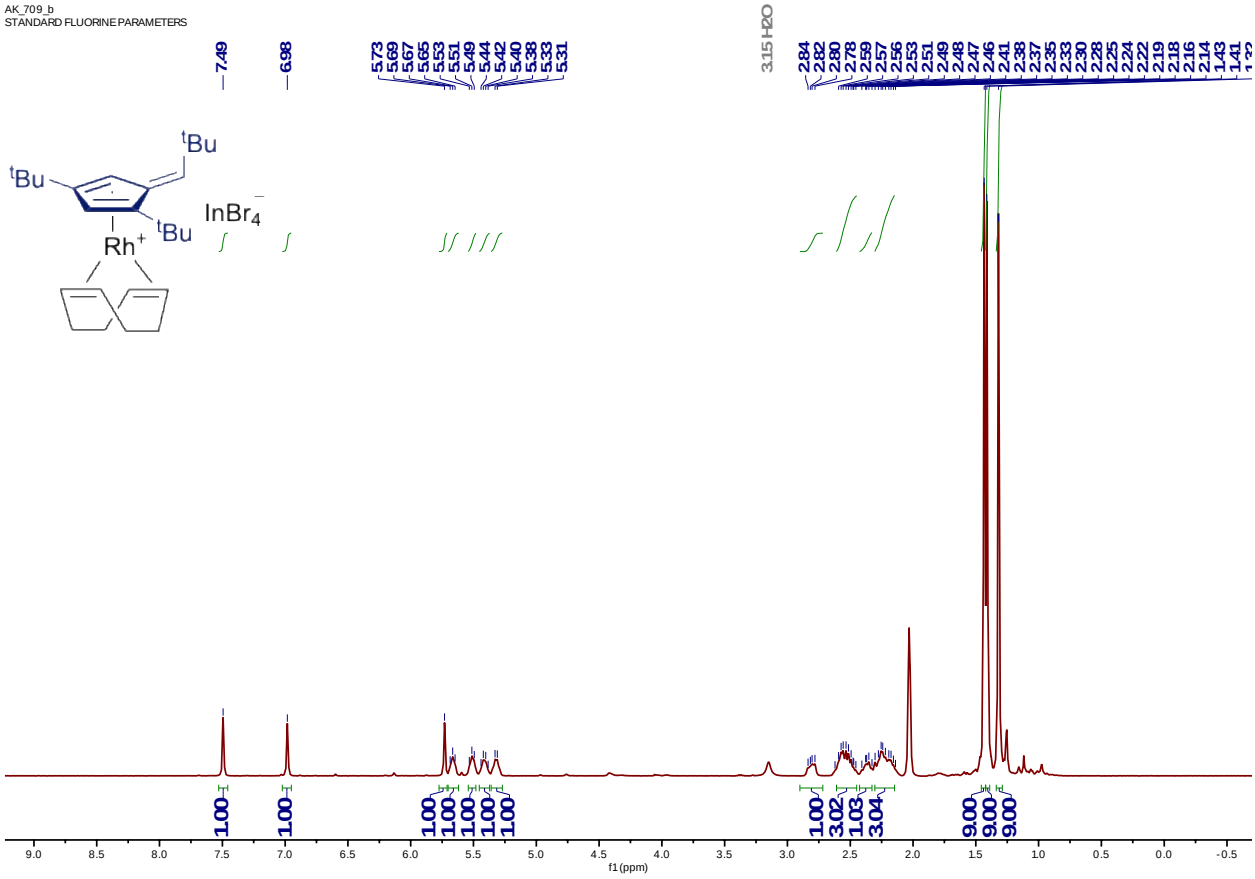
Observed reflections [$I > 2\sigma(I)$]	3503	10698	9962	6388	8182
Parameters	289	608	687	289	621
R1	0.0705	0.0294	0.0482	0.0171	0.0417
wR2	0.1650	0.0702	0.1327	0.0433	0.0968
GOF	1.213	1.065	1.100	1.060	1.109
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	1.750/-0.904	1.099/-0.879	2.345/-2.122	1.552/-0.550	1.051/-0.800

Table S2. Crystal data and structure refinement parameters.

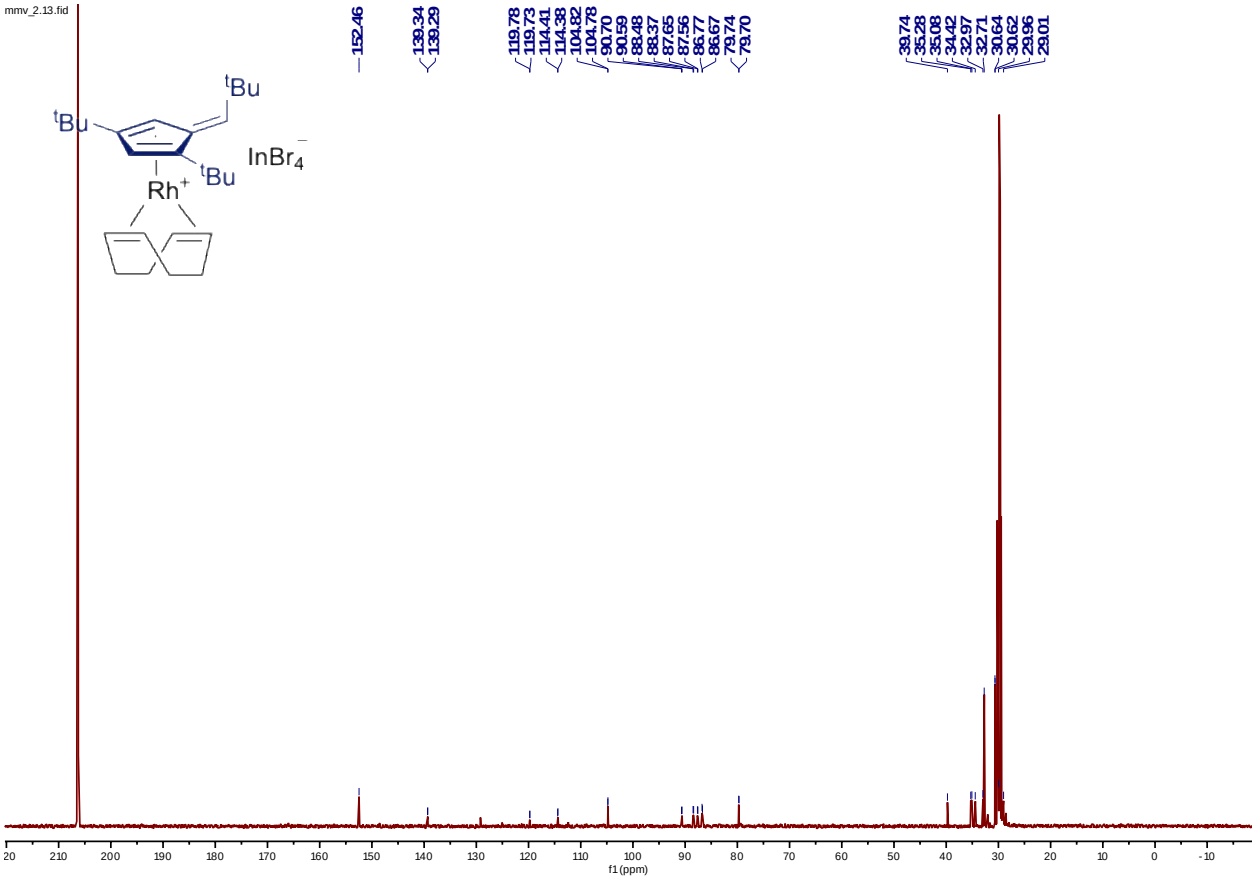
	2OH-Br	**2**OH-Cl	**2**OMe-Cl	**5**OMe	**4**$InBr_4$
Empirical formula	$C_{38}H_{64}Br_4Cl_6O_2Rh_2$	$C_{38}H_{64}Cl_{10}O_2Rh_2$	$C_{38}H_{66}Cl_4O_2Rh_2$	$C_{27}H_{45}ORh$	$C_{26}H_{42}Br_4InRh$
Formula weight	1291.05	1113.21	902.52	488.54	891.96
T, K	100	100	120	120	100
Crystal size, mm	0.03×0.15×0.15	0.05×0.1×0.15	0.01×0.01×0.35	0.01×0.01×0.35	0.03×0.03×0.15
Crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	P-1	P-1	$Pca2_1$	$P2_12_12_1$	$P2_1/n$
Z	1	1	8	4	4
a, Å	10.2647(3)	10.1497(3)	25.3786(10)	9.922(6)	15.871(3)
b, Å	10.4313(3)	10.4552(3)	14.1588(6)	15.460(10)	12.1783(17)
c, Å	12.9342(4)	12.8567(4)	23.2064(9)	16.460(11)	16.655(3)
α, °	82.315(2)	81.7540(10)	90	90	90
β, °	73.935(2)	74.7190(10)	90	90	107.520(10)
γ, °	67.629(2)	67.4720(10)	90	90	90
V, Å^3	1230.05(7)	1214.27(6)	8338.8(6)	2525(3)	3069.9(8)
D_{calc} (g cm^{-1})	1.743	1.522	1.438	1.285	1.930
Linear absorption, μ (cm^{-1})	42.75	12.6	10.78	6.91	65.08
F(000)	640	568	3744	1040	1728
$2\theta_{max}$, °	52	52	54	52	50
Reflections measured	24487	24762	67086	24640	21908
Independent reflections	4814	4768	18157	4951	5398
Observed reflections [$I > 2\sigma(I)$]	4276	4298	14558	3053	3403
Parameters	261	261	870	274	314
R1	0.0400	0.0608	0.0616	0.0655	0.1583
wR2	0.1017	0.1765	0.1026	0.1594	0.4089
GOF	1.042	1.114	1.033	0.957	1.084
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	1.748/-1.368	1.909/-0.761	1.107/-1.967	0.983/-0.764	2.710/-1.294

NMR spectra

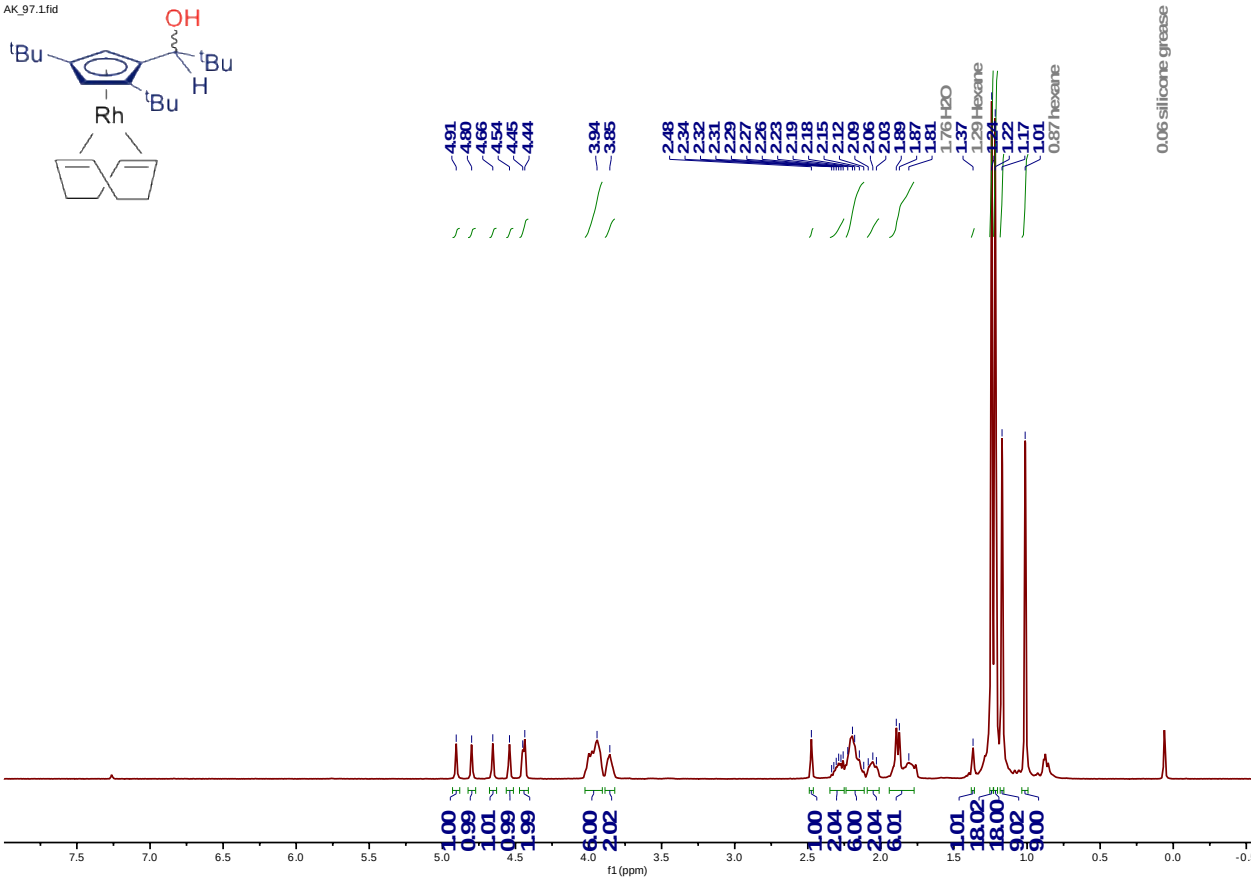
^{1}H spectrum of [(η^{5}-1,3,6-^{t}Bu-fulvene)Rh(1,5-C_8H_{12})]$^{+}InBr_4^{-}$ (**4**$InBr_4$)



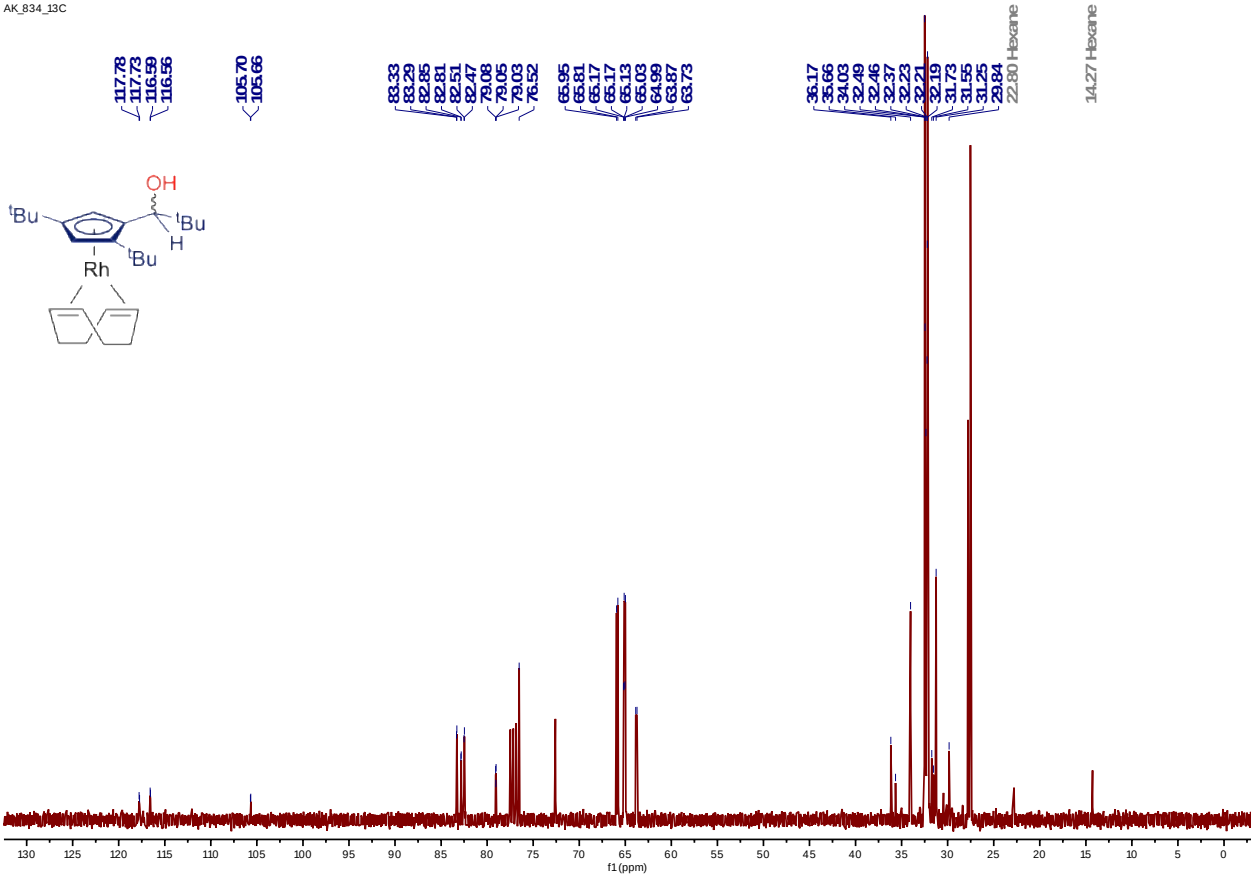
^{13}C spectrum of [(η^{5}-1,3,6-^{t}Bu-fulvene)Rh(1,5-C_8H_{12})]$^{+}InBr_4^{-}$ (**4**$InBr_4$)



