Supplementary Information

Planar chiral arene ruthenium complexes derived from R-carvone

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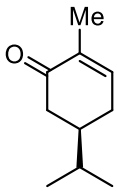
General Information

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. N-methoxy-p-methylbenzamide[1] (**6**), diazo compound[2,3] (**8**), ((*1R*,*2S*,*5R*-2-isopropyl-5-methylcyclohexyl)oxy)-diphenylphosphane (menthoxy-PPh_2),[4] and N-vinylpivalamide[5] were prepared according to the literature procedures. All other reagents were obtained from commercial sources (Macklin, Dalchem, TCI, Vekton) and used without further purification. NMR spectra were measured using Bruker Avance 300 and Varian Inova 400 spectrometers. Chemical shifts (δ) are given in ppm relative to solvent residual signals for $CDCl_3$ (^{1}H: δ = 7.27 ppm; ^{13}C: δ = 77.2 ppm), DMSO-d_6 (^{1}H: δ = 2.50 ppm; ^{13}C: δ = 39.52 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad. Coupling constants (J) are given in Hz. Enantiomeric excess values were measured using Shimadzu HPLC equipped with Daicel Chiralpak IA-3 (4.6 × 150 mm) column and diode array detector, flow rate 1 mL/min was adjusted in all experiments. GS-MS analysis was done using GCMS-QP2020 instrument (Shimadzu, Japan) with column temperature set at 250 °C. High-resolution mass spectra were recorded using LCMS-9030 instrument (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Measurements were carried out in positive ion mode; samples were dissolved in acetonitrile and injected into the mass-spectrometer chamber from an HPLC system LC-40 Nexera (Shimadzu, Japan). The following parameters were used: capillary voltage 4.0 kV; mass scanning range: m/z 150–2000; external calibration with solution NaI in MeOH/H_2O; drying and heating gases (nitrogen) (each 10 L/min); nebulizing gas (nitrogen) (3 L/min); interface temperature: 250 °C; flow rate 95% acetonitrile 0.4 mL/min. Molecular ions in the spectra were analyzed and matched with the appropriately calculated m/z and isotopic profiles in the LabSolutions v.5.114 program.

Synthesis of diene ligands

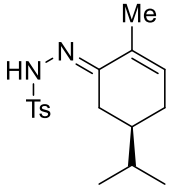
Synthesis of (R)-5-isopropyl-2-methylcyclohex-2-en-1-one (carvotanacetone) (1).



1

The synthesis was conducted following the literature procedure.[6] From 7.7 g (51 mmol) of *R*-carvone 6.5 g (83%) of carvotanacetone (**1**) was obtained after distillation. The compound contained ca. 8% of the double hydrogenation product according to GC/MS and GC/FID. The reaction can be also carried out using heterogeneous catalyst PtO_2.[7] However, we observed larger amounts of the double hydrogenation product in this case. ^{1}H NMR data was in agreement with those reported previously.

Synthesis of (S)-N'-(5-isopropyl-2-methylcyclohex-2-en-1-ylidene)-4-methylbenzene-sulfonohydrazide (2).

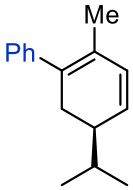


2

The synthesis was performed similar to the literature procedure in air.[8] To a solution of carvotanacetone **1** (6.50 g, 42.7 mmol, 1 equiv.) in MeOH (22 mL), p-toluenesulfonyl hydrazide (8.40 g, 45.1 mmol, 1.06 equiv.) was added in one portion at room temperature and the reaction mixture was brought to reflux with a heatgun. To the resulting hot clear solution, a two drops of concentrated aqueous HCl were added, which started exothermic reaction with spontaneous self-sustaining reflux and precipitate formation. After cooling to room temperature, the reaction mixture was kept at ambient conditions for 24 hours. The precipitate of the product was further purified by crystallization from boiling methanol (additional 110 mL was needed to achieve complete dissolution at

reflux). After filtration of white solid (9.14 g), the mother liquor was evaporated (caution: solution tends to splash at the end of evaporation) and the residue was crystallized again from hot MeOH (40 mL) to give additional 1.48 g of white crystals. Total yield 10.62 g (33.1 mmol, 78 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 2H), 7.69 (br s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.05 (d, J = 6.1 Hz, 1H), 2.64 (dd, J = 15.8, 3.5 Hz, 1H), 2.42 (s, 3H, Me^{Ts}), 2.23 – 2.07 (m, 1H), 1.89 – 1.61 (m, 2H + Me), 1.60 – 1.40 (m, 2H), 0.86 (dd, J = 6.5, 2.0 Hz, 6H, ^{i}Pr). ^{1}H NMR data was in agreement with those reported previously.[9]

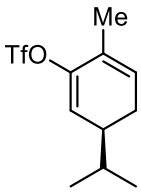


3a

Synthesis of (R)-3-isopropyl-6-methyl-2,3-dihydro-1,1'-biphenyl (3a)

Freshly distillated dioxane (40 ml) was added to a mixture of hydrazone **2** (640 mg, 2.0 mmol, 1 equiv.), XPhos ligand (143 mg, 0.3 mmol, 15 mol%), $Pd_2dba_3{\cdot}CHCl_3$ (124 mg, 0.12 mmol, 6 mol%), ^{t}BuOLi (385 mg, 4.8 mmol, 2.4 eq.) and bromobenzene (315 mg, 2.0 mmol, 1 eq.). The resulting suspension was stirred and refluxed for 24 hours. Dioxane was then evaporated in vacuum, the residue was suspended in hexane and eluted through a short silica gel pad (3 cm). The hexane solution was evaporated to give the crude product as colorless liquid (340 mg, 80%, 85% purity according to GC-MS), which was used without further purification. We could not achieve complete purification even by preparative TLC, due to low polarity of the target diene **3a** and similar polarity of the admixtures.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (t, J = 7.6 Hz, 2H, Ph), 7.25-7.18 (m, 3H, Ph), 5.92 (d, J = 9.7 Hz, 1H), 5.77 (dd, J = 9.7, 3.4 Hz, 1H), 2.42 (m, 2H), 2.25 (m, 1H), 1.80 – 1.70 (m, 1H^{iPr} + Me), 0.93 (m appears as t, 6H, ^{i}Pr). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.3, 131.8, 130.1, 129.4, 128.4, 128.1, 126.7, 126.3, 40.8, 33.1, 31.4, 20.1 (Me^{iPr}), 20.0 (Me^{iPr}), 18.8 (Me). GS-MS: major peaks 210.1 ($C_{16}H_{18}$ = $[M-2H]^+$), 214.2 ($C_{16}H_{22}$ = $[M+2H]^+$) due to disproportionation.

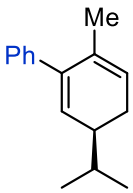


4

Synthesis of (S)-3-isopropyl-6-methylcyclohexa-1,5-dien-1-yl trifluoromethanesulfonate (4).

A solution of carvotanacetone **1** (1.30 g, 8.53 mmol, 1 equiv.) in THF (2 mL) was added to a 50 mL Schlenk flask containing a precooled (−78 °C) solution of LDA (9.38 mmol, 1.1 equiv.) in THF (25 mL). The resulting solution was stirred for 1 hour at -78 °C. Then a solution of $PyNTf_2$ (3.36 g, 9.38 mmol, 1.1 equiv.) in 10 mL of THF was added dropwise. The resulting solution was left to warm up to room temperature overnight. After the indicated time, distilled H_2O (20 mL) was slowly added to the mixture. Then the solution was transferred to a separatory funnel and extracted with Et_2O (3x20 mL) The organic phase was separated, washed with brine (50 mL), dried over anhydrous Na_2SO_4 and evaporated in vacuum. The obtained oil was dissolved in hexane, passed through a small silica gel pad (3 cm). Evaporation produces the desired crude product as colorless liquid (1.80 g, 74%), which was used without further purification.

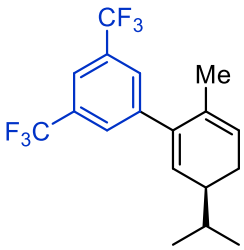
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.69 (s, 1H), 5.64 (s, 1H), 2.38 (m, 1H), 2.25 – 2.13 (m, 2H), 1.80 (s, 3H), 1.75 – 1.66 (m, 1H), 1.10 – 0.74 (m, 6H). ^{1}H NMR data was in agreement with those reported previously.[10]



3b

Synthesis of (S)-3-isopropyl-6-methyl-3,4-dihydro-1,1'-biphenyl (3b). A mixture of dioxane (21 mL) and H_2O (7 mL) was added to a 50 ml Schlenk flask containing solid $PhB(OH)_2$ (643 mg, 5.28 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (123 mg, 0,18 mmol, 5 mol-%), and K_2CO_3 (972 mg, 7.03 mmol, 2 equiv.) The mixture was stirred for 5 min. Then triflate **4** (1.00 g, 3.52 mmol, 1 equiv.) was added and the mixture was heated at 90 °C for 24 hours. After the indicated time the solution was cooled to room temperature and extracted with EtOAc (3x20 mL). The organic phase was separated, washed with brine (50 mL), dried over anhydrous Na_2SO_4 and evaporated in vacuum. The obtained oil was dissolved in hexane and passed through a small pad of silica gel (3 cm). After evaporation of the solvent the crude product was obtained as colorless oil (635 mg, 85 % yield) and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.13 (m, 5H, Ph), 5.72 (br s, 2H), 2.26 – 2.07 (m, 3H), 1.85 – 1.71 (m, 1H), 1.68 (s, 3H, Me), 1.00 – 0.90 (m, 6H, ^{i}Pr). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.9, 140.7, 132.2, 130.0, 128.5, 127.9, 126.6, 123.5, 40.9, 31.2, 26.1, 20.7, 20.3, 20.2. GS-MS: major peaks 210.1 ($C_{16}H_{18}$ = $[M-2H]^+$), 214.2 ($C_{16}H_{22}$ = $[M+2H]^+$), due to disproportionation.

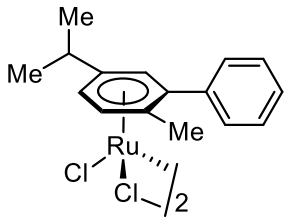


3c

Synthesis of (S)-3-isopropyl-6-methyl-3',5'-bis(trifluoromethyl)-3,4-dihydro-1,1'-biphenyl (3c). A mixture of dioxane (21 mL) and H_2O (7 mL) was added to a 50 ml Schlenk flask containing $ArB(OH)_2$ (1.36 g, 5.28 mmol, 1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (123 mg, 0,18 mmol, 5 mol-%), and K_2CO_3 (972 mg, 7.03 mmol, 2 equiv.) The mixture was stirred for 5 min. Then triflate **4** (1.00 g, 3.52 mmol, 1 equiv.) was added and the mixture was heated at 90 °C for 24 hours. After the indicated time the solution was cooled to room temperature and extracted with EtOAc (3x20 mL). The organic phase was separated, washed with brine (50 mL), dried over anhydrous Na_2SO_4 and evaporated in vacuum. The obtained oil was dissolved in hexane and passed through a small pad of silica gel (3 cm). After evaporation of the solvent the crude product was obtained as colorless oil (1.13 g, 92 % yield) and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (s, 1H), 7.63 (s, 2H), 5.77 (br s, 2H), 2.30 – 2.07 (m, 3H), 1.90 – 1.70 (m, 1H), 1.62 (s, 3H, Me), 1.00 – 0.90 (m, 6H, ^{i}Pr). ^{19}F NMR (282 MHz, $CDCl_3$): δ = −62.88 (s). ^{13}C NMR spectrum was complicated because of ^{13}C-^{19}F spin-coupling as well as presence of several admixtures (purity of **3c** is ca. 85% according to GC-MS). GS-MS: major peaks 305.1 ($C_{15}H_{11}F_6$ = $[M-^iPr]^+$), 348.1 ($C_{18}H_{18}F_6$ = $[M]^+$), 348.1 ($C_{18}H_{18}F_6$ = $[M]^+$), 350.1 ($C_{18}H_{20}F_6$ = $[M+2H]^+$).

Synthesis of ruthenium complexes



5a

Synthesis of ruthenium complex (5a). $RuCl_3 \cdot xH_2O$ (60 mg, 0.27 mmol, 1 equiv.) was added to a Schlenk flask containing aqueous EtOH (1 mL). Then diene **3a** or **3b** (350 mg, 1.62 mmol, 6 equiv.) was added to it and the resulting solution was refluxed for 3 hours. After cooling to room temperature the brown solution was evaporated in vacuo and the obtained residue was dissolved in chloroform (1 mL). The resulting solution was passed through a small pad of celite, additionally washed with chloroform and then the solvent was evaporated. The brownish solid residue was dissolved in the minimum amount of chloroform (~ 0.5 mL) and diethyl ether (~ 3 mL) was added to it until precipitation began. The resulting suspension was centrifuged and the red solution was decanted from solid by-products. Then hexane (~ 5 mL) was added to the red solution to give the precipitate of the product, which was filtered, washed with hexane (10 mL) and dried in vacuum. The complex was obtained as orange powder (71 mg, 71 % yield, ~ 90 % ee). To increase the enantiomeric purity, the product was dissolved in the minimum amount of DCE and crystallized by slow diffusion of hexane vapors into the solution to give orange microcrystals (34 mg, 34 % yield, ≥ 95 % ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.60 (m, 2H, Ph), 7.46 – 7.33 (m, 3H, Ph), 5.73 (d, J = 5.7 Hz, 1H, coord. arene), 5.63 (d, J = 5.7 Hz, 1H, coord. arene), 5.56 (s, 1H, coord. arene), 3.01 (hept, J = 6.9 Hz, 1H, CH^{iPr}), 2.07 (s, 3H, Me), 1.33 (d, J = 6.9 Hz, 3H, CH_3^{iPr}), 1.27 (d, J = 6.9 Hz, 3H, $zCfH_3^{iPr}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 134.4 (Ph), 130.5 (Ph), 128.7 (Ph), 128.6 (Ph), 98.3, 97.6, 92.8, 86.5, 82.8, 80.6, 30.6, 23.2, 21.9, 19.1. HRMS (ESI): Exact mass calculated for $C_{32}H_{36}Cl_3Ru_2^+$ = $[M-Cl]^+$ 728.9964, found 728.9979; calculated for $C_{18}H_{21}ClNRu^+$ = $[monomer-Cl+MeCN]^+$ 388.0401, found: 388.0408. Characteristic patterns due to isotopes of ruthenium and chlorine were observed.

To assess the optical purity of the obtained complex, stock solution of menthoxy-PPh_2 (2.0 mg, 0.006 mmol, 1.1 equiv.) was added to the solution of **5a** (0.005 mmol, 1 equiv.) in $CDCl_3$ (600 µL), which led to the formation of the mixture of two diastereomeric adducts. ^{1}H NMR spectrum of this mixture was recorded, and the enantiomeric purity was assessed via the integration of signals of the arene ligand protons (Figure S1). ^{31}P NMR signals coincided for both diastereomers.

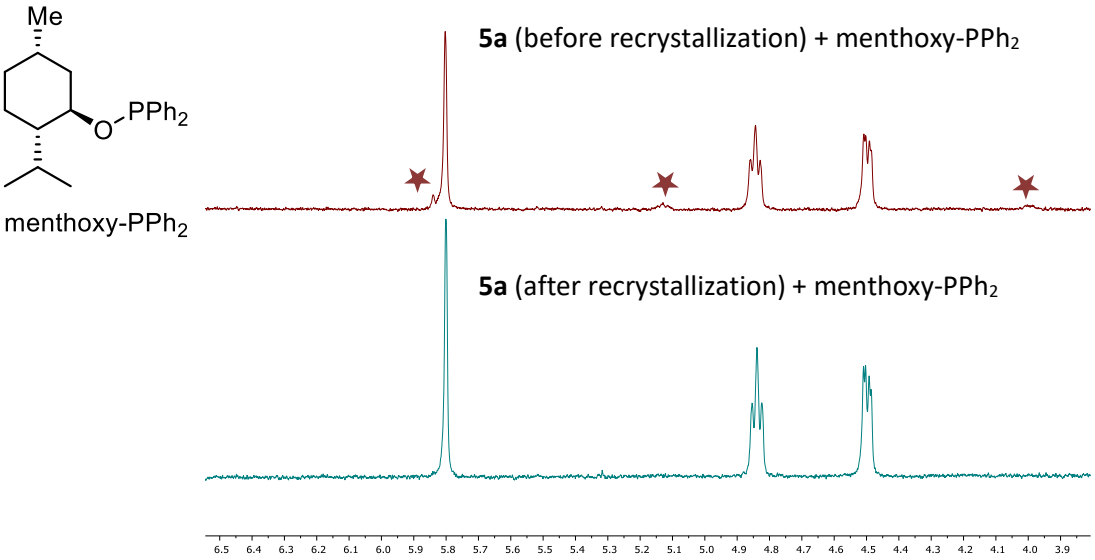
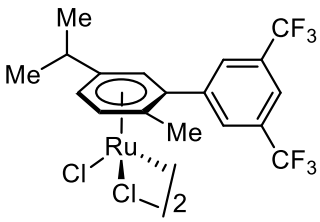


Figure S1. Fragments of ^{1}H NMR spectra of diastereomeric adducts of **5a** with menthoxy-PPh_2. Signals from the minor diastereomer are marked with asterisks.



5b

Synthesis of ruthenium complex (4b). $RuCl_3 \cdot xH_2O$ (50 mg, 0.22 mmol, 1 equiv.) was added to a Schlenk flask containing aqueous EtOH (1 mL). Then diene **3c** (467 mg, 1.34 mmol, 6 equiv.) was added and the resulting solution was refluxed for 3 hours. After cooling to room temperature the red solution was evaporated in vacuo and the obtained residue was dissolved in chloroform (1 mL). The resulting solution was passed through a small pad of celite, additionally washed with chloroform and then the solvent was evaporated. Red solid residue was dissolved in the minimum amount of chloroform (~ 0.5 mL) and hexane (~ 8 mL) was added. The resulted suspension was cooled at −30° C and left overnight. Orange precipitate formed was filtered, washed with hexane (10 mL) and dried in vacuo. The complex was obtained as orange powder (86 mg, 75 % yield, ~80 % ee). ^{1}H and ^{19}F NMR spectra of the product indicated that in solution complex **4b** exists as a 3:1 mixture of homochiral and heterochiral dimers. To increase the enantiomeric purity, the product was dissolved in the minimum amount of DCE and crystallized by slow diffusion of hexane vapors into the solution. After crystallization the complex was obtained as orange microcrystals (38 mg, 33% yield, ≥ 95 % ee). X-ray quality crystals of **5b** were grown by slow diffusion of hexane vapors into the saturated solution in DCE.

NMR spectra signals of homochiral dimer are provided here. Spectra of the mixture are more sophisticated, see copy of NMR for details. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 2H), 7.90 (s, 1H), 5.83 (d, J = 5.8 Hz, 1H), 5.71 (d, J = 6.0 Hz, 1H), 5.59 (s, 1H), 3.02 (p, J = 6.9 Hz, 1H), 2.02 (s, 3H), 1.33 (d, J = 7.0 Hz, 3H), 1.29 (d, J = 6.9 Hz, 3H).).^{13}C NMR (101 MHz, $CDCl_3$) δ =132.1 (q, J = 32.9 Hz), 131.0, 99.1, 98.1, 89.9, 86.8, 83.6, 81.8, 30.7, 23.1, 21.9, 18.6. Some of the ^{13}C signals were not included in this list due to the difficulty of their assignment. HRMS (ESI): Exact mass calculated for $C_{36}H_{32}Cl_3F_{12}Ru_2^+$ = [M−Cl]$^+$ 1000.9459, found 1000.9480; calculated for $C_{20}H_{19}ClF_6NRu^+$ = [monomer−Cl+MeCN]$^+$ 524.0148, found: 524.0167. Characteristic patterns due to isotopes of ruthenium and chlorine were observed.