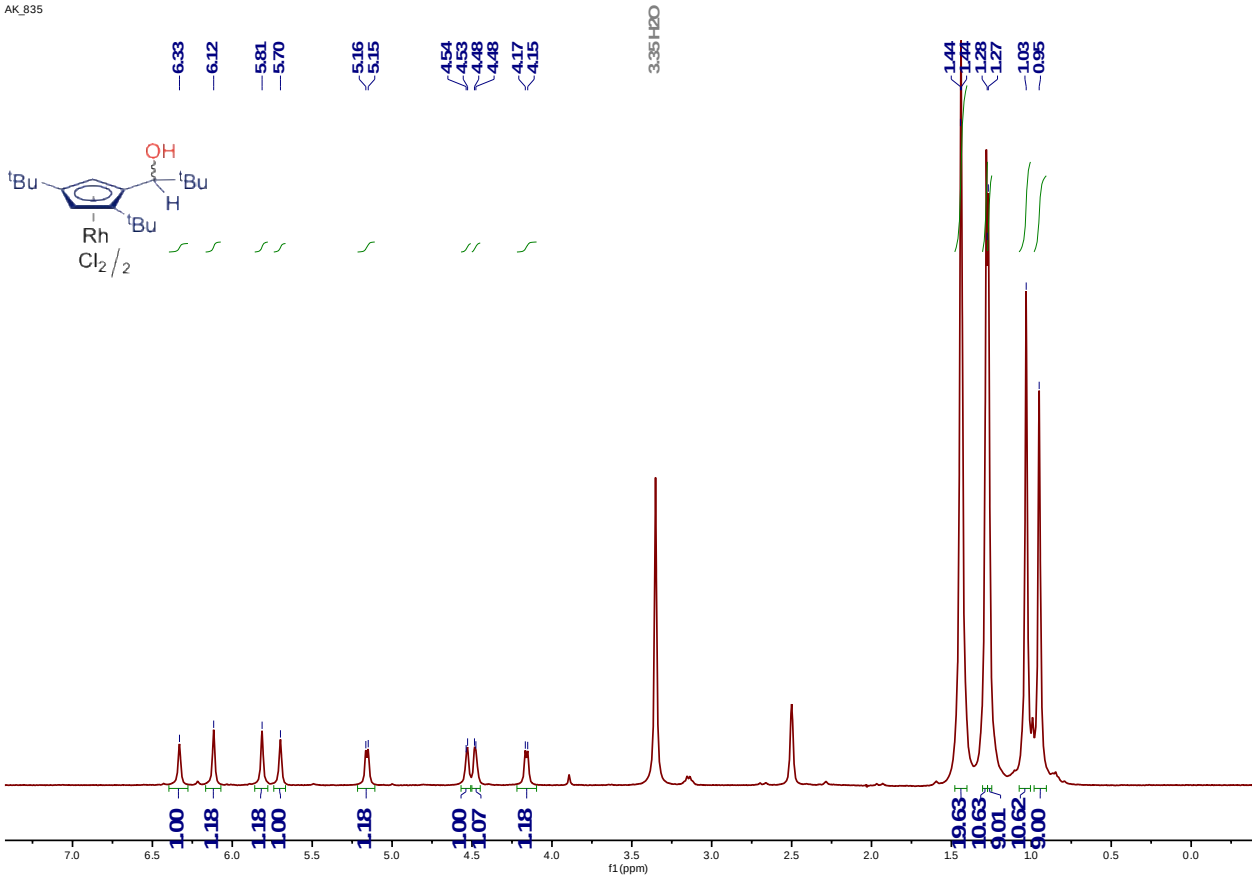
^{1}H spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(OH)CHC$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (**5**OH).



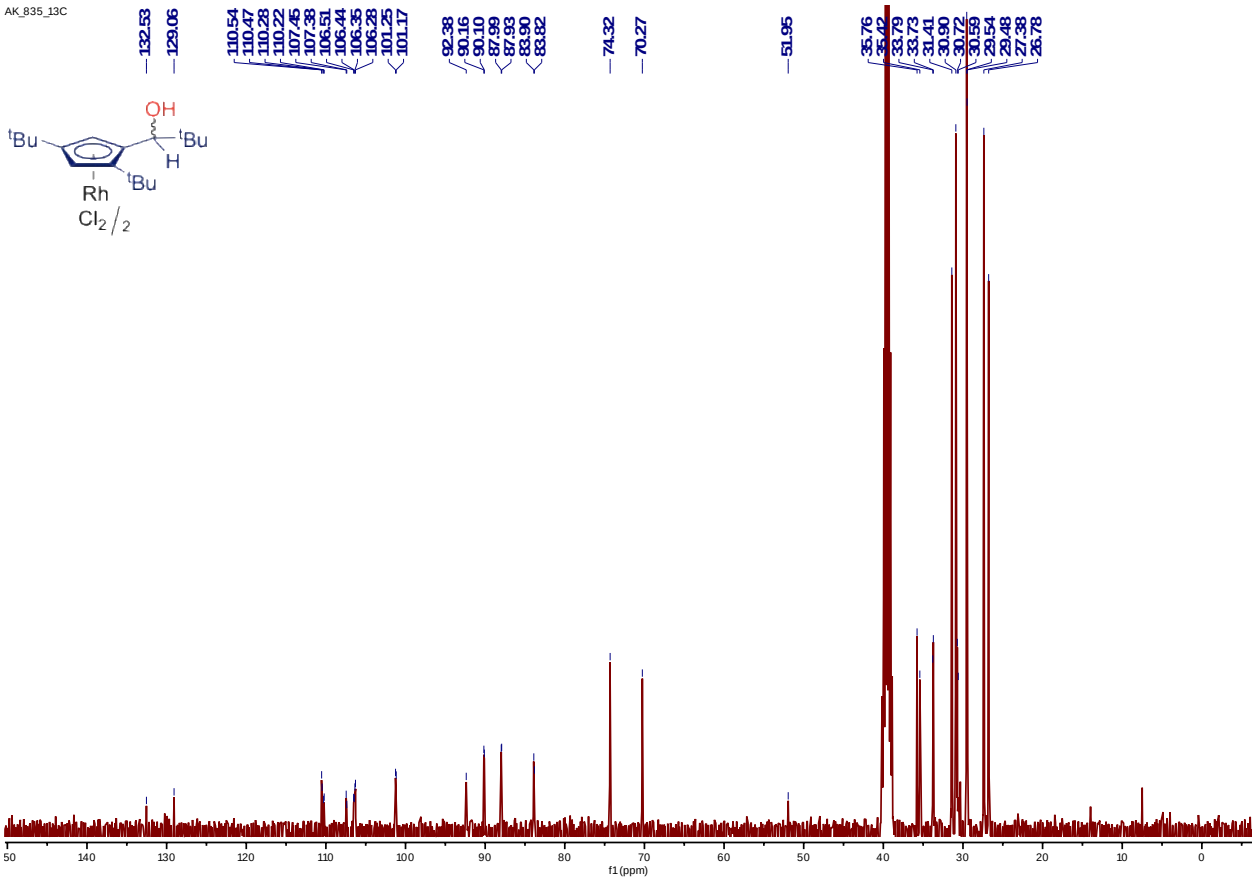
^{13}C spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(OH)CHC$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (**5**OH).



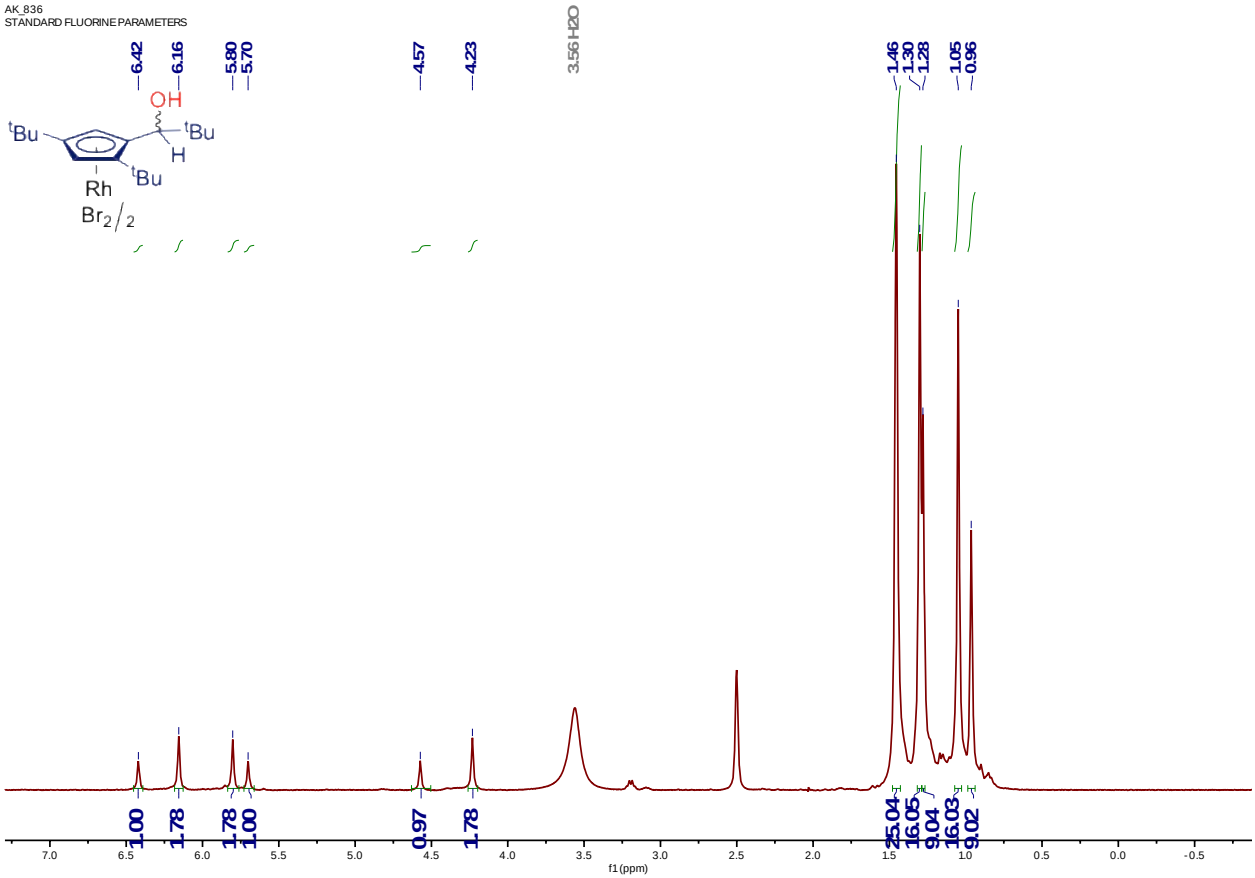
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(HO)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (**2**OH-Cl).



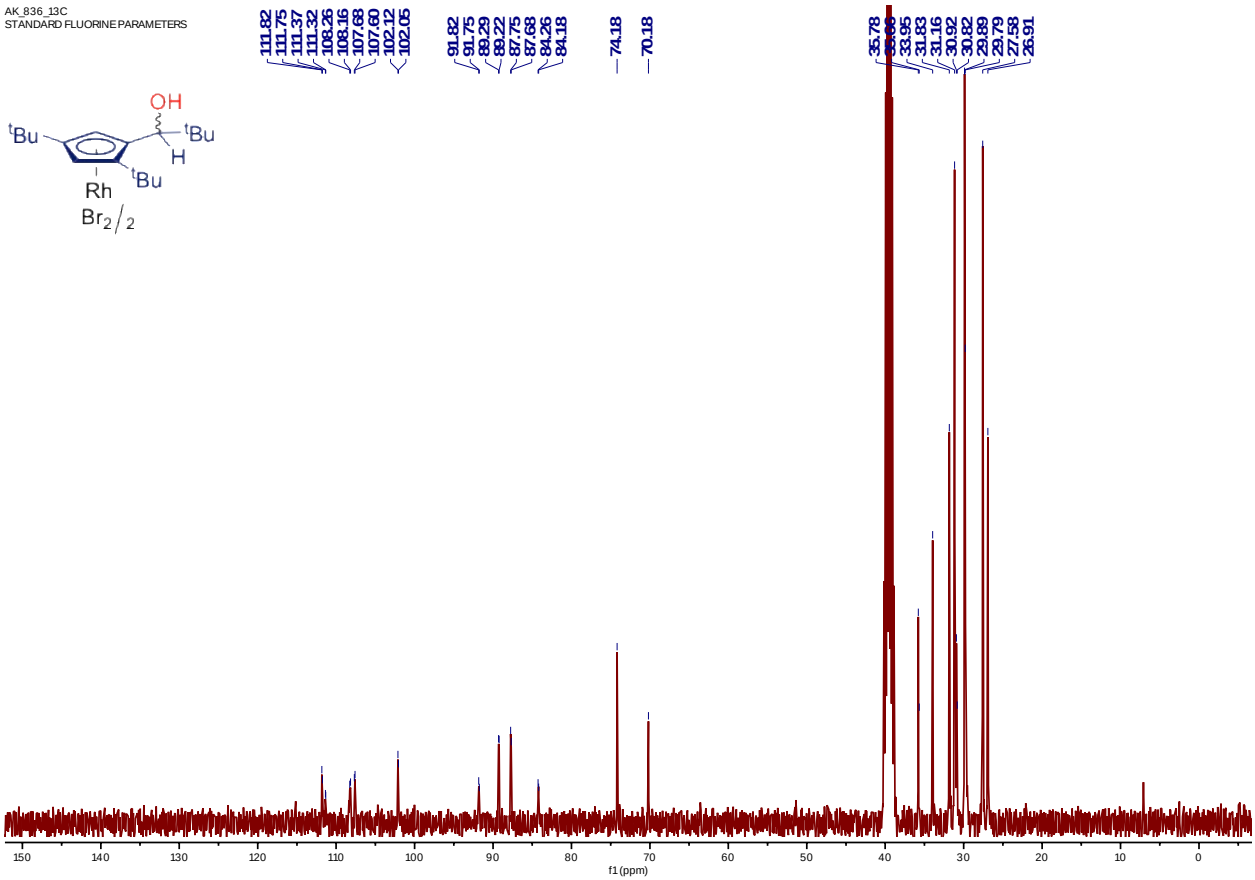
^{13}C spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(HO)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (**2**OH-Cl).