To assess the optical purity of the obtained complex, stock solution of menthoxy-PPh_2 (2.0 mg, 0.006 mmol, 1.1 equiv.) was added to the solution of **5b** (0.005 mmol, 1 equiv.) in $CDCl_3$ (600 µL), at which point the mixture of two diastereomeric adducts formed. Then the ^1H NMR spectrum was recorded, and the enantiomeric purity was assessed via the integration of signals of the arene ligand protons (Figure S2). ^{31}P and ^{19}F NMR signals coincided for both diastereomers.

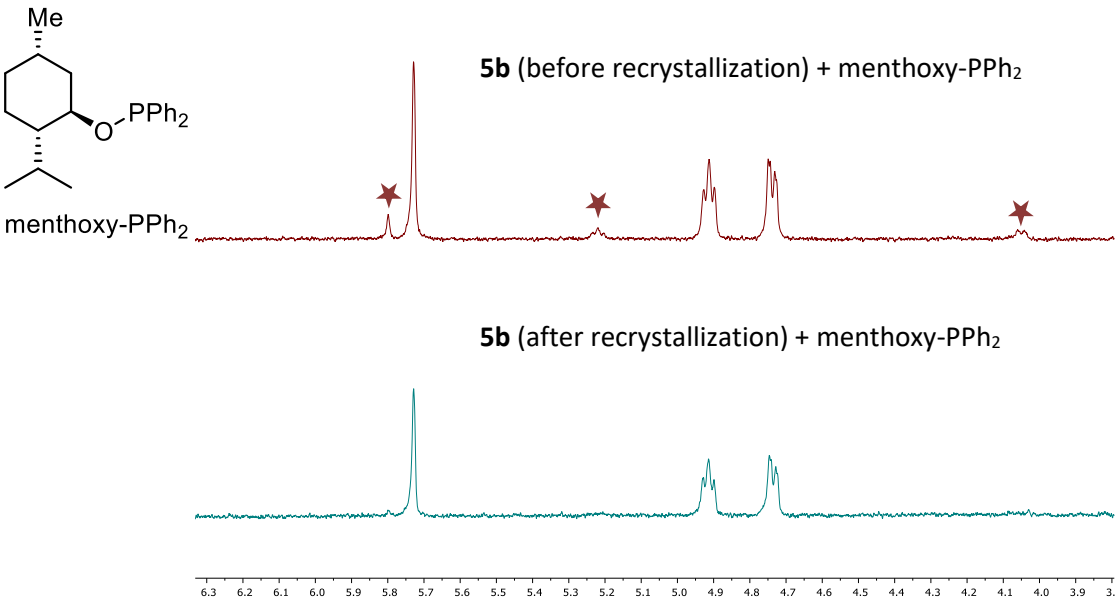
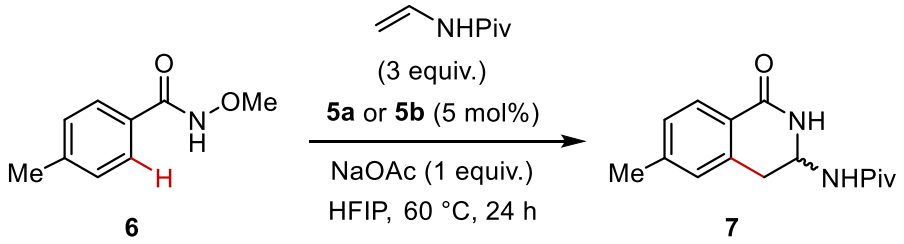


Figure S2. Fragments of ^1H NMR spectra of diastereomeric adducts of complex **5b** with menthoxy-PPh_2. Signals from the minor diastereomer are marked with asterisks.

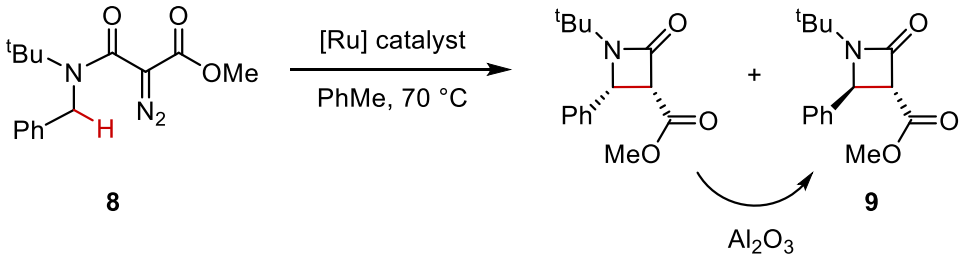
Catalytic reaction of N-methoxy-p-methylbenzamide with N-pivalamide



N-methoxy-p-methylbenzamide (20.0 mg, 0.12 mmol, 1 equiv.), complex (*pR*)-**5a** or (*pR*)-**5b** (4.5 or 6.2 mg, 0.006 mmol, 5 mol-%), NaOAc (10.0 mg, 0.012 mmol, 1 equiv.) and N-pivalamide (40 mg, 0.36 mmol, 3 equiv.) were placed in a 20 x 45 mm vial equipped with a stir bar. HFIP (0.4 mL) was added and the reaction was stirred at 60 °C for 24 h. The mixture was then transferred to a round bottom flask. Silica was added and volatiles were evaporated under reduced pressure. The remaining silica was subjected on the top of short silica gel column and the product was eluted with hexane:EtOAc mixture (1:2). After evaporation of the solvent and drying the product was obtained as white powder. Yield: 22 mg (71%) for **5a**, 24 mg (77%) for **5b**.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.06 (d, J = 6.9 Hz, 1H), 8.27 (s, 1H), 7.85 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.57 – 7.46 (m, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 5.62 (dt, J = 6.9, 4.4 Hz, 1H), 3.21 (dd, J = 16.3, 5.2 Hz, 1H), 3.10 (dd, J = 16.3, 5.2 Hz, 1H), 2.32 (s, 3H). ^{1}H NMR data was in agreement with those reported previously.[11] Enantiomeric ratio: 61:39 (for **5a**) or 74:26 (for **5b**). HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 ml/min; tr(major) = 14.1 min, tr (minor) = 14.8 min.

General procedure for catalytic carbene insertion



In air, ruthenium catalyst was added to a solution of the diazo compound **8** (29 mg, 0.1 mmol) in toluene (10 mL). The resulting mixture was heated in a closed vessel at 70 °C. Then the solvent was evaporated and the crude mixture was analyzed by ^{1}H NMR to determine the ratio of cis- and trans-isomers of **9**. Then the crude product was purified by flash column chromatography on silica gel with hexane/EtOAc mixtures as eluent. The compound obtained was dissolved in EtOAc, filtered through a neutral alumina pad (~2 cm) to induce complete epimerization into trans-isomer, and evaporated to give pure **9**. In the case of the catalyst **5a**, the yield of **9** was 25 mg (96%). The obtained compound was then analyzed by chiral HPLC to determine the ratio of enantiomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.30 (m, 5H, Ph), 4.86 (d, J = 2.3 Hz, 1H), 3.78 (s, 3H, OMe), 3.72 (d, J = 2.3 Hz, 1H), 1.27 (s, 9H, ^{t}Bu). ^{1}H NMR data was in agreement with those reported previously.[2] HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 95:5, 1.0 ml/min; tr(minor) = 5.8 min, tr(major) = 6.7 min.

Table S1. Investigation of catalytic carbene insertion.

Catalyst	**Time, h**	**Yield, %**	**Ratio of isomers cis:trans**	***er***
$[(cymene)RuCl_2]_2$, 0.5 mol.%	2	91	> 20:1	NA
$[(^t$Bu-tetraline$)RuCl_2]_2$,[11] 1 mol.%	2	87	10:1	59:41
Complex **5a**, 0.5 mol.%	3	> 95	10:1	58:42
Complex **5b**, 0.5 mol.%	3	> 95	5:1	57:43

X-ray diffraction study

X-ray diffraction data for **5b** were collected at 120 K with a Bruker APEXII Quazar diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Structure was solved using Intrinsic Phasing with the ShelXT structure solution program in Olex2 and then refined with the XL 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 Table S2. CCDC 2378241 contains the supplementary crystallographic data.

Table S2. Crystal data for **5b**.

Empirical formula	$C_{36}H_{32}Cl_4F_{12}Ru_2$	Linear absorption, μ (cm^{-1})	10.81
Formula weight	1036.55	F(000)	2048
T, K	120	$2\theta_{max}$, °	50
Crystal system	Orthorhombic	Reflections measured	9727
Space group	I222	Independent reflections	3591
Z	4	Observed reflections [$I > 2\sigma(I)$]	2133
a, Å	10.894(3)	Parameters	305
b, Å	15.115(4)	R1	0.0699
c, Å	24.808(7)	wR2	0.1509
α, °	90	GOF	1.064
β, °	90	$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e $Å^{-3}$)	0.973/-0.732
γ, °	90	Flack parameter	-0.06(5)
V, $Å^3$	4085(2)	Hooft parameter	-0.09(6)
D_{calc} (g cm^{-1})	1.686		

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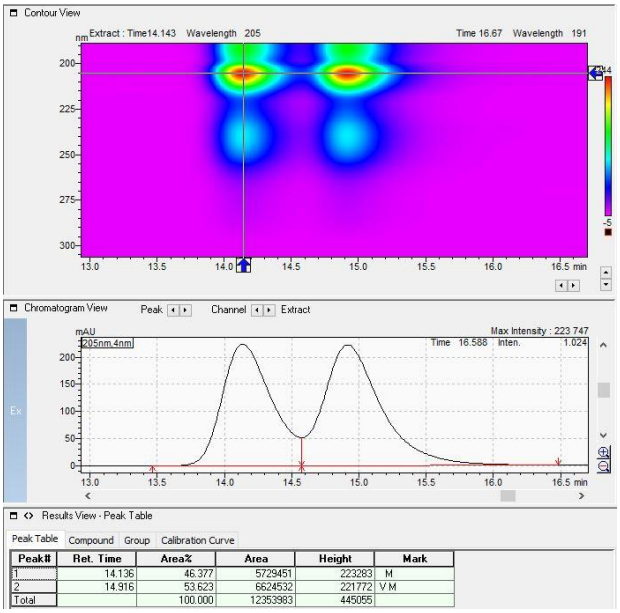
Chiral HPLC data

Figure S3. HPLC chromatogram for racemic (left) and enantioenriched (right) product **7**.



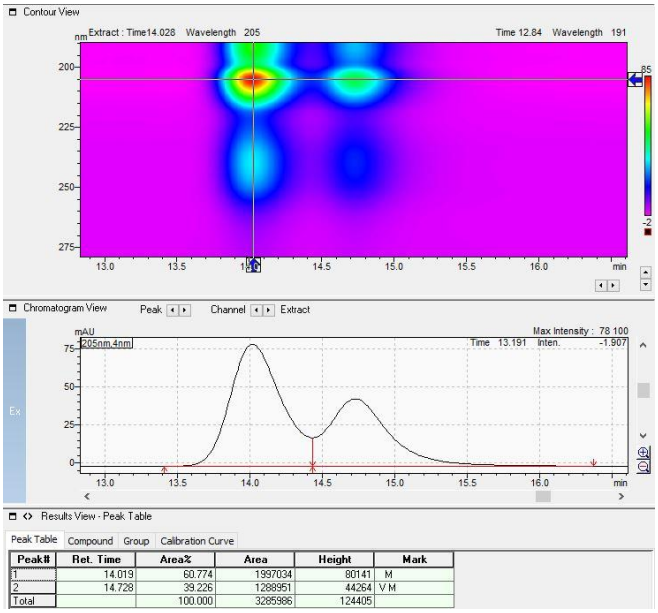
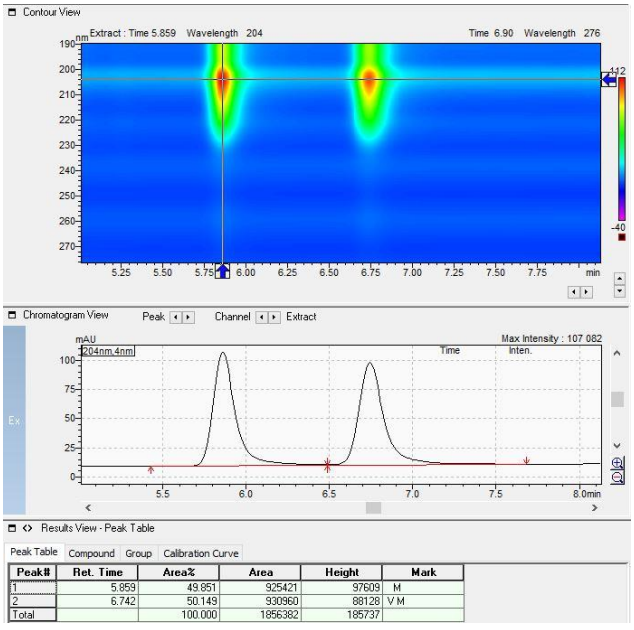
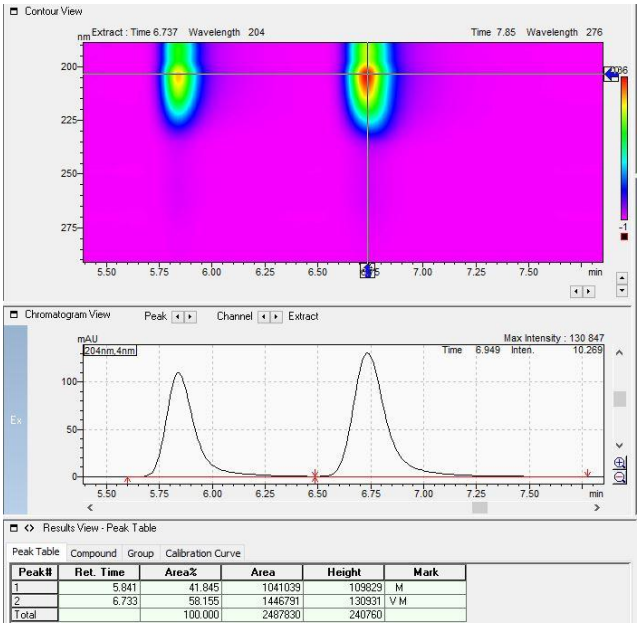


Figure S4. HPLC chromatogram for racemic (left) and enantioenriched (right) product **9**.





Copies of NMR spectra

Figure S5. ^{1}H NMR spectrum of tosyl hydrazone **2** in $CDCl_3$

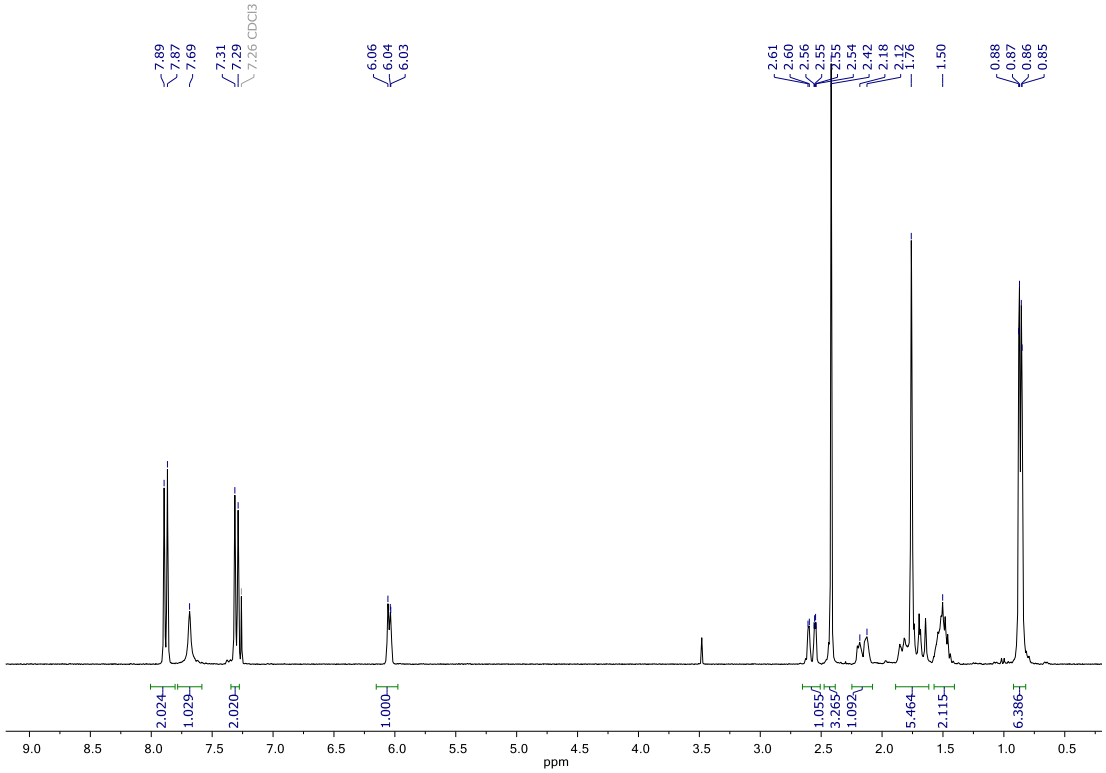


Figure S6. ^{1}H NMR spectrum of diene **3a** in $CDCl_3$ (ca. 85% purity according to GC-MS)

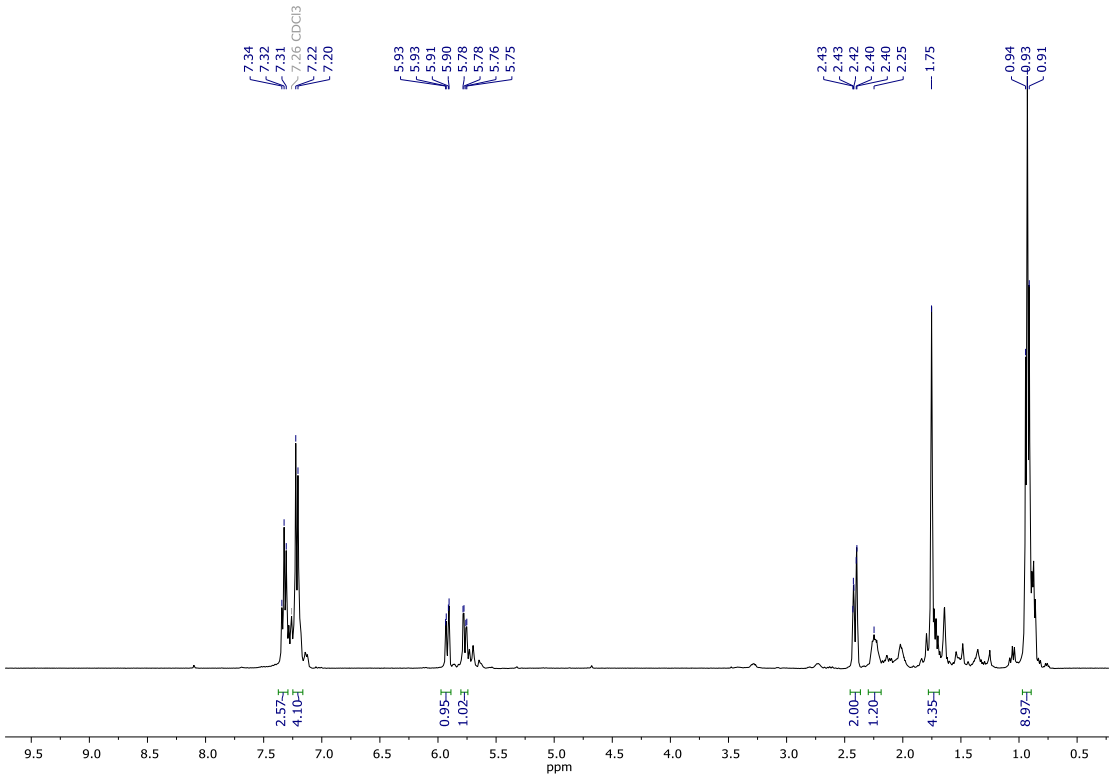


Figure S7. ^{13}C NMR spectrum of diene **3a** in $CDCl_3$ (ca. 85% purity according to GC-MS)