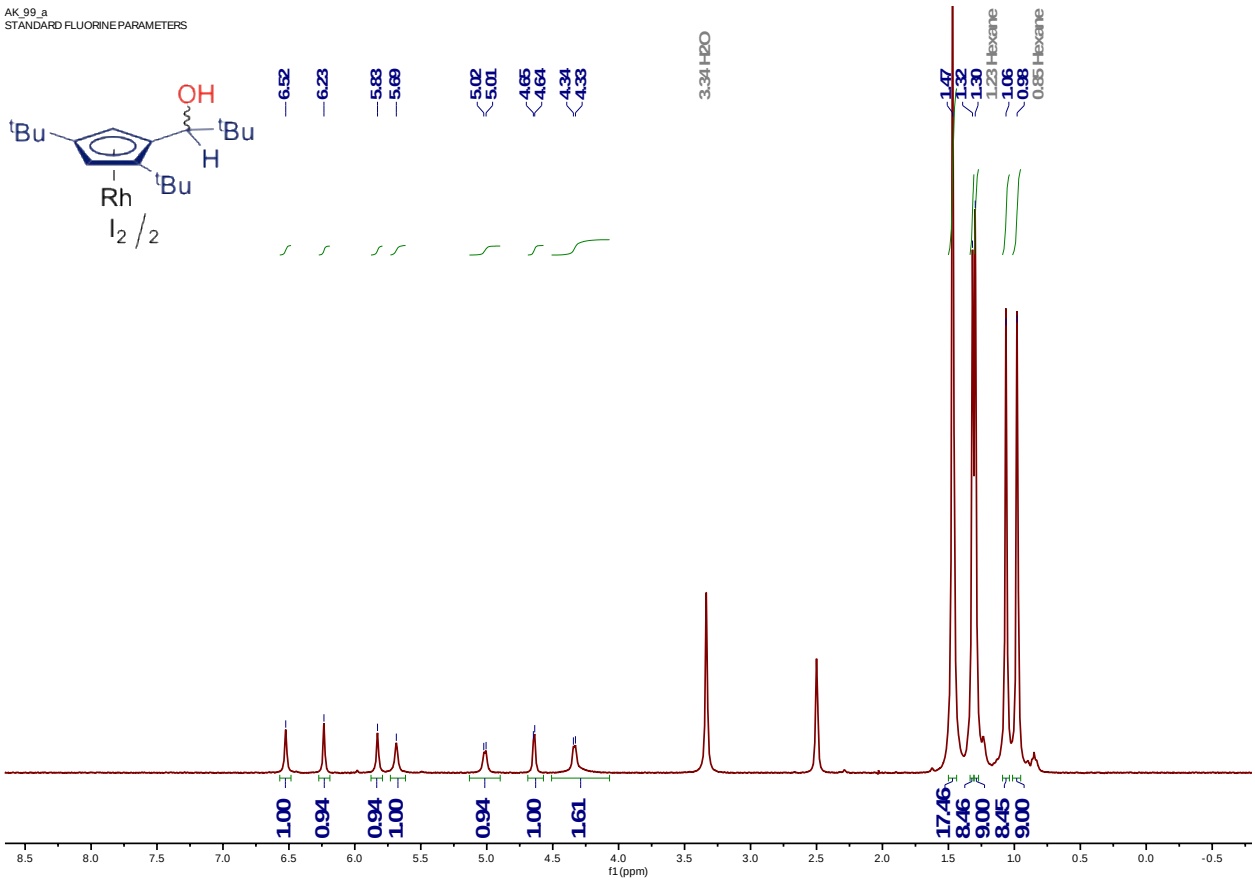
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(HO)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (**2**OH-Br). dr 1:1.78



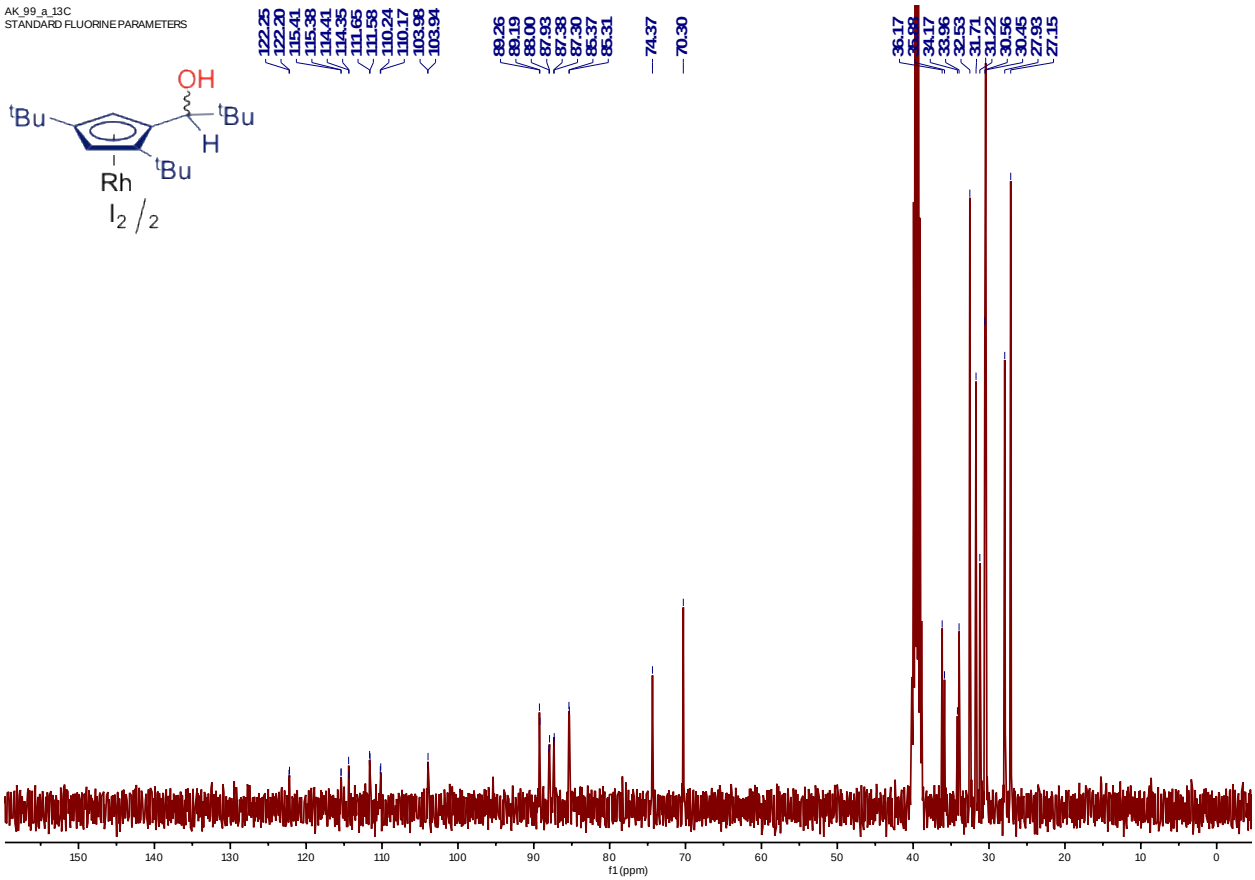
^{13}C spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(HO)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (**2**OH-Br).



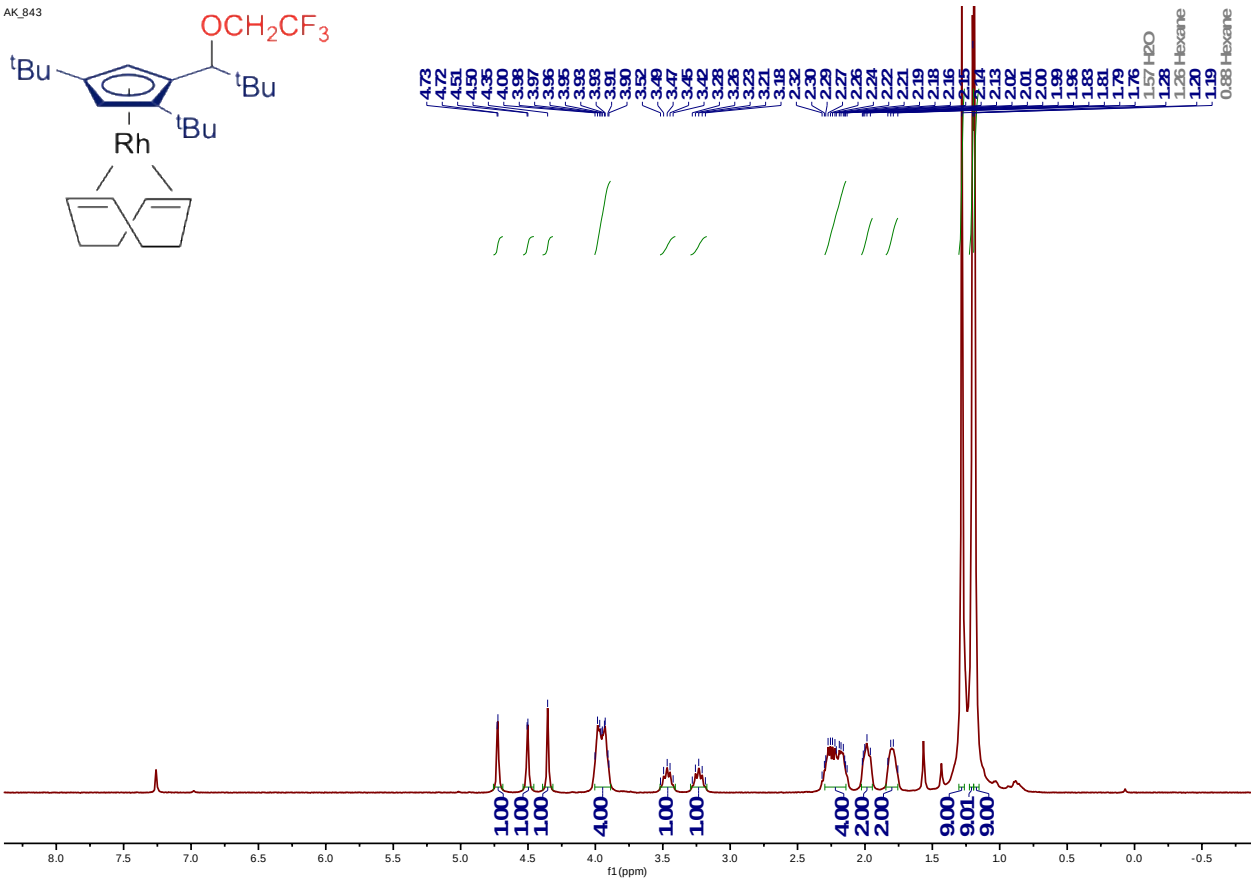
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(HO)CHC$_5$H$_2$)RhI$_2$]$_2$ (**2**OH-I). dr 1: 0.94



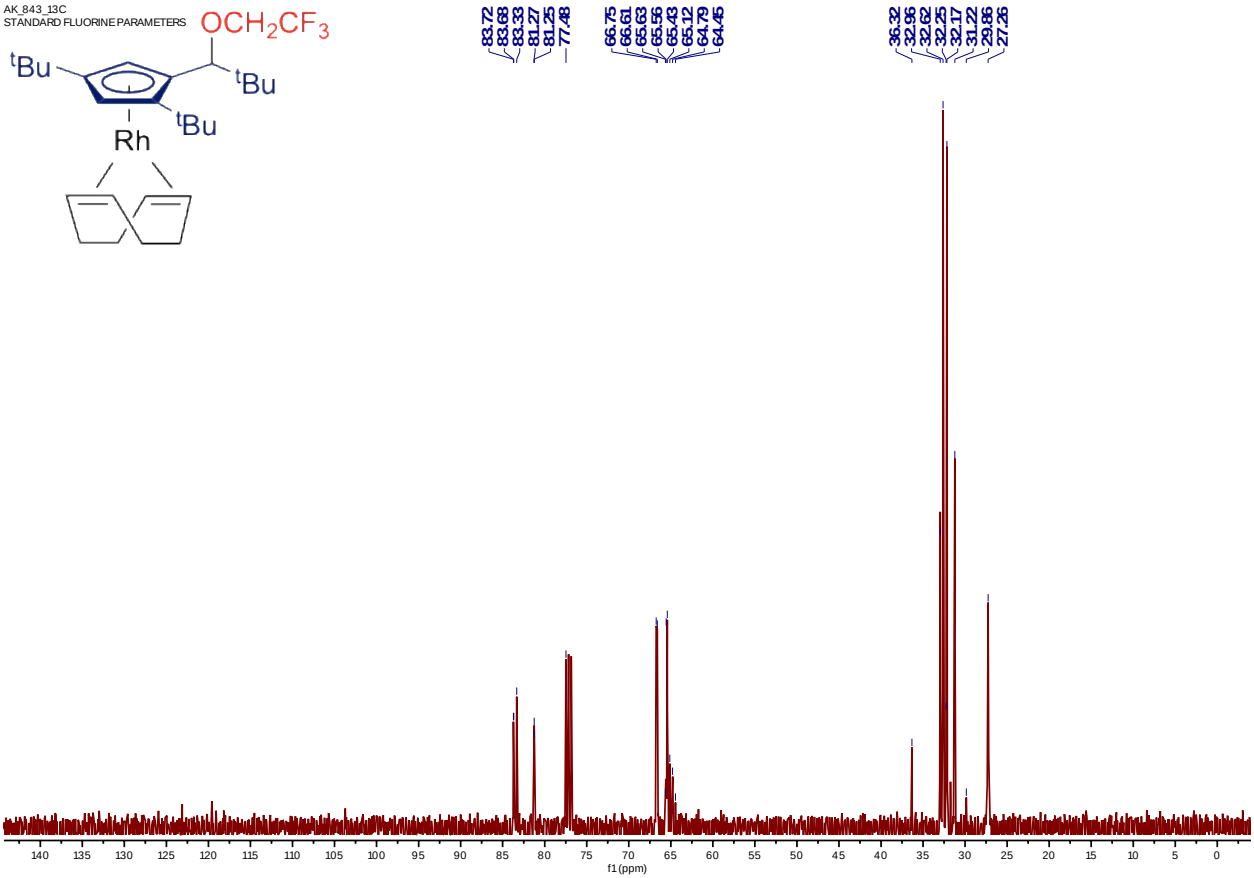
^{13}C spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(HO)CH-C$_5$H$_2$)RhI$_2$]$_2$ (**2**OH-I).



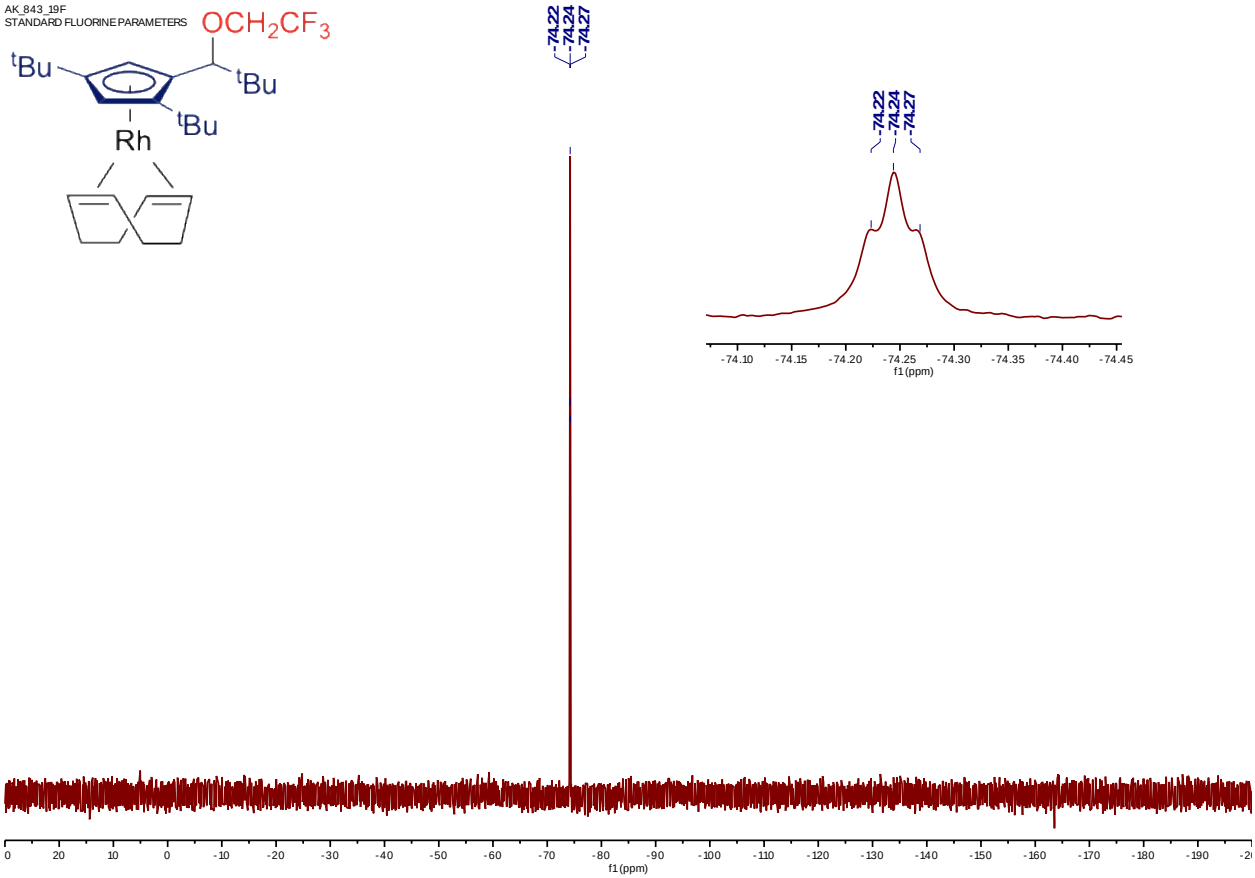
^{1}H Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF_3CH_2O)CH-C_5H_2)Rh(1,5-C_8H_{12}) (**5**OCH_2CF_3).