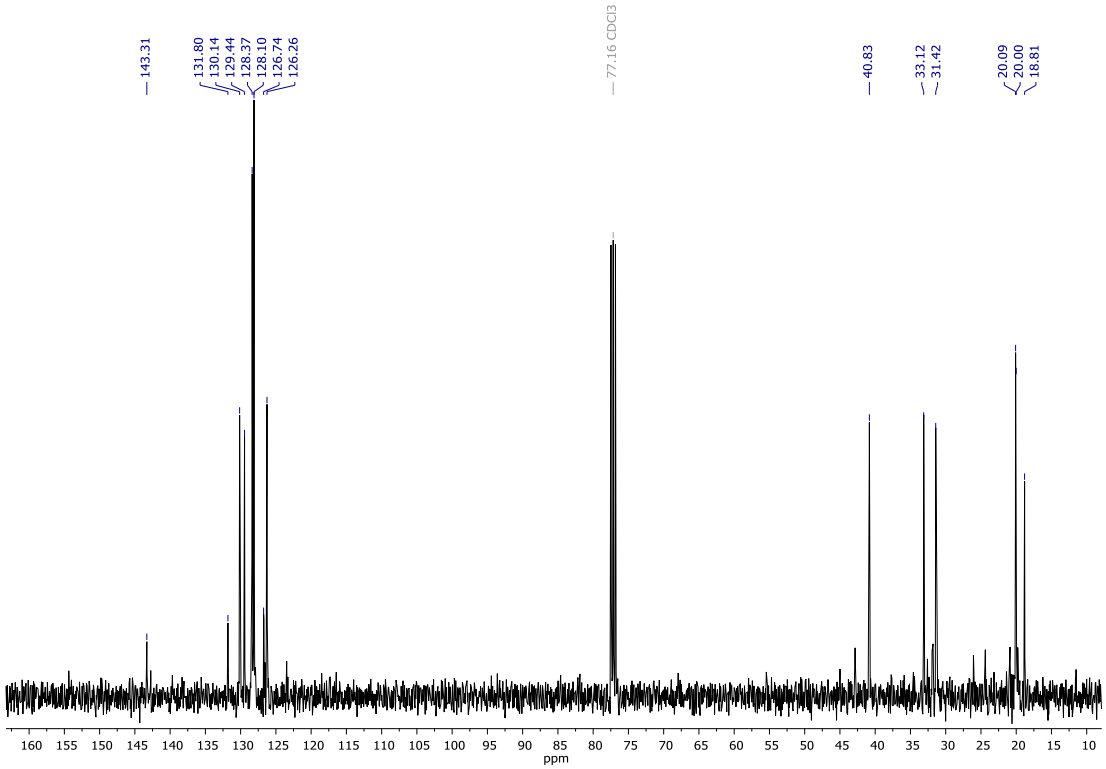


Figure S8. ^{1}H NMR spectrum of triflate **4** in $CDCl_3$

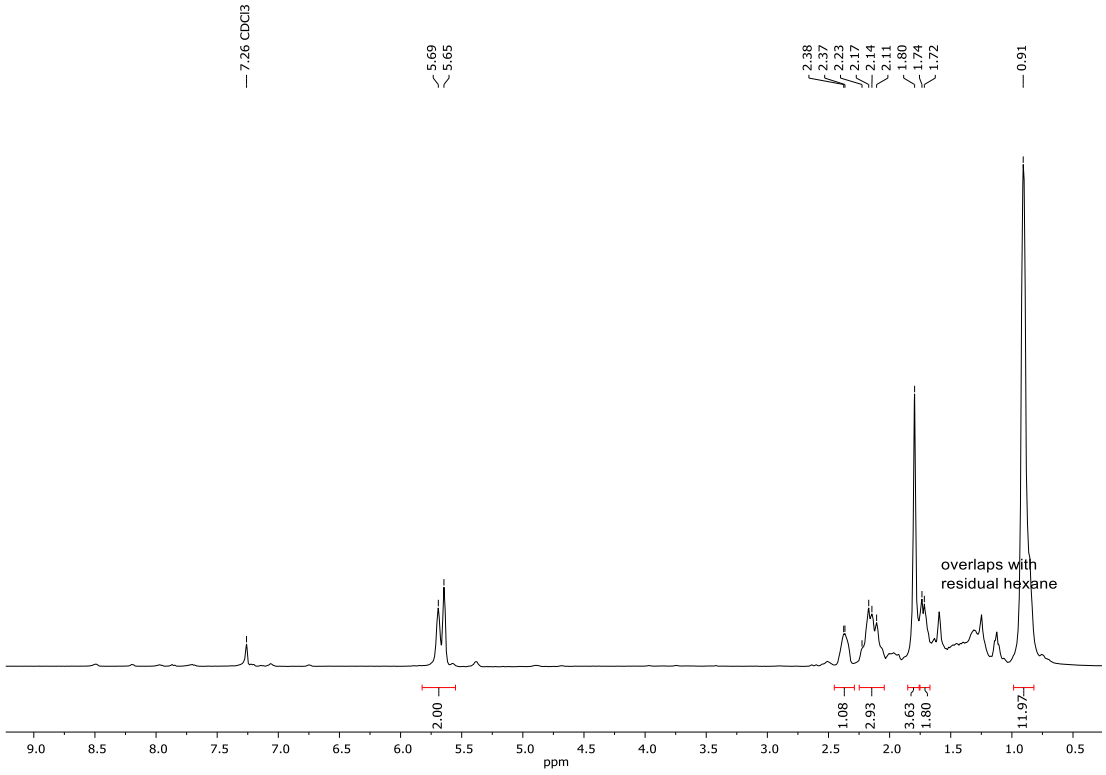


Figure S9. ^{19}F NMR spectrum of triflate **4** in $CDCl_3$

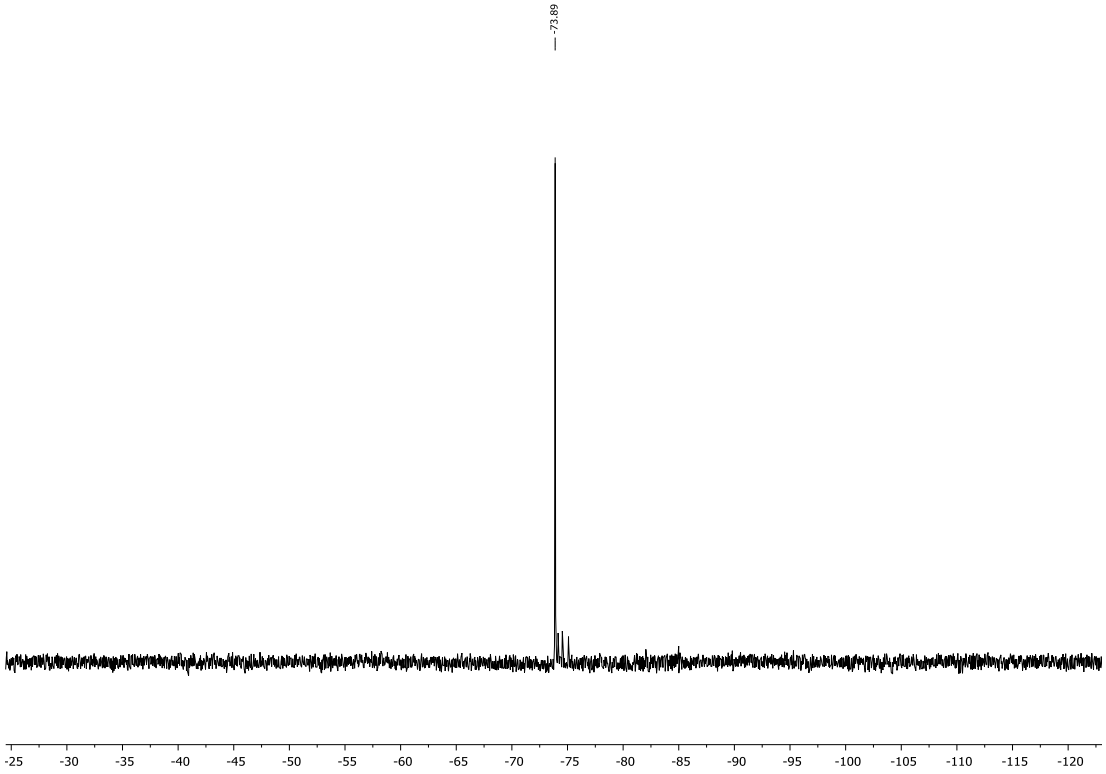


Figure S10. ^{1}H NMR spectrum of diene **3b** in $CDCl_3$ (ca. 85% purity according to GC-MS)