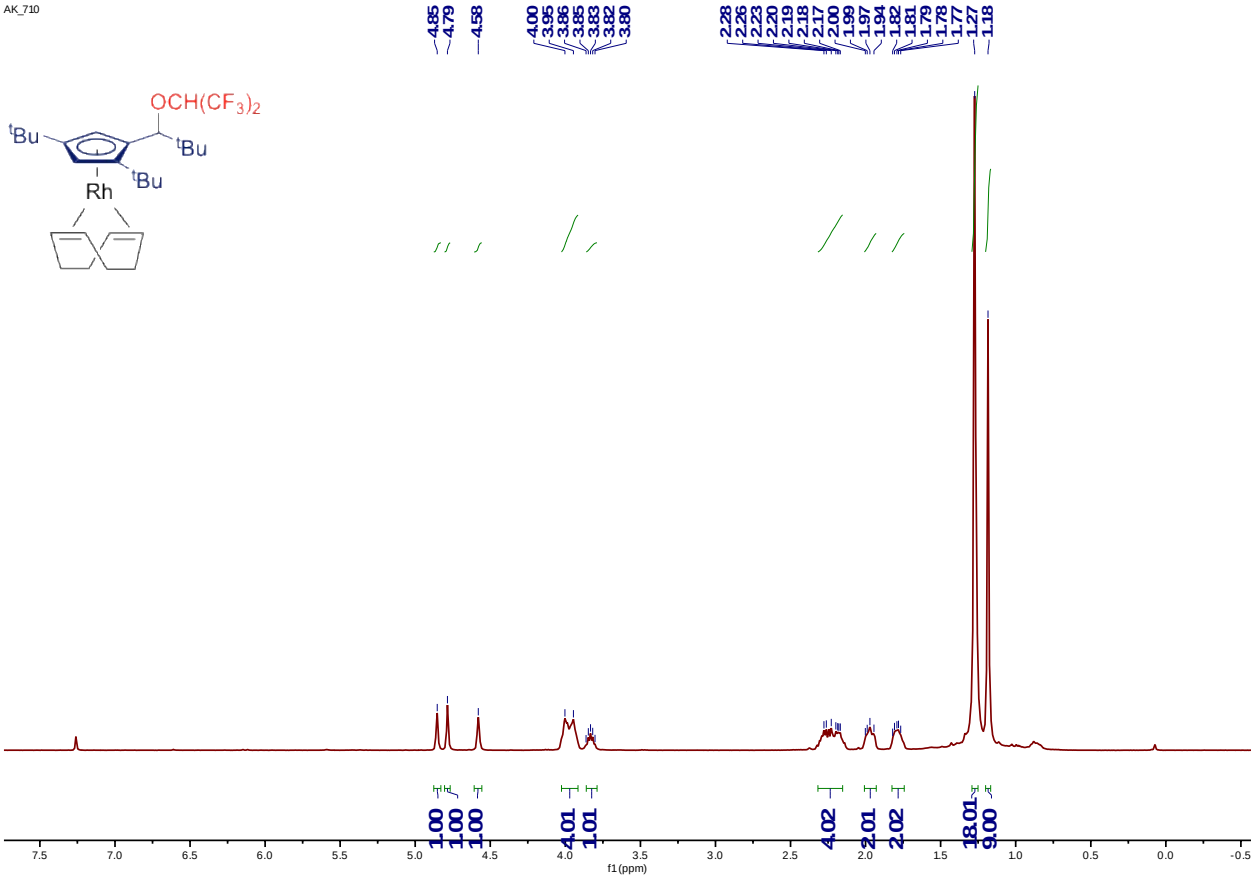
^{13}C Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF_3CH_2O)CH-C_5H_2)Rh(1,5-C_8H_{12}) (**5**OCH_2CF_3).



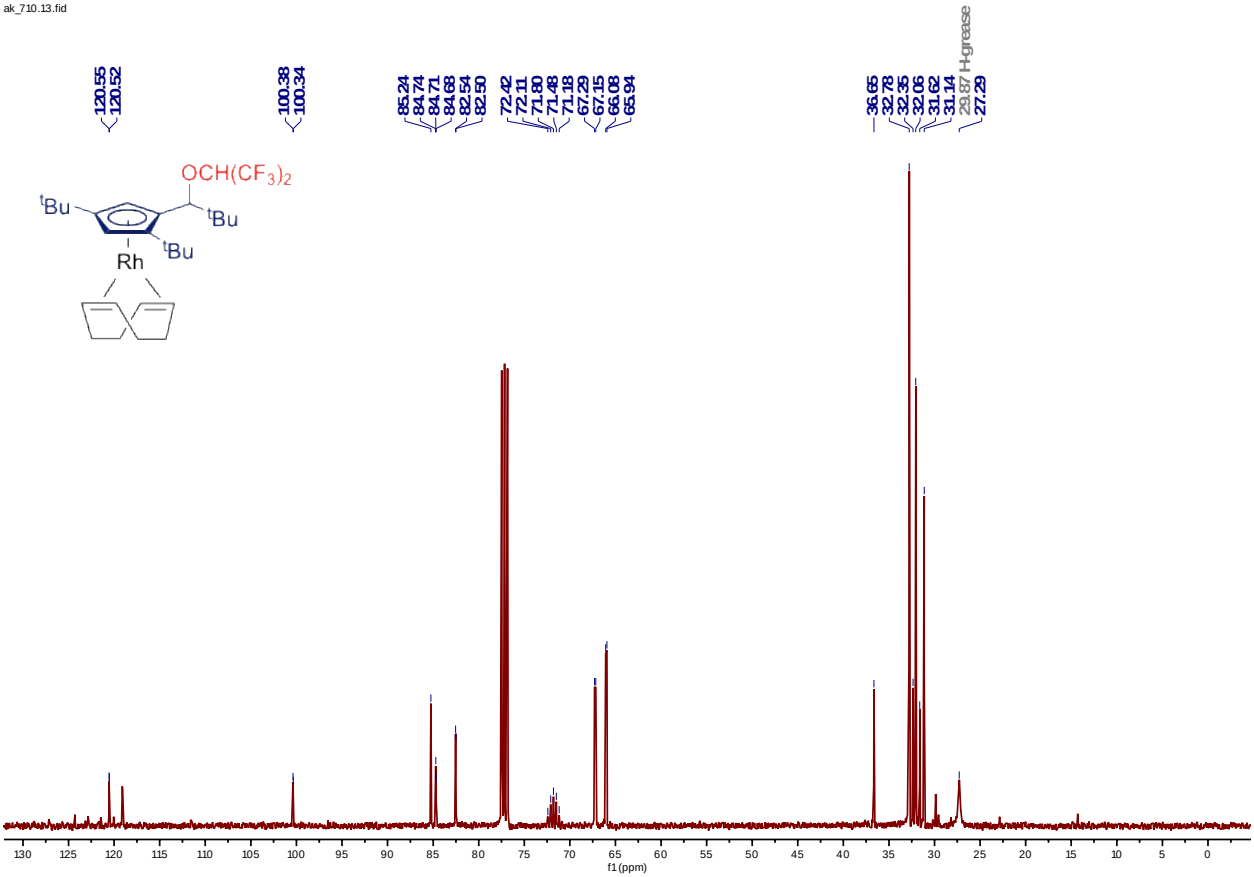
^{19}F Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF$_3$CH$_2$O)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (**5**OCH$_2$CF$_3$).



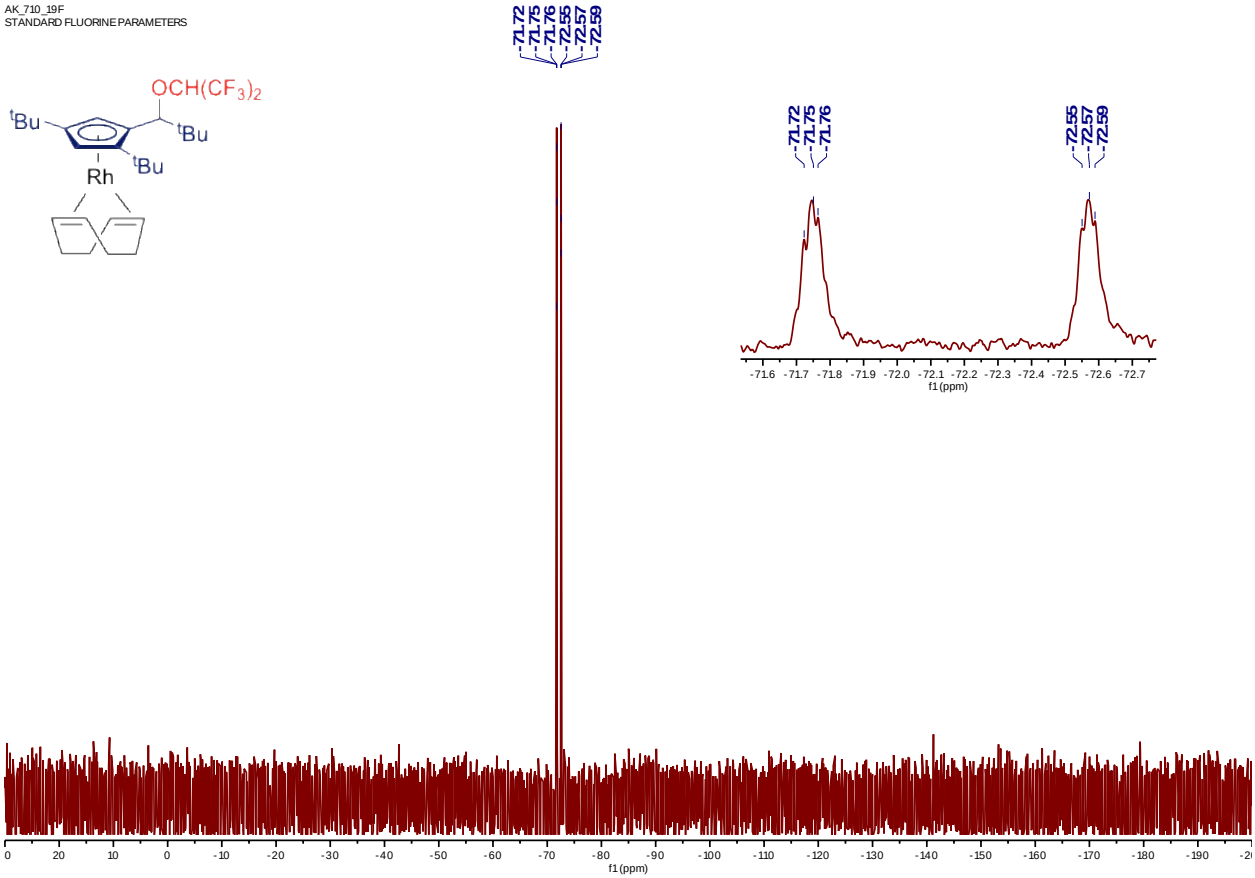
^{1}H Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (**5**OCH(CF$_3$)$_2$).



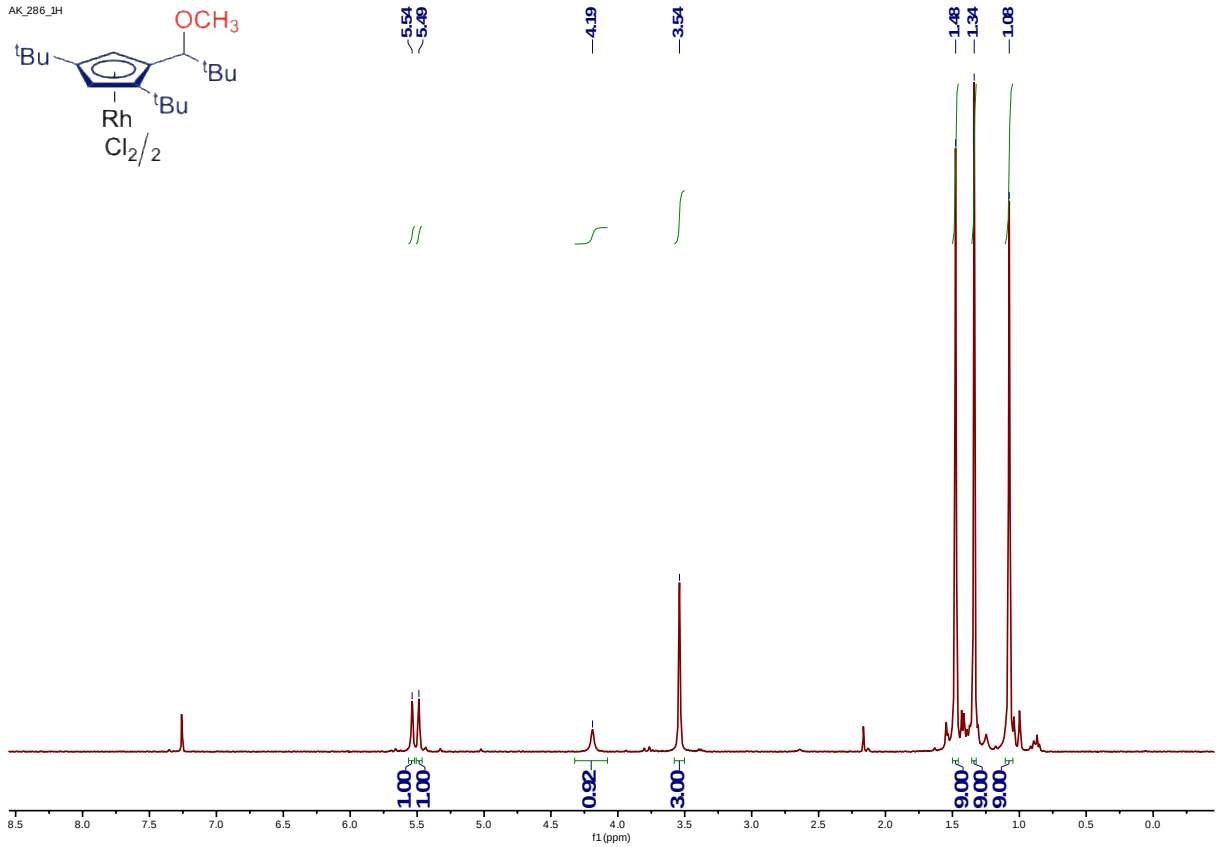
^{13}C Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (**5**OCH(CF$_3$)$_2$).



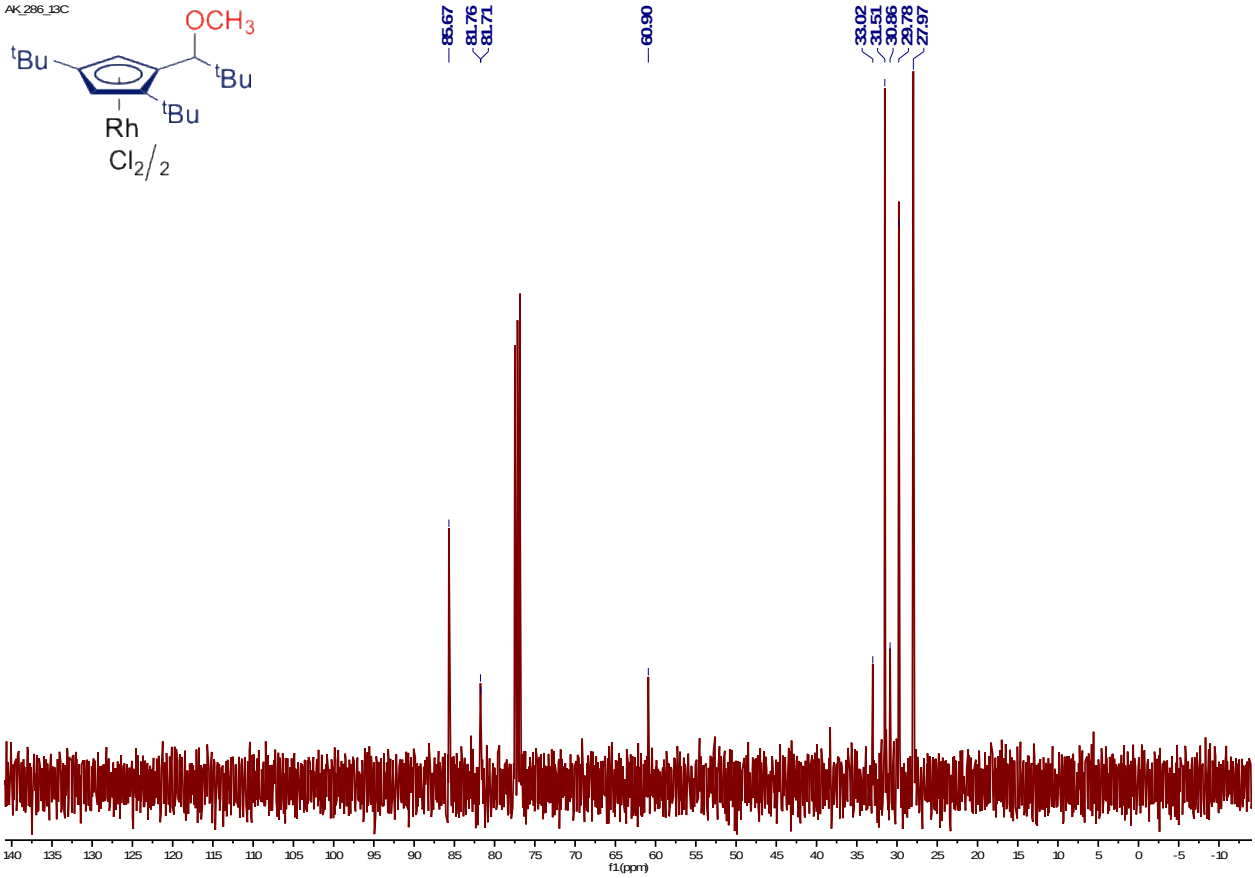
^{19}F Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (**5**OCH(CF$_3$)$_2$).



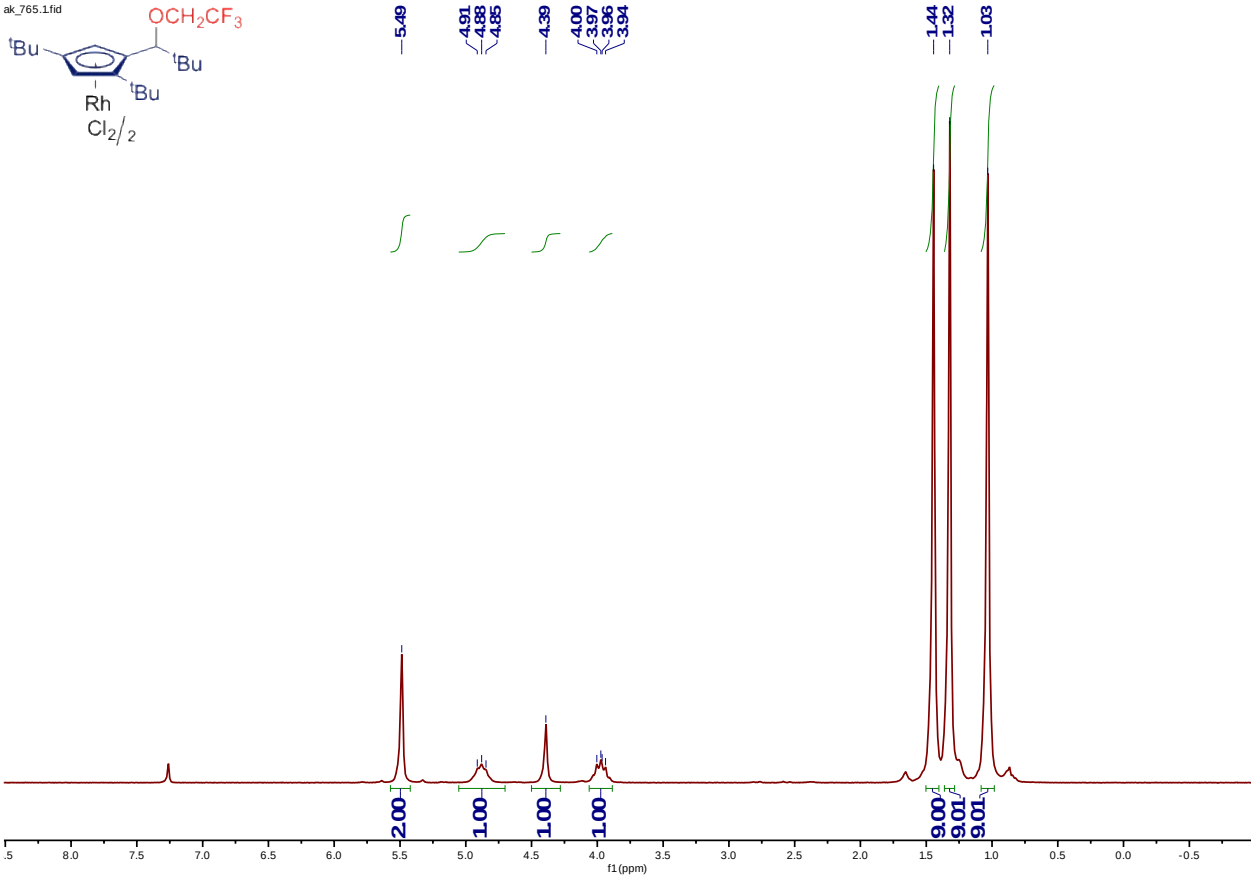
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CH$_3$O)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (**2**OCH$_3$-Cl).



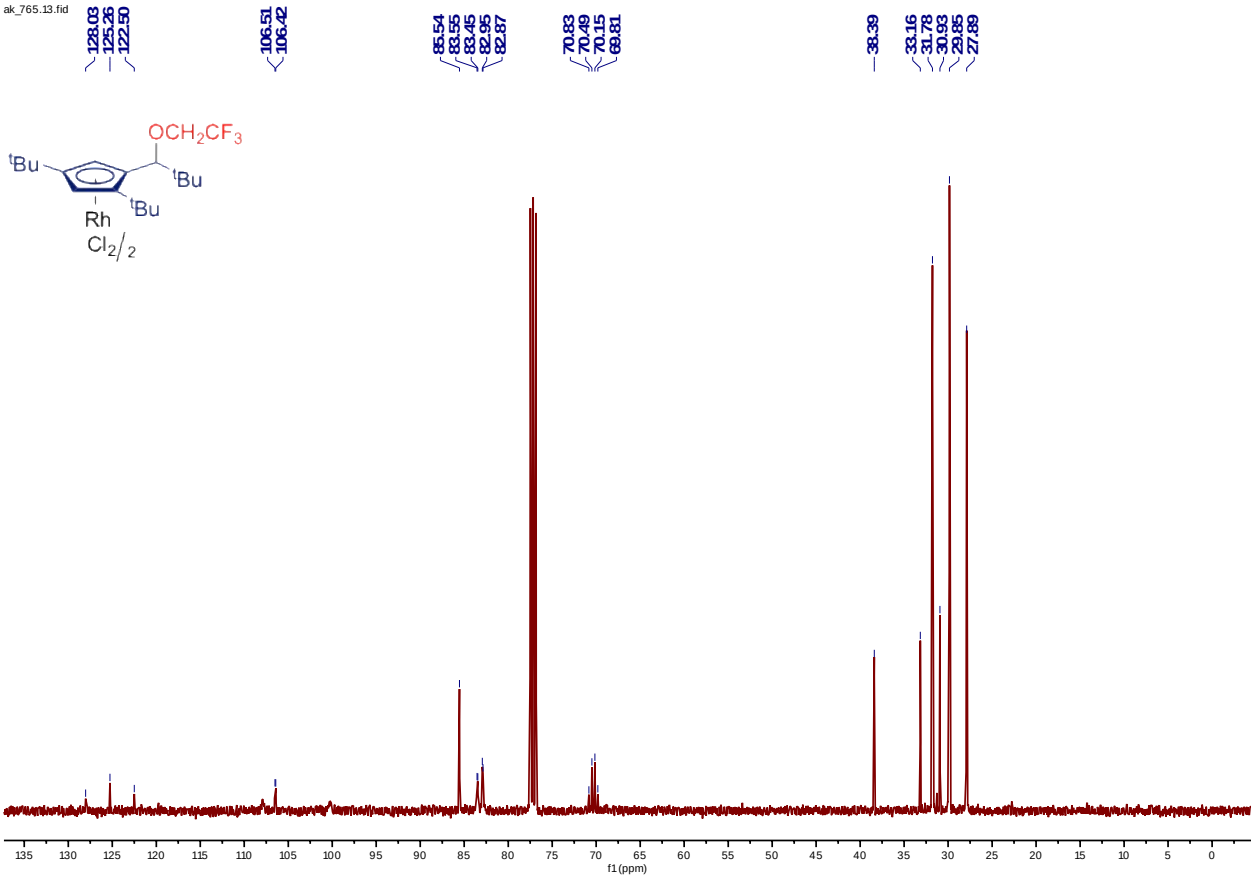
^{13}C spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$]$_2$ (**2**OCH$_3$-Cl).



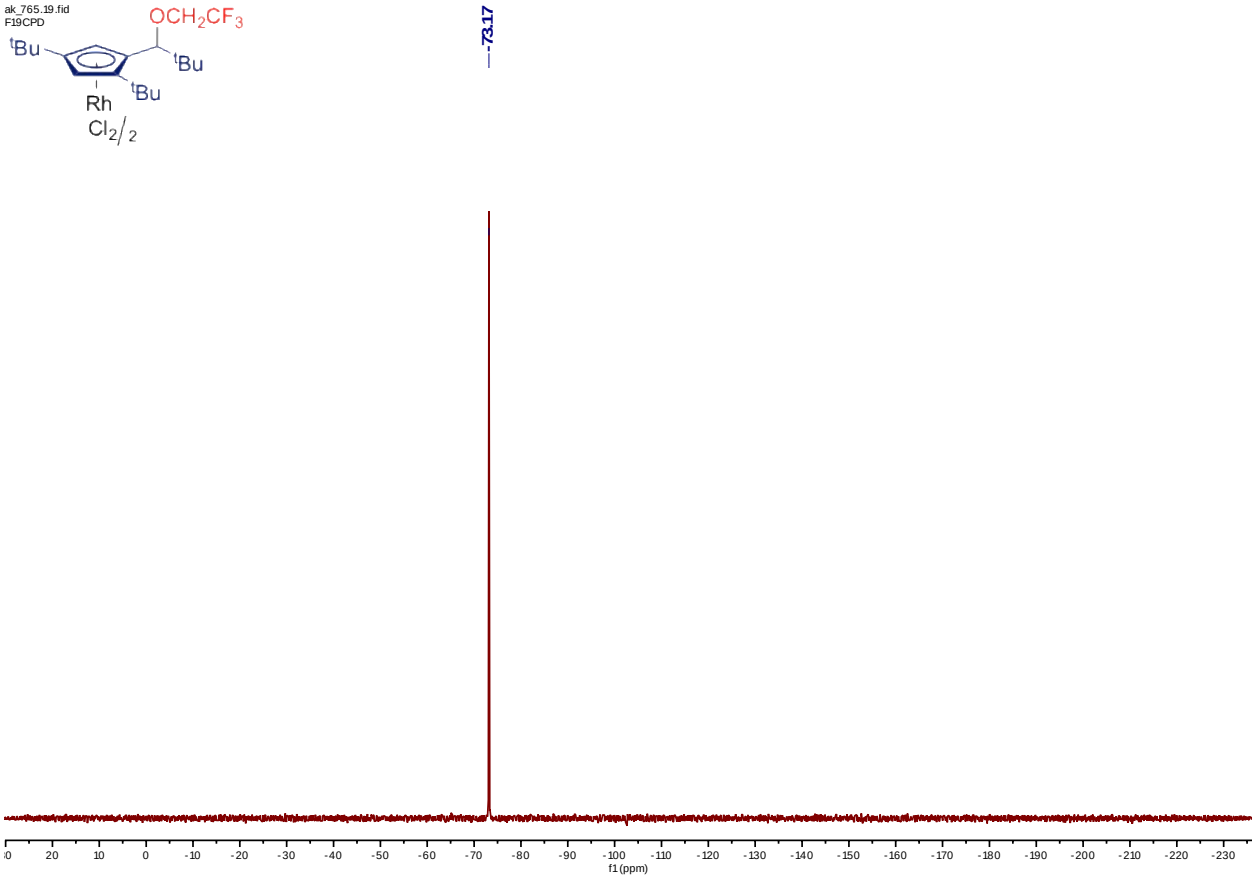
^{1}H Spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF_3CH_2O)CH-C_5H_2)$RhCl_2$]$_2$ (**2**OCH_2CF_3-Cl).



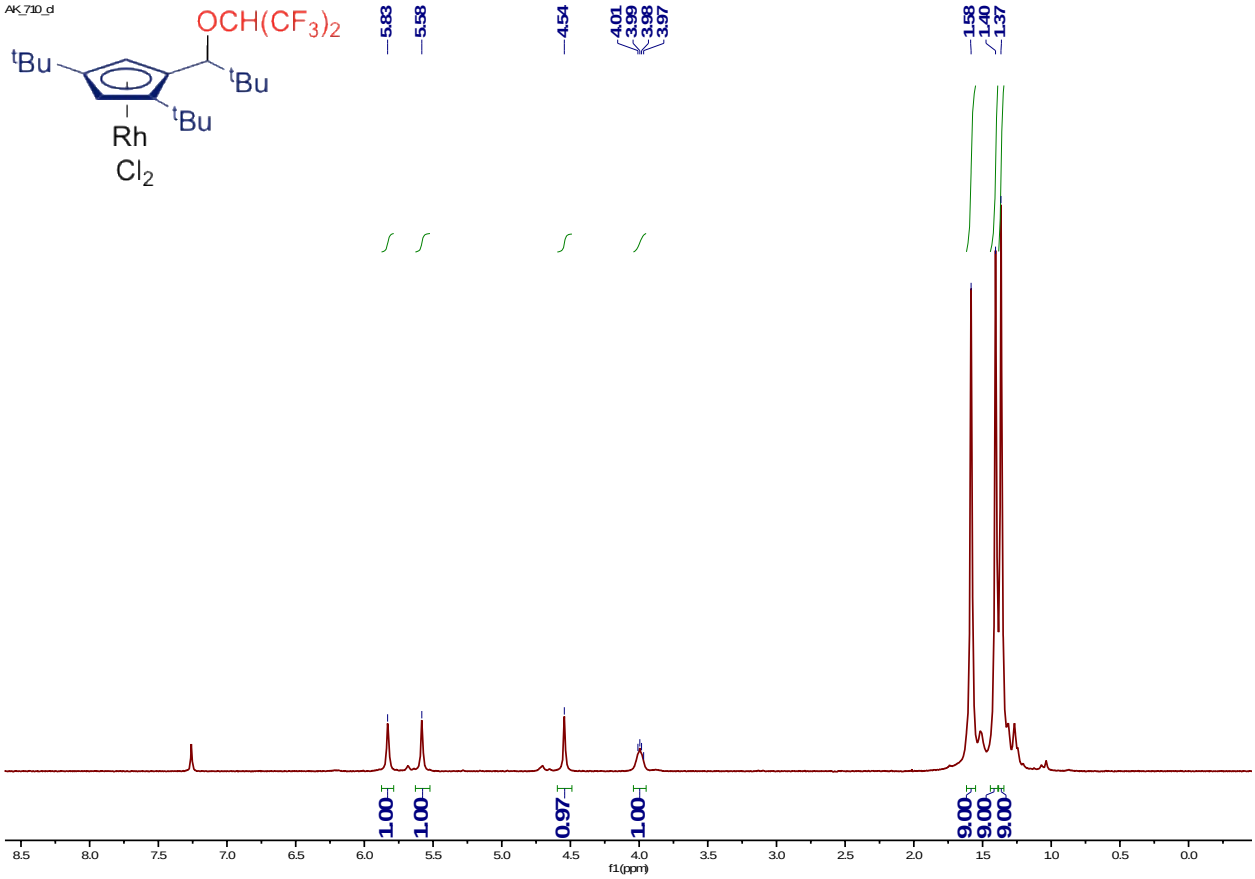
^{13}C Spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF_3CH_2O)CH-C_5H_2)$RhCl_2$]$_2$ (**2**OCH_2CF_3-Cl).



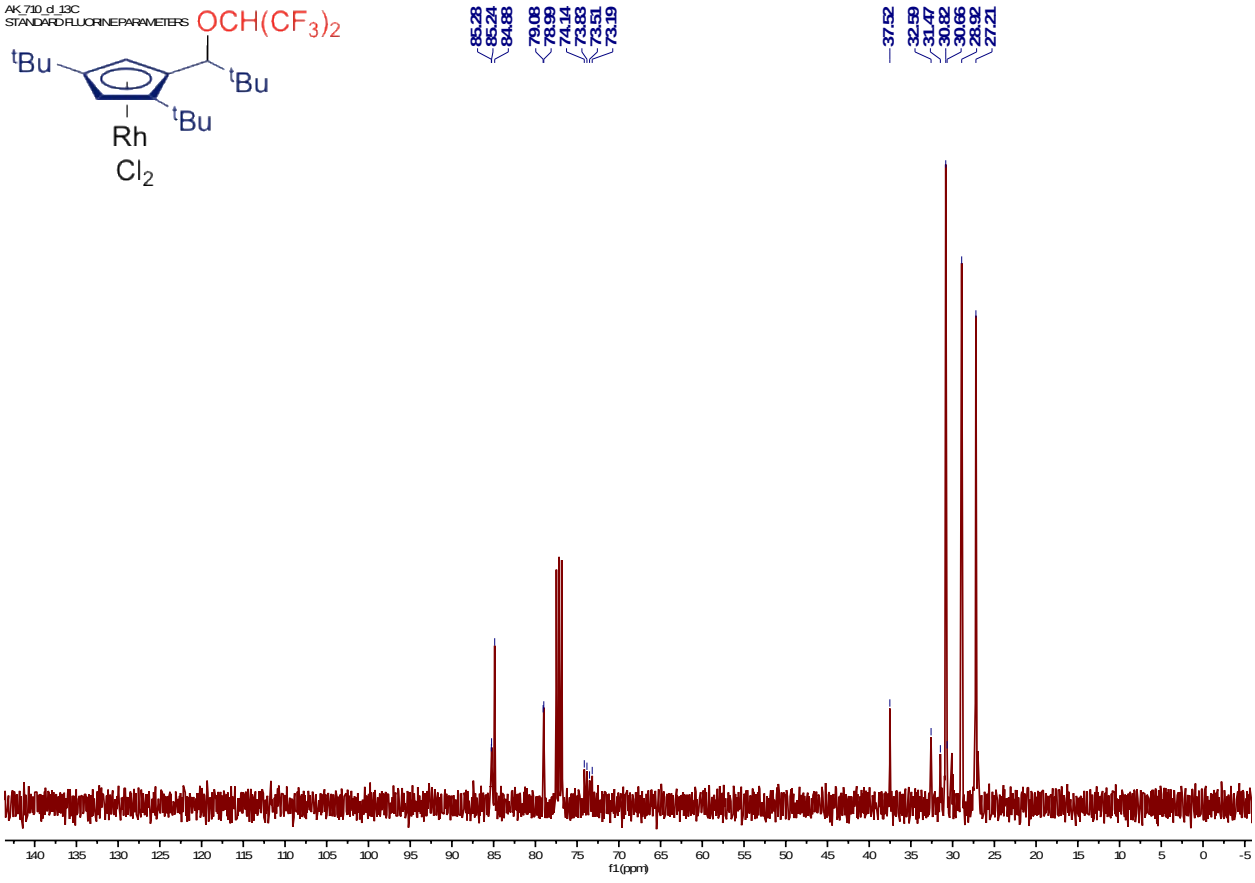
^{19}F Spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CF_3CH_2O)CH-C_5H_2)$RhCl_2$]$_2$ (**2**OCH_2CF_3-Cl).