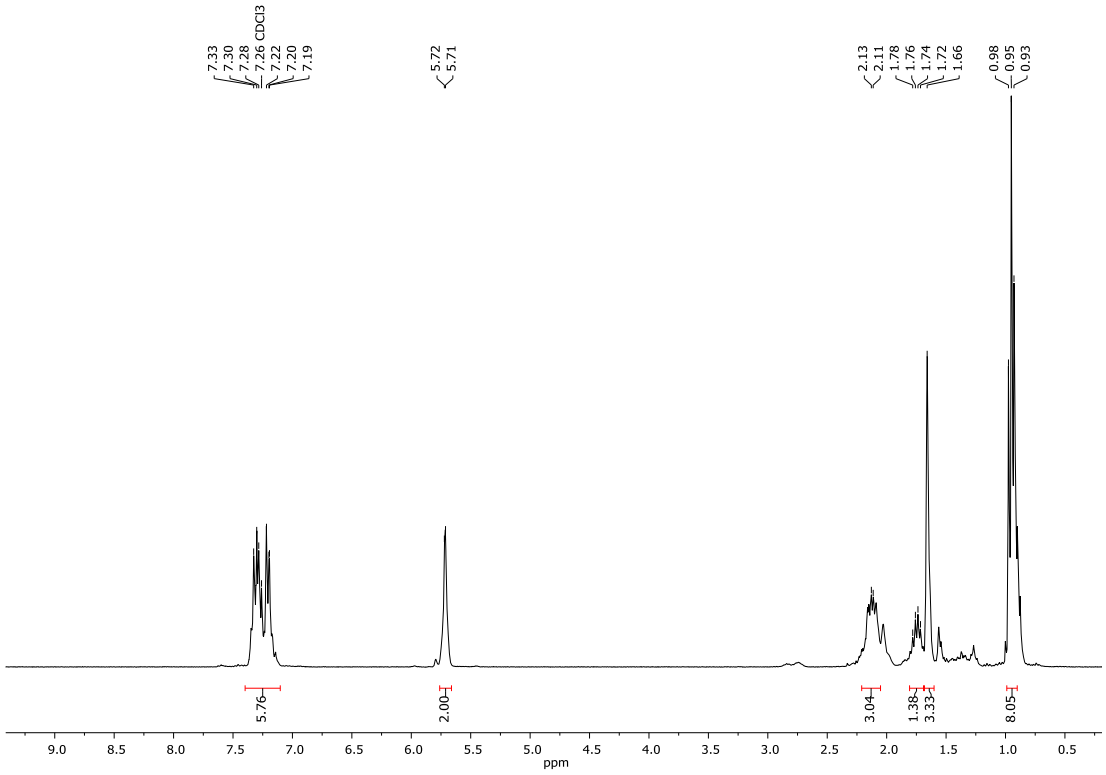


Figure S11. ^{13}C NMR spectrum of diene **3b** in $CDCl_3$ (ca. 85% purity according to GC-MS)

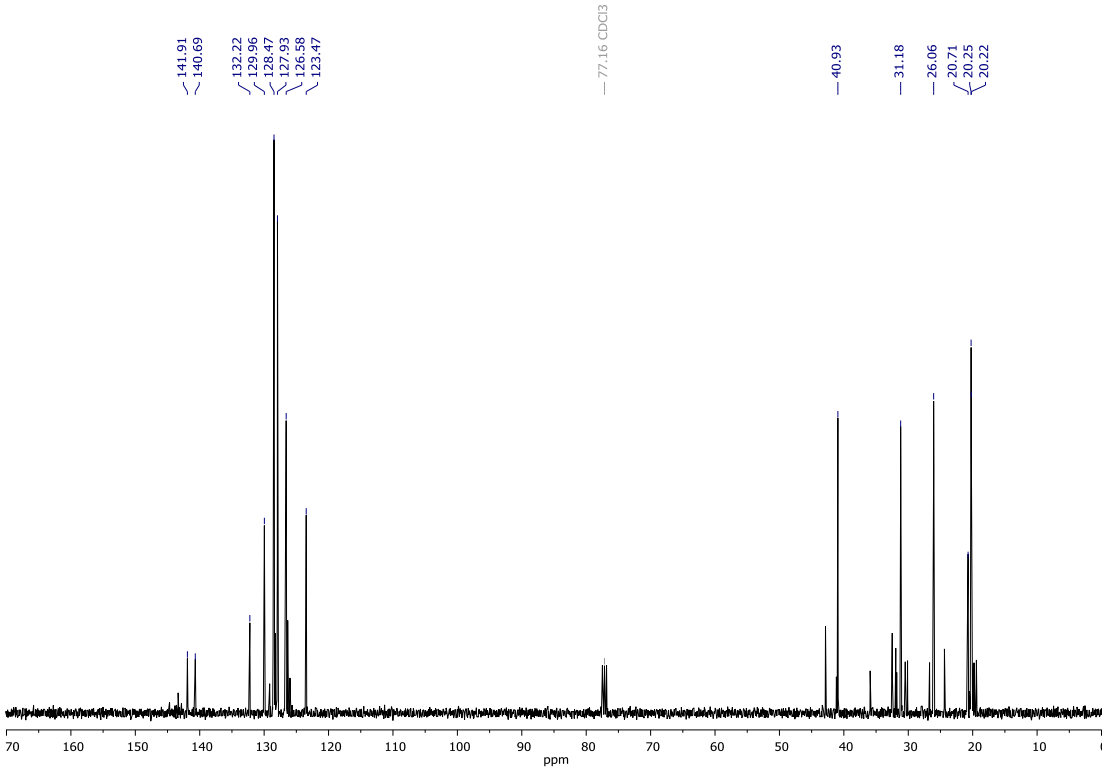


Figure S12. ^{1}H NMR spectrum of diene **3c** in $CDCl_3$ (ca. 85% purity according to GC-MS)