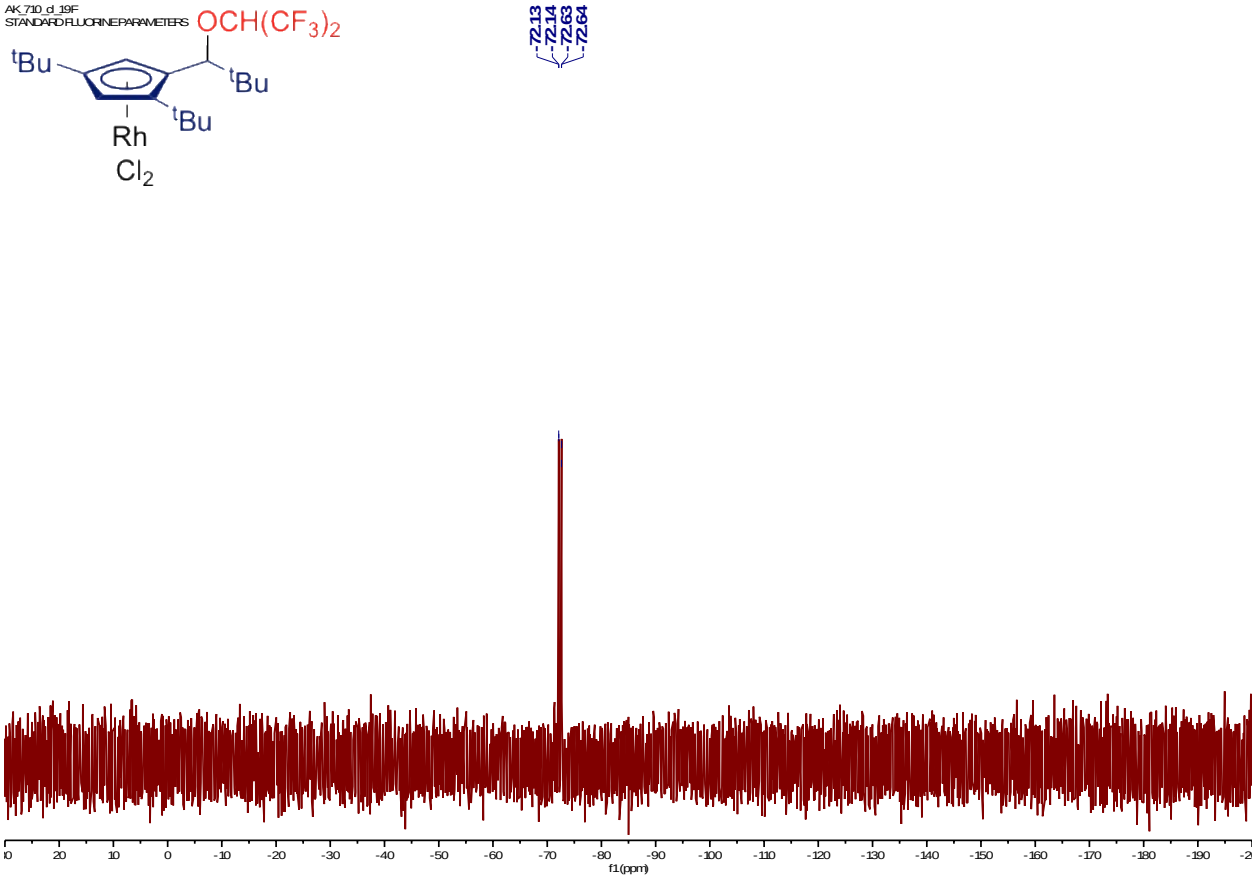
^{1}H spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$ (**2**OCH(CF$_3$)$_2$-Cl).



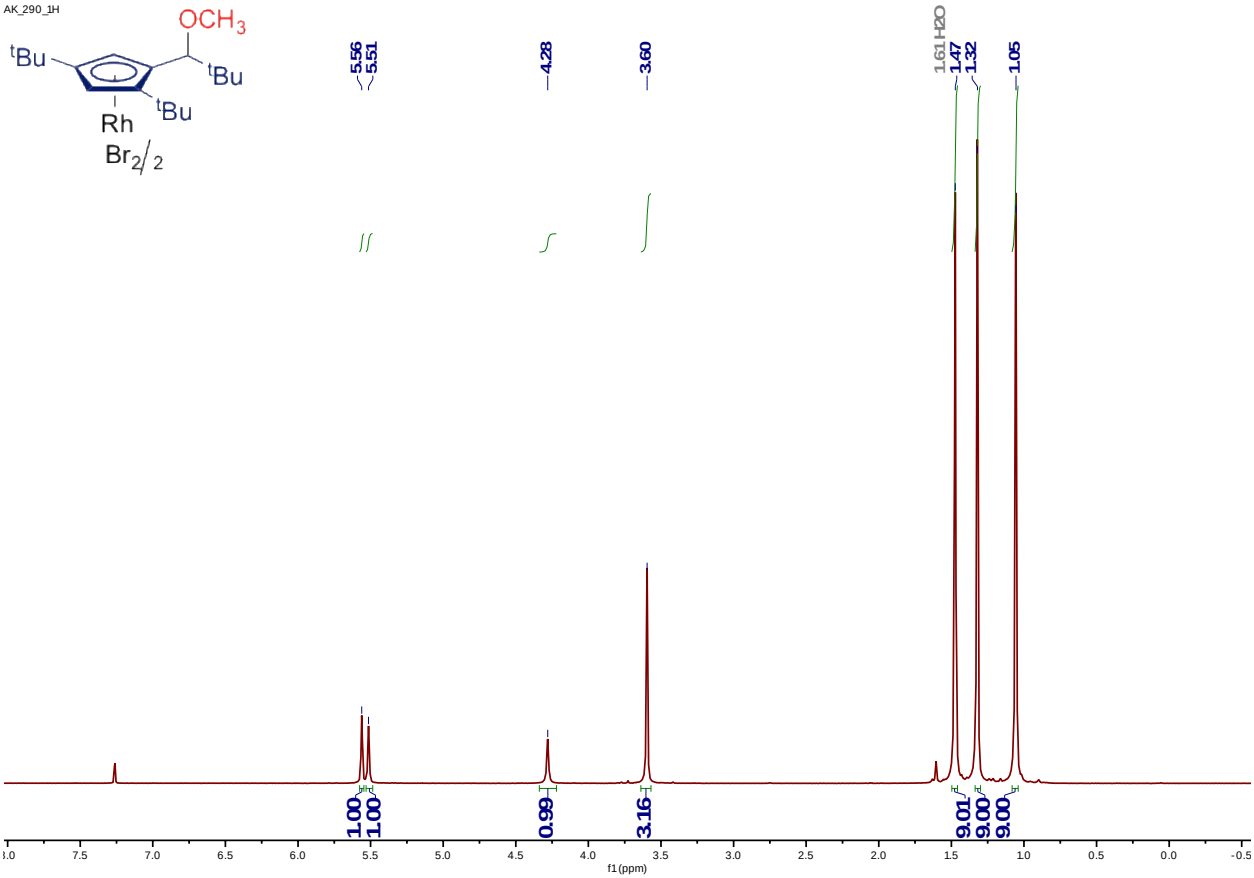
^{13}C spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$ (**2**OCH(CF$_3$)$_2$-Cl).



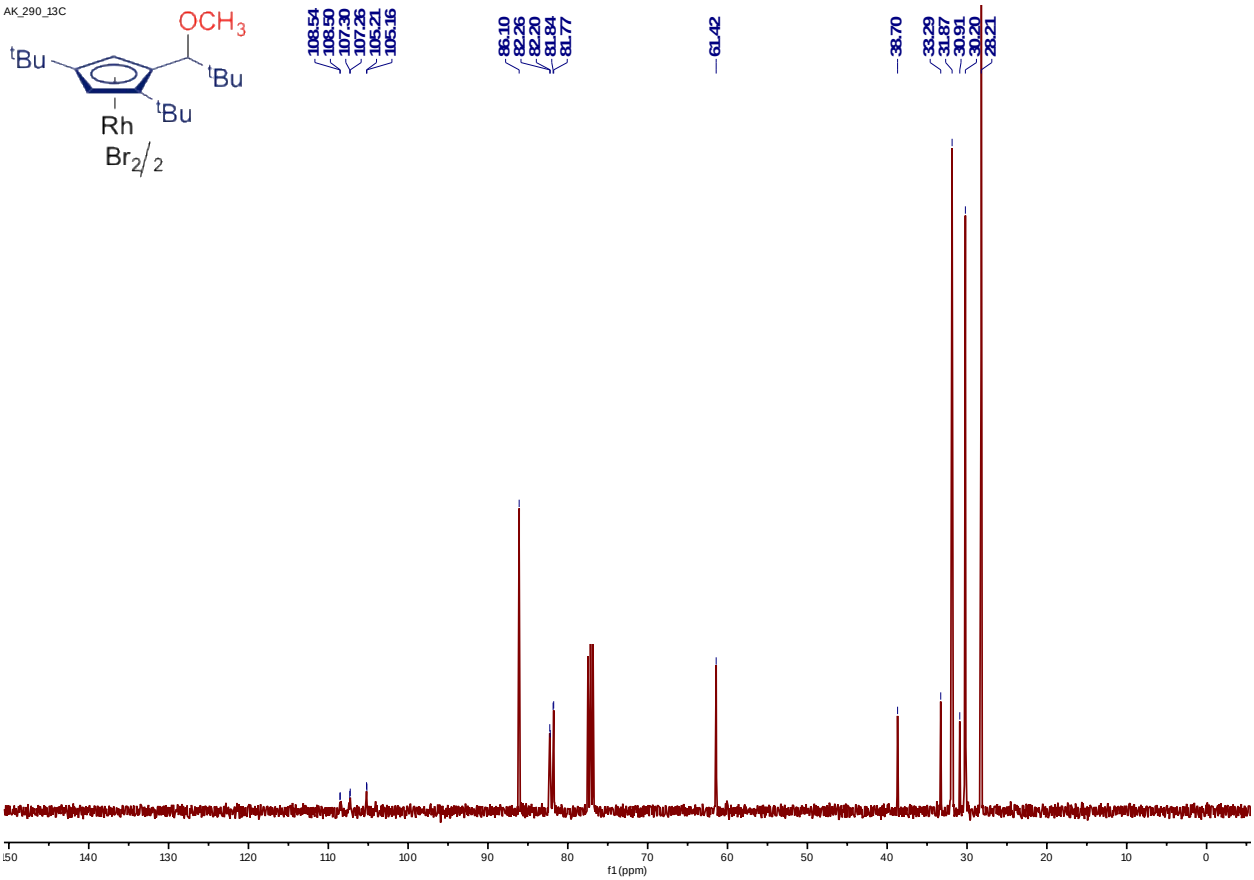
^{19}F spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$ (**2**OCH(CF$_3$)$_2$-Cl).



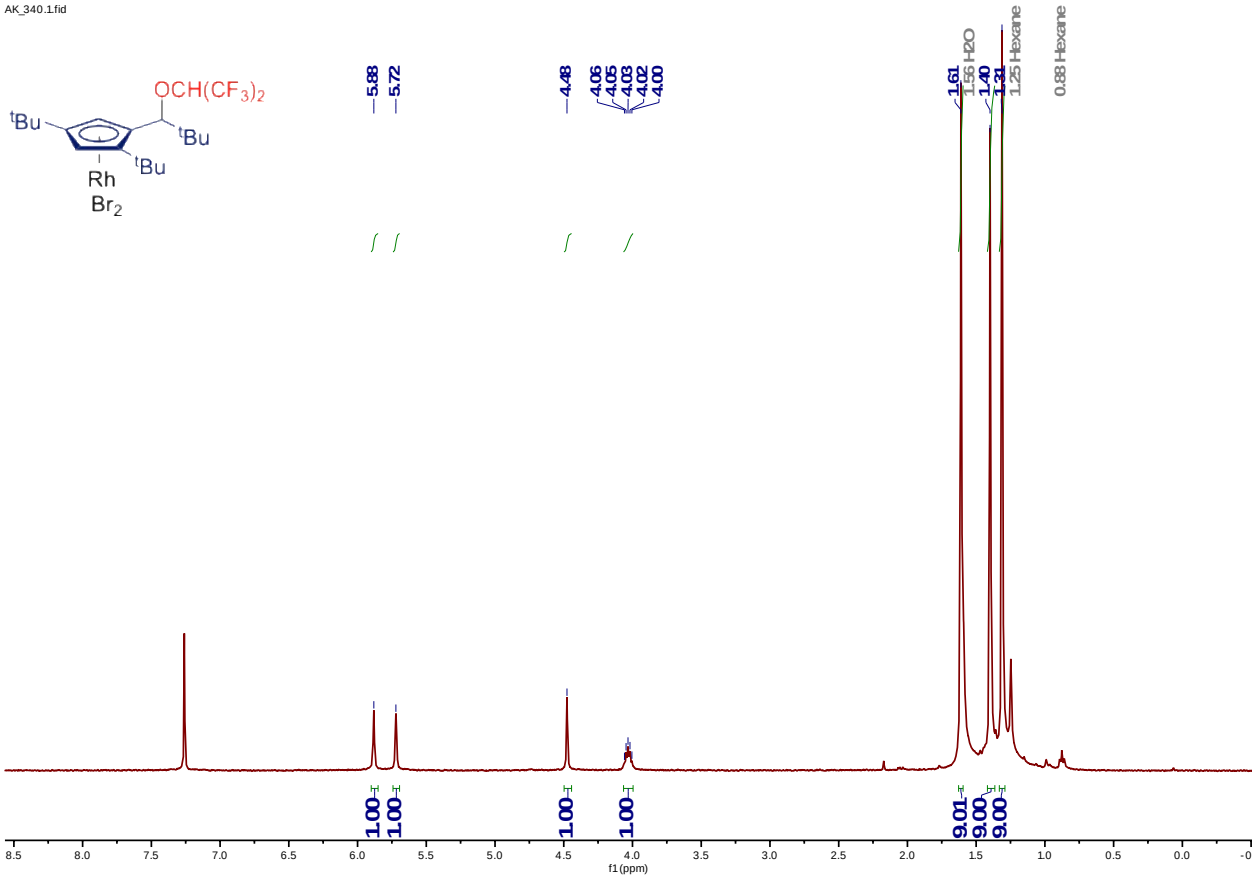
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CH$_3$O)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (**2**OMe-Br).



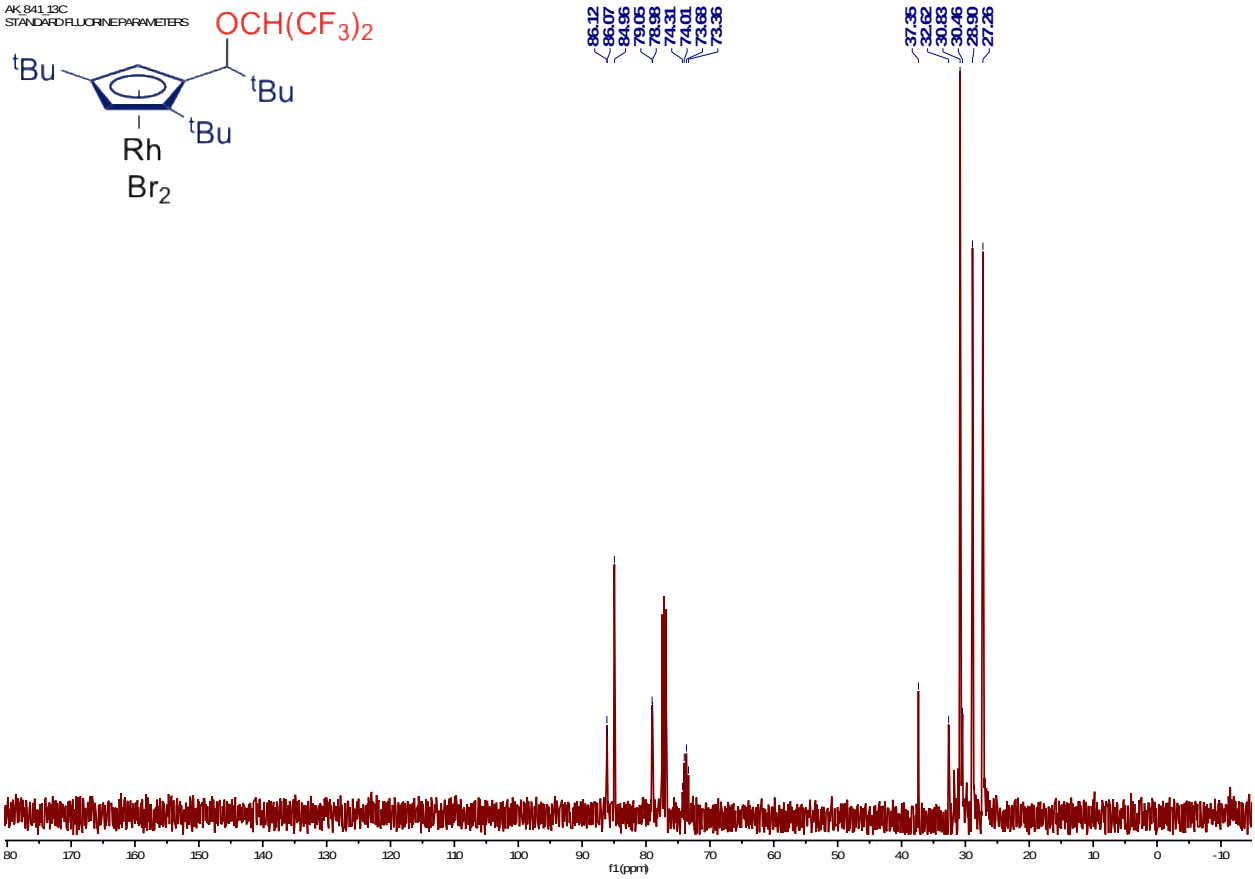
^{13}C spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu(CH$_3$O)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (**2**OMe-Br).