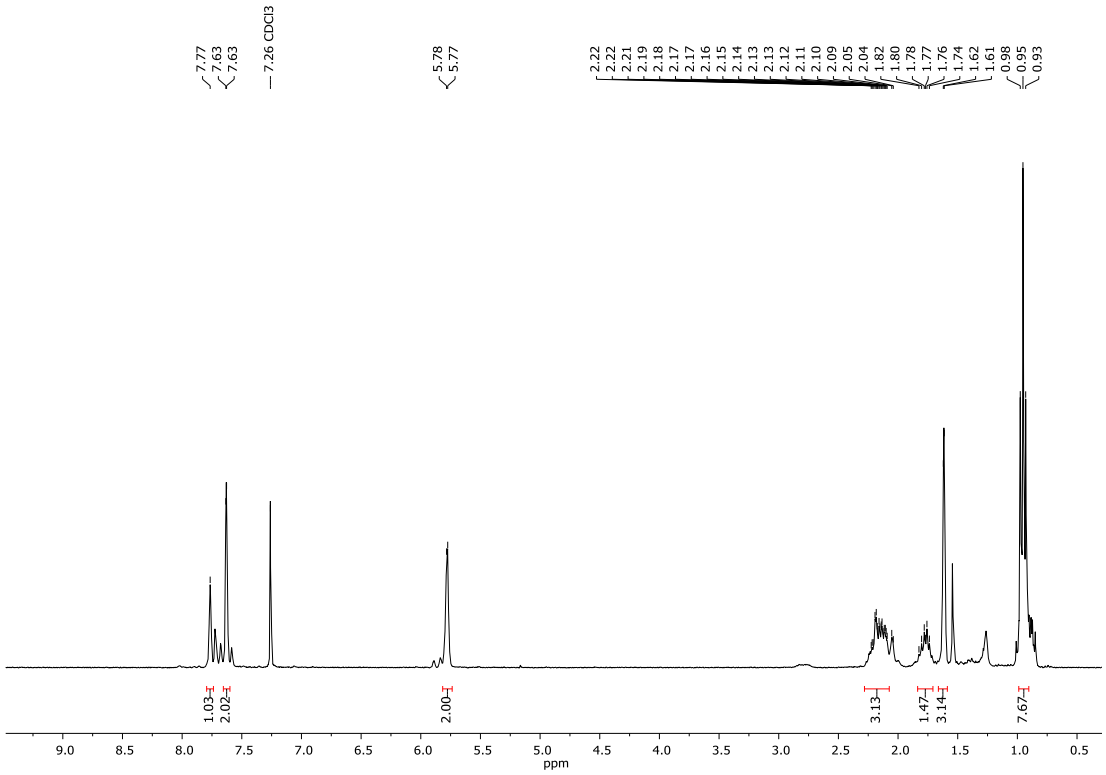


Figure S13. ^{19}F NMR spectrum of diene **3c** in $CDCl_3$

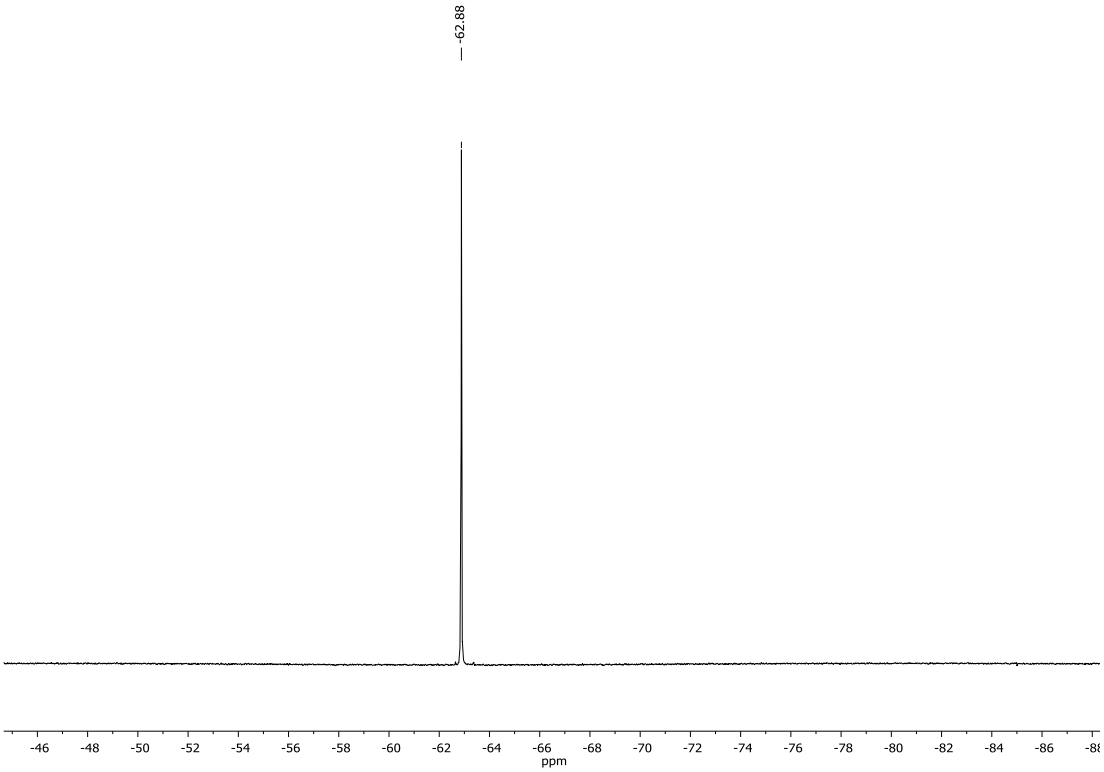


Figure S14. ^{1}H NMR spectrum of ruthenium complex **5a** in $CDCl_3$

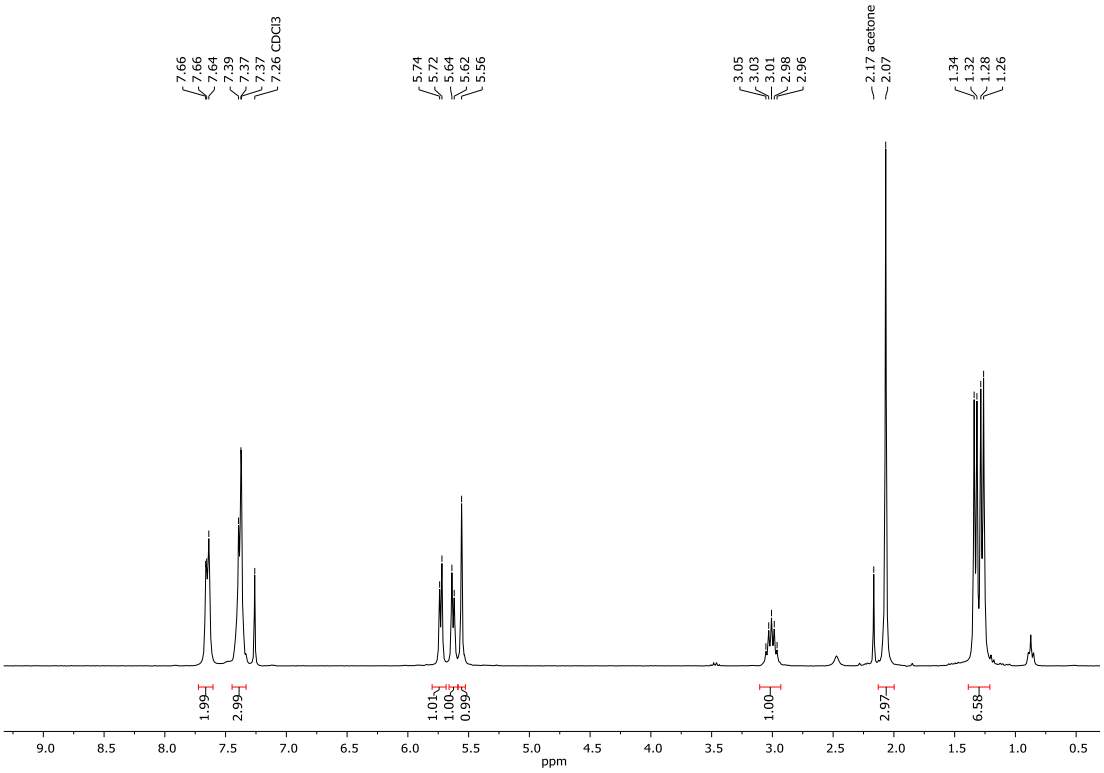


Figure S15. ^{13}C NMR spectrum of ruthenium complex **5a** in $CDCl_3$

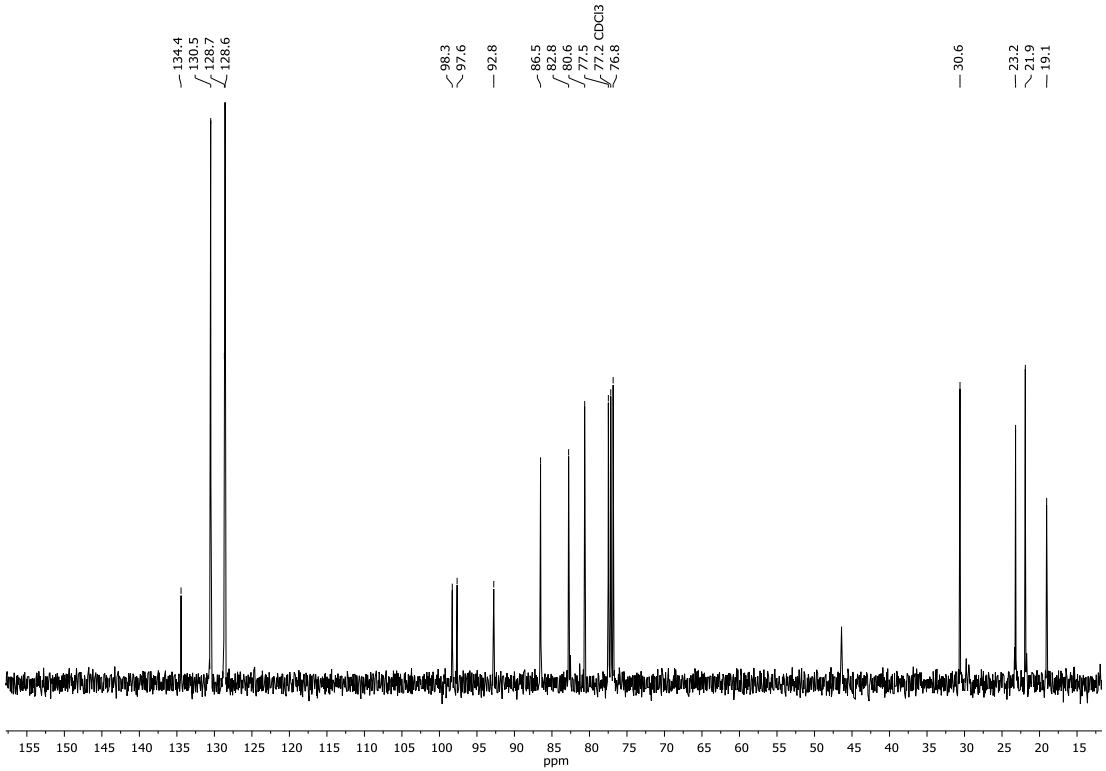


Figure S16. ^{1}H NMR spectrum of ruthenium complex **5b** in $CDCl_3$

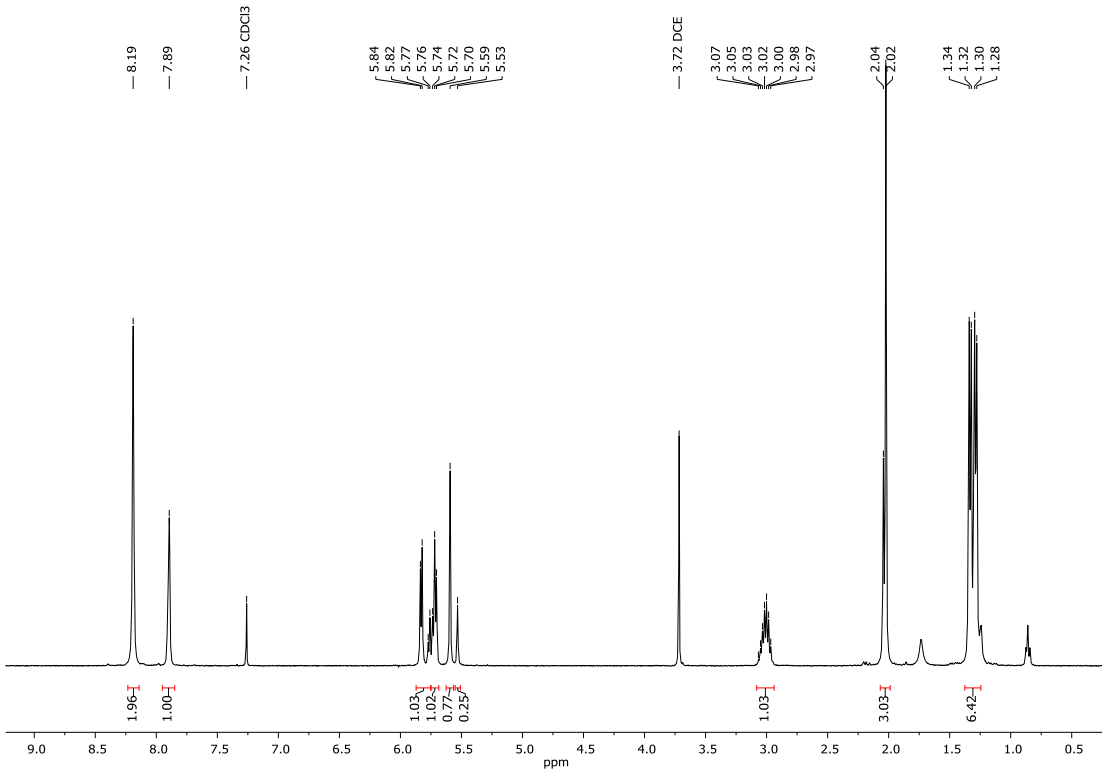


Figure S17. ^{13}C NMR spectrum of ruthenium complex **5b** in $CDCl_3$