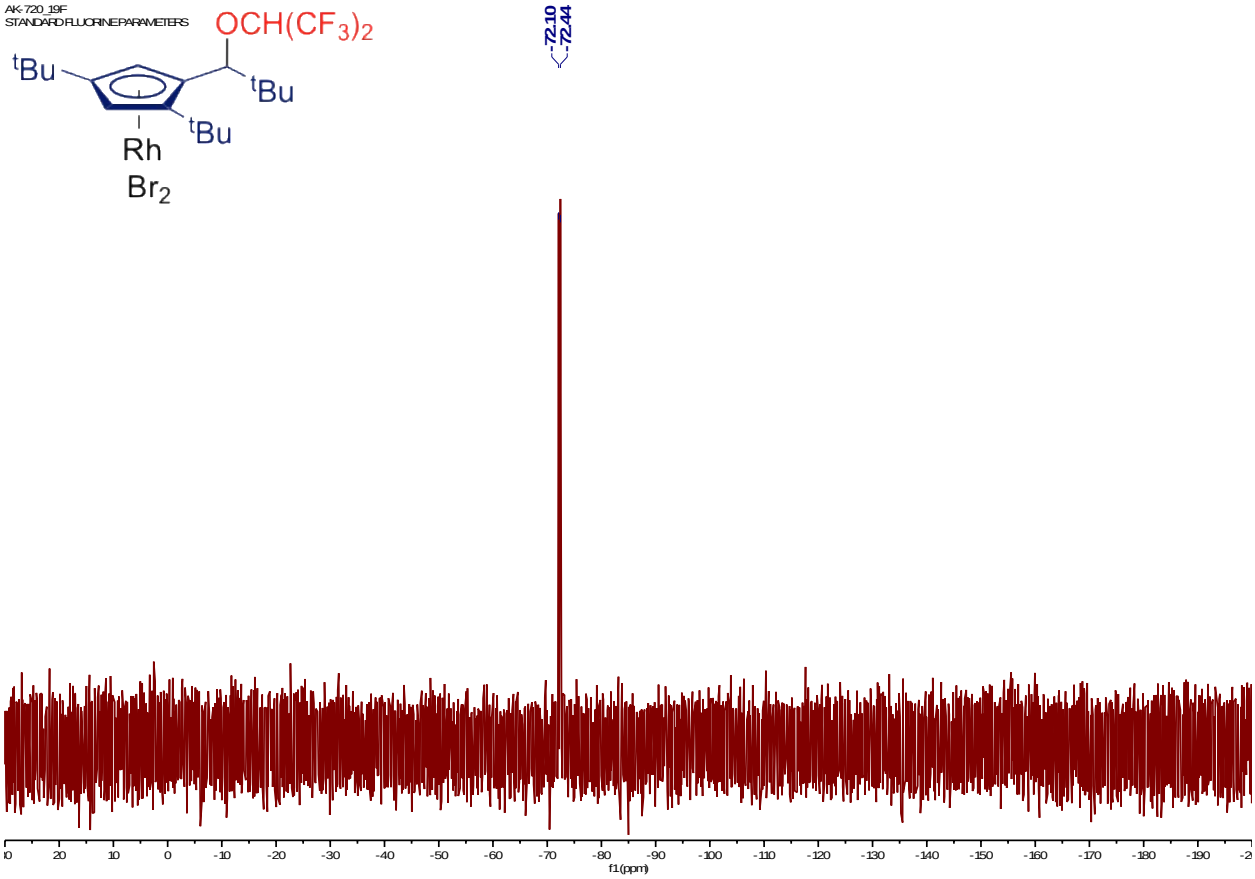
^{1}H spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhBr$_2$ (**2**OCH(CF$_3$)$_2$-Br).



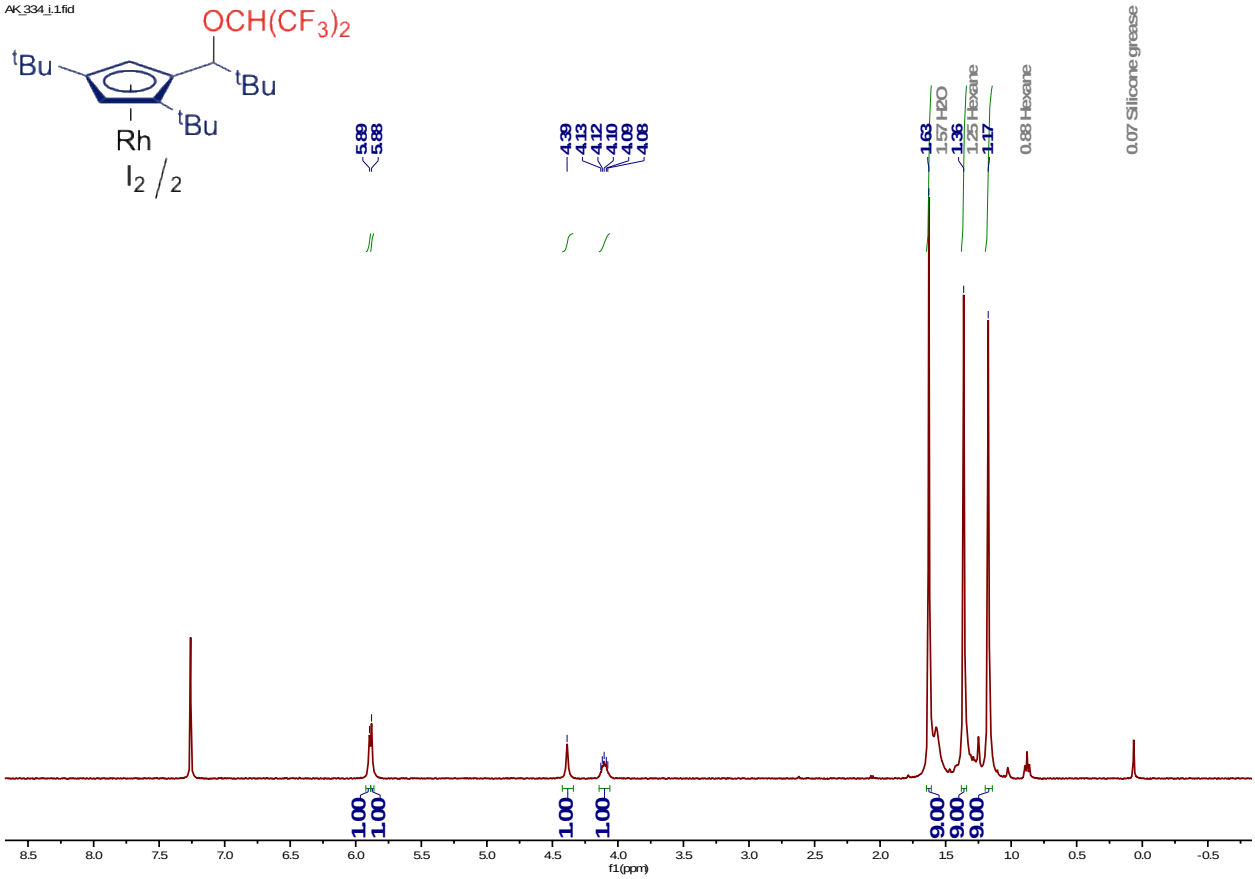
^{13}C spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhBr$_2$ (**2**OCH(CF$_3$)$_2$-Br).



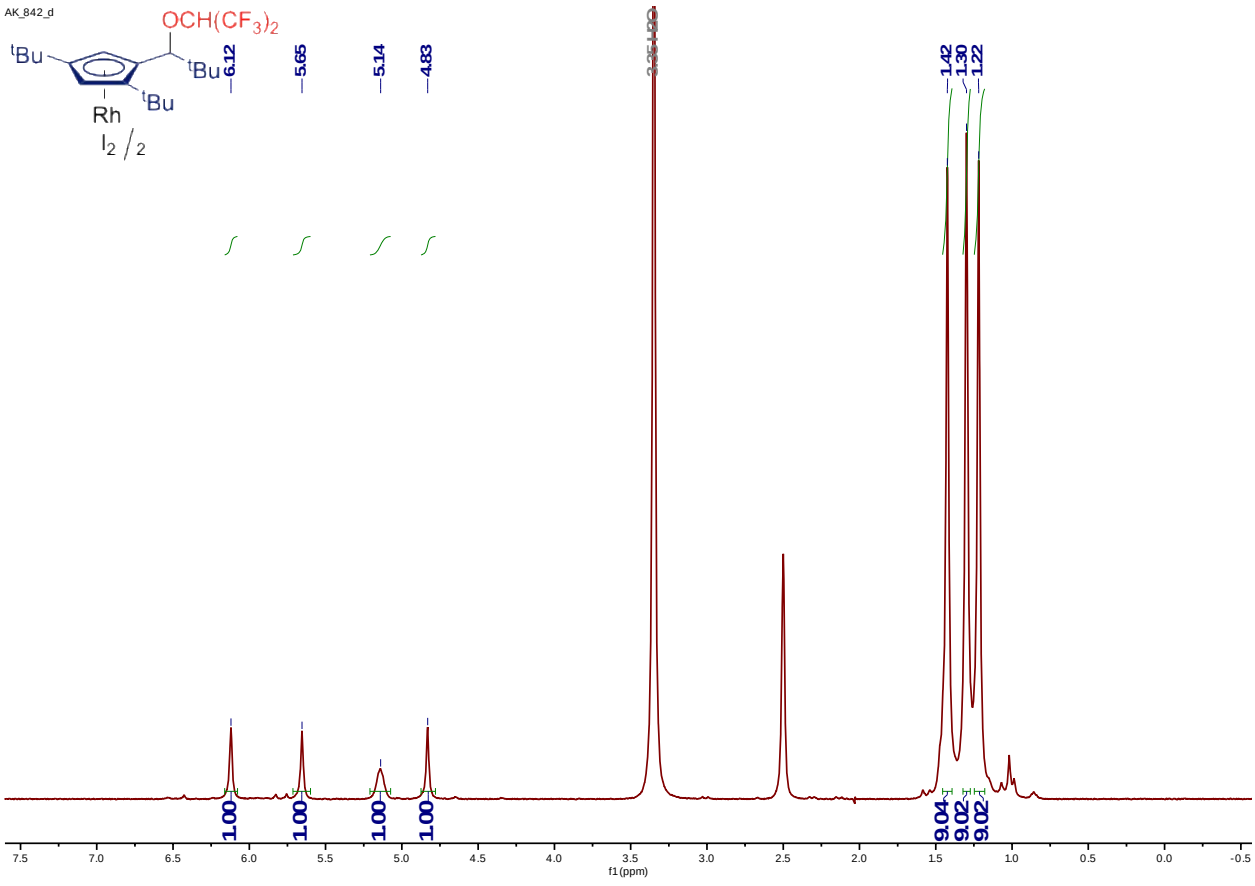
^{19}F Spectrum of (η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhBr$_2$ (**2**OCH(CF$_3$)$_2$-Br).



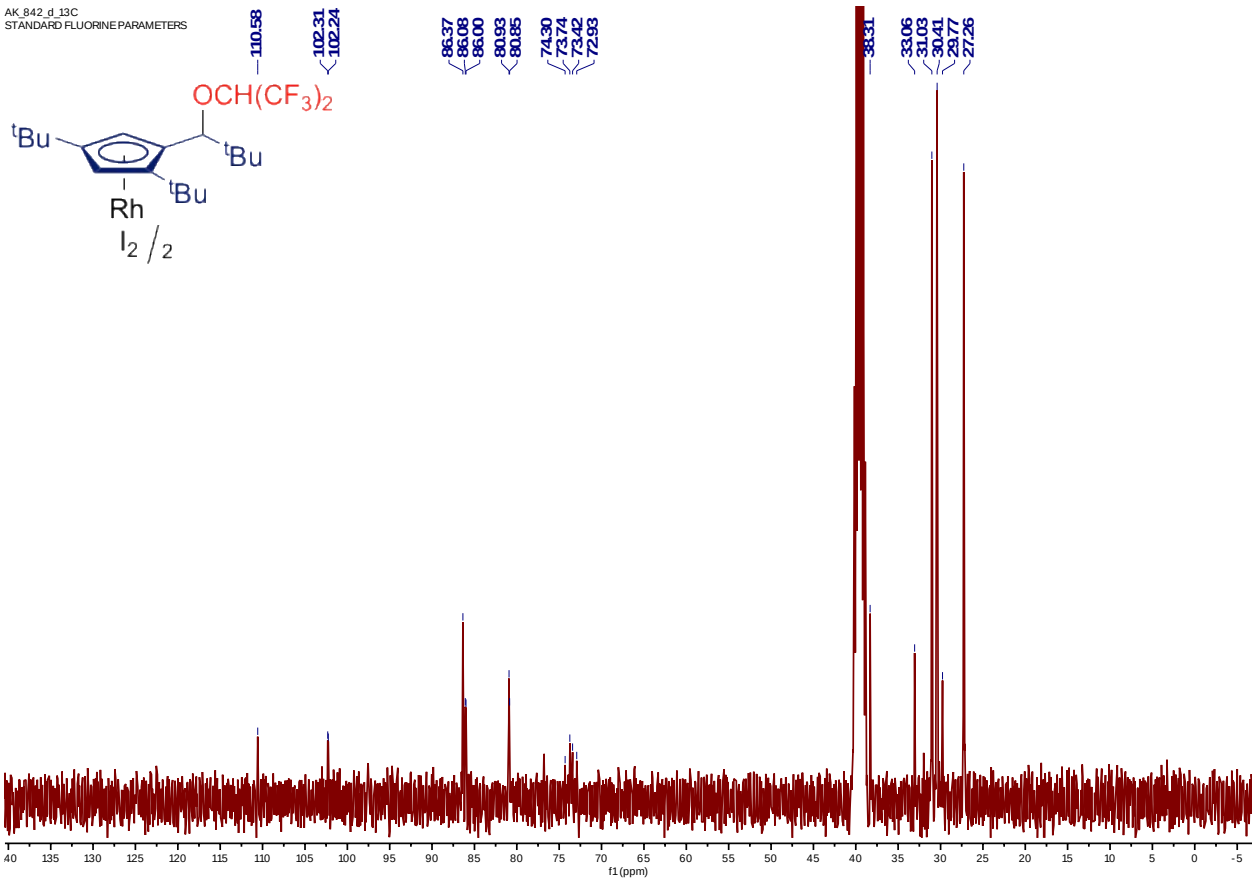
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhI$_2$]$_2$ (**2**OCH(CF$_3$)$_2$-I) in CDCl$_3$.



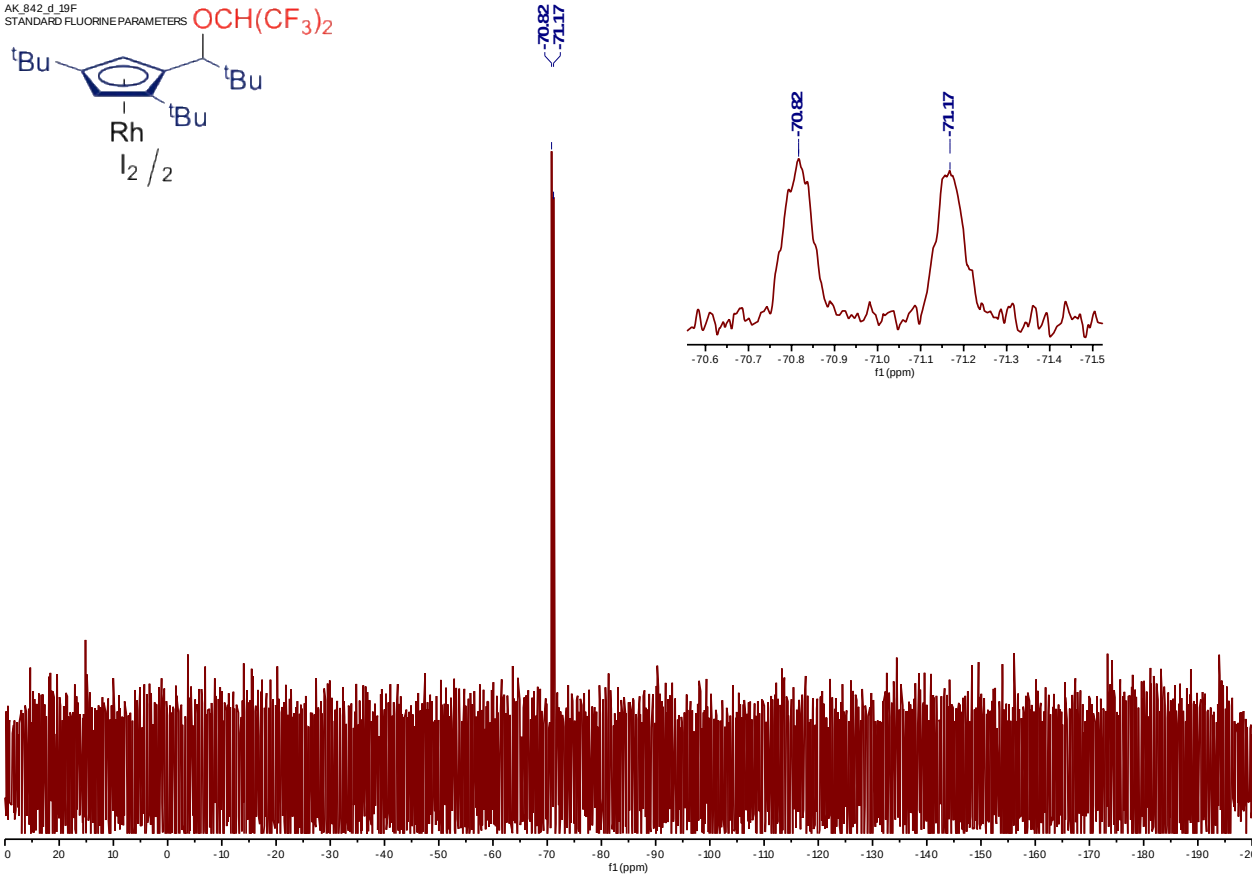
^{1}H spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhI$_2$]$_2$ (**2**OCH(CF$_3$)$_2$-I) in DMSO-d$_6$.



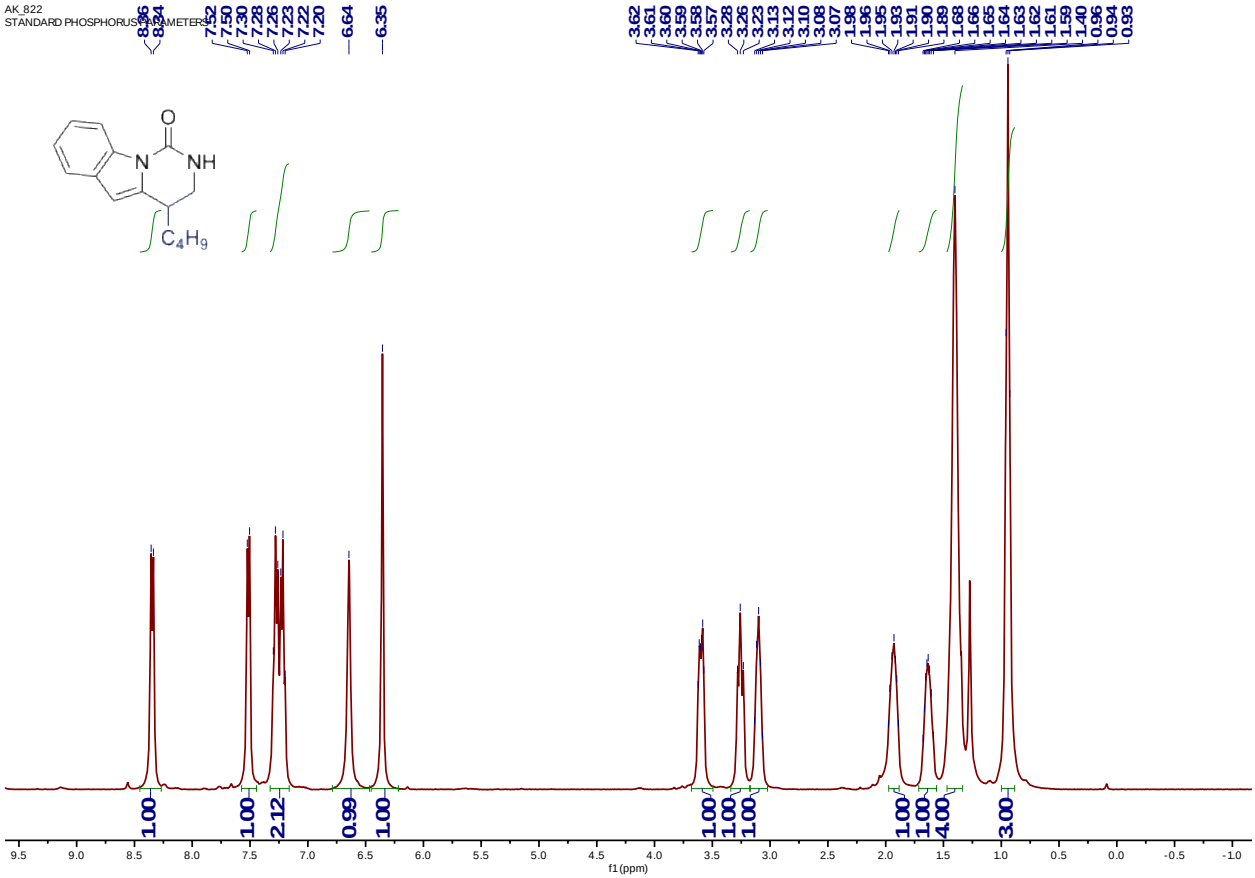
^{13}C spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CHC$_5$H$_2$)RhI$_2$]$_2$ (**2**OCH(CF$_3$)$_2$-I).



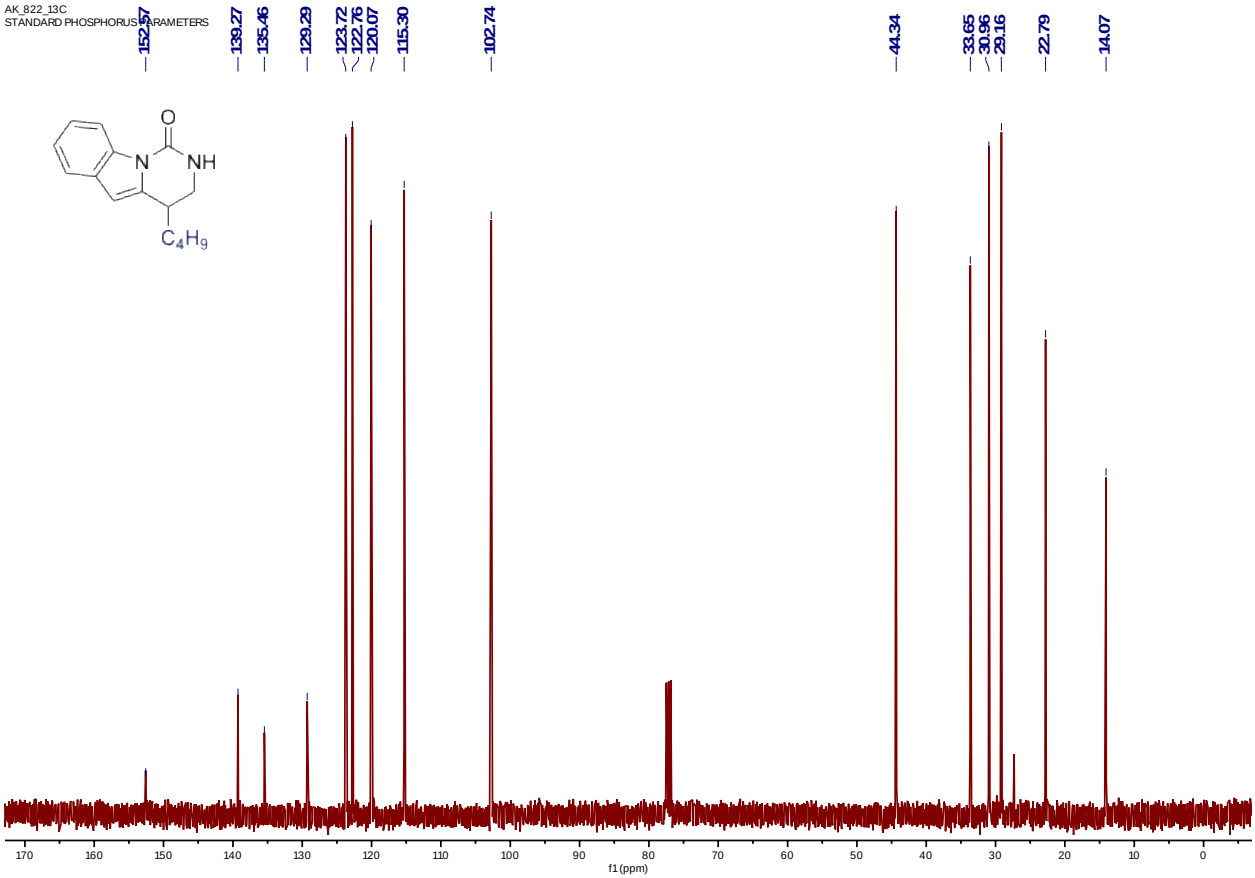
^{19}F spectrum of [(η^5-1,3-^{t}Bu$_2$-4-^{t}Bu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhI$_2$]$_2$ (**2**OCH(CF$_3$)$_2$-I).



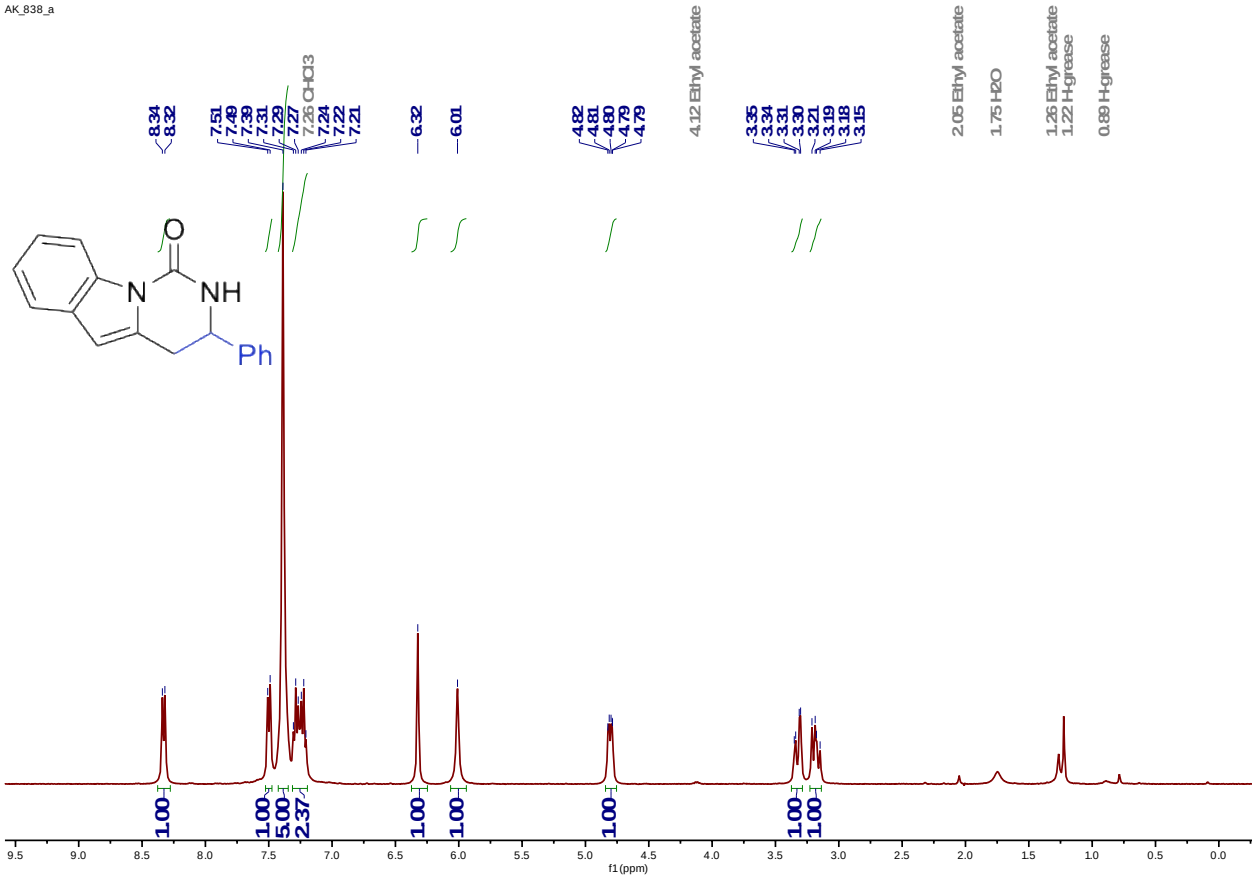
^{1}H spectrum of **12**.



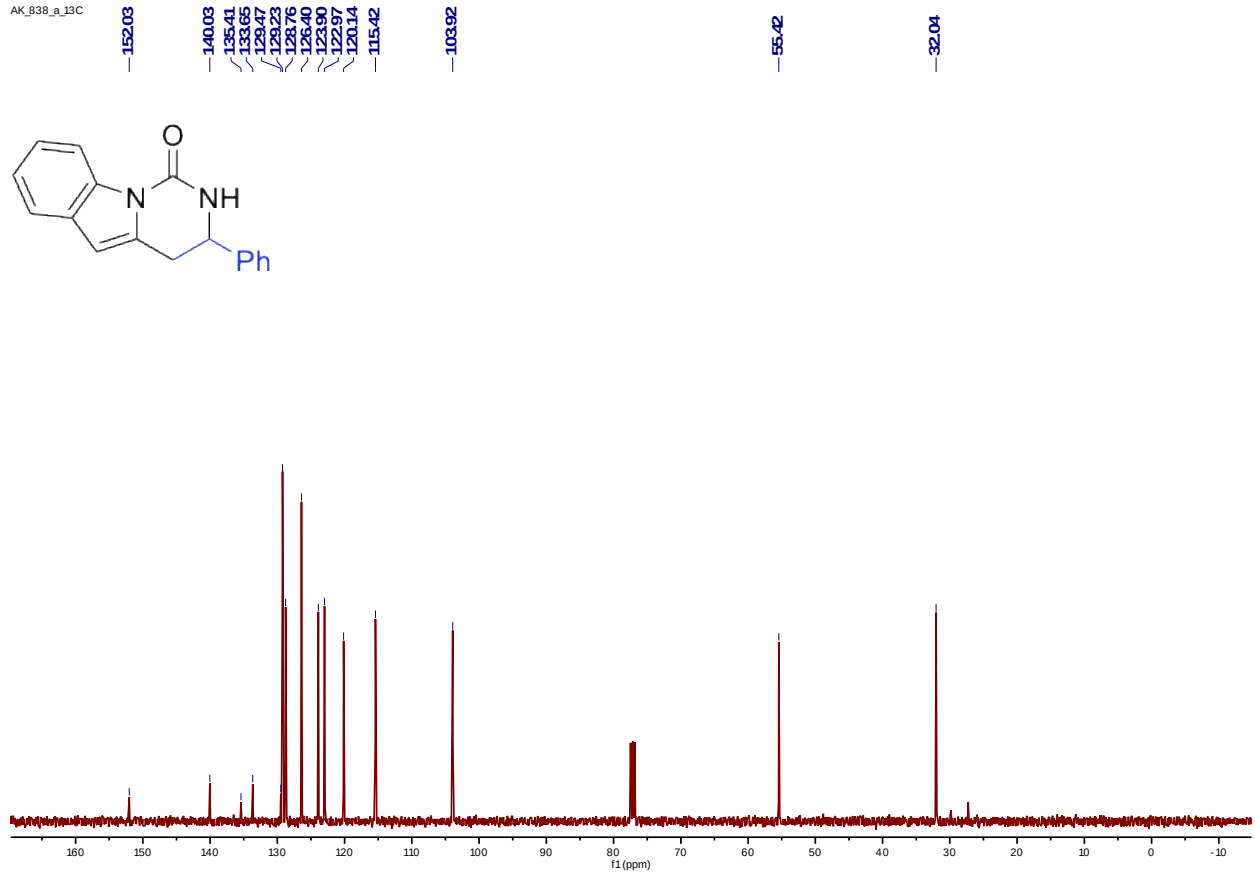
^{13}C spectrum of **12**.



^{1}H spectrum of **15a**.



^{13}C spectrum of **15a**



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