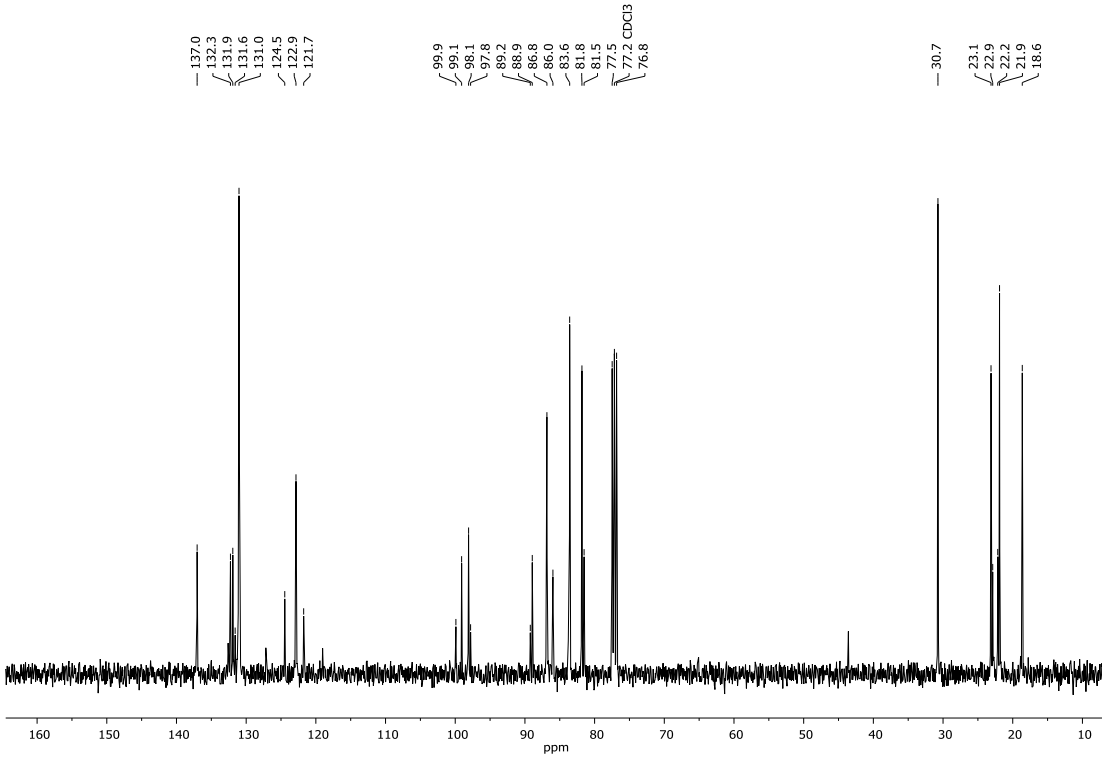


Figure S18. ^{19}F NMR spectrum of ruthenium complex **5b** in $CDCl_3$

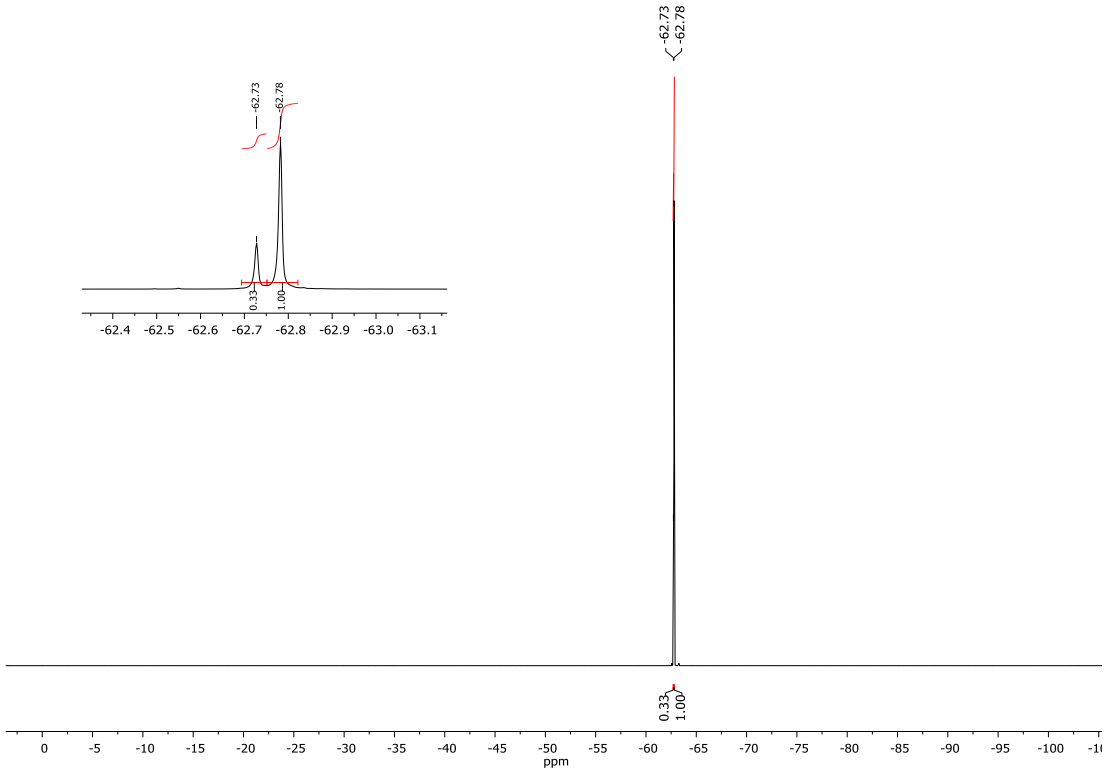


Figure S19. ^{1}H NMR spectrum of complex **5a** in the presence of menthoxy-PPh_2 in $CDCl_3$

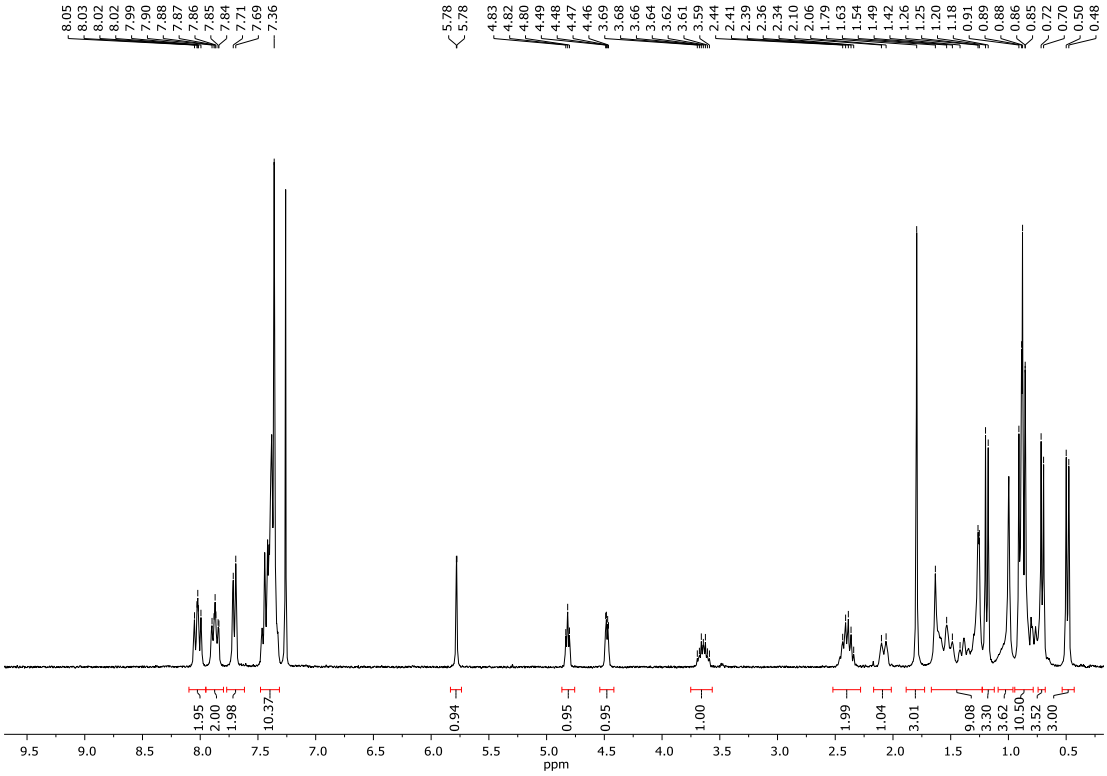


Figure S20. ^{31}P NMR spectrum of complex **5a** in the presence of menthoxy-PPh_2 in $CDCl_3$

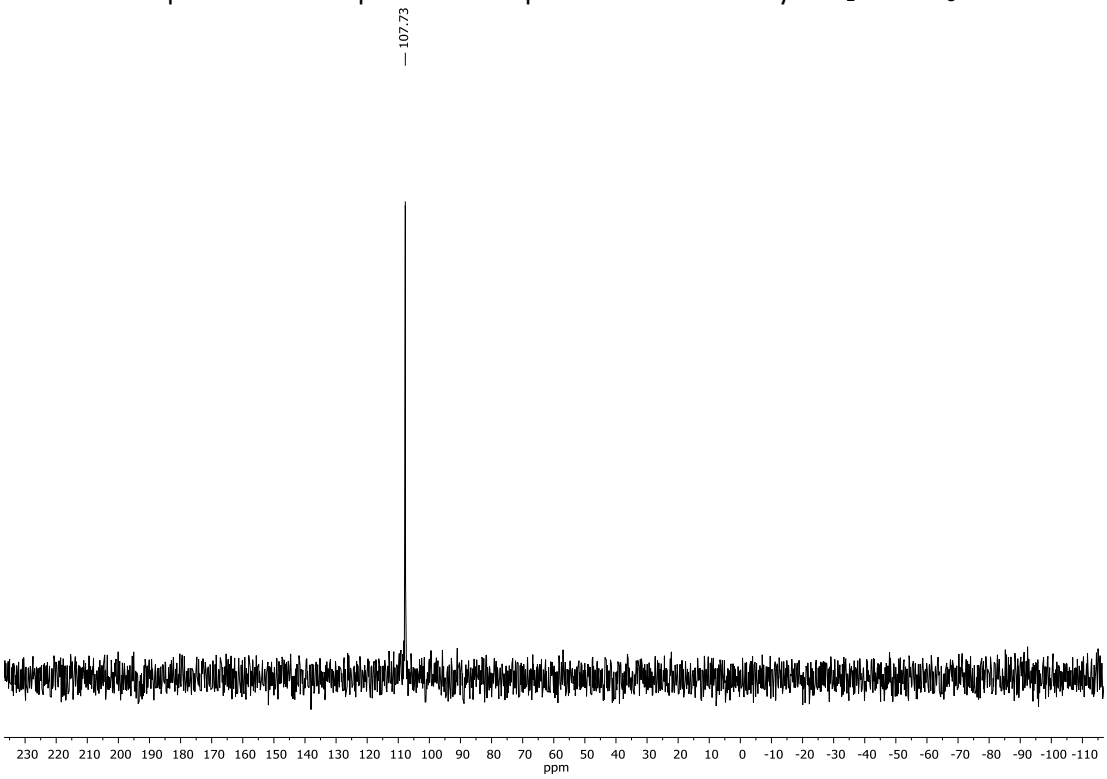


Figure S21. ^{1}H NMR spectrum of complex **5b** in the presence of menthoxy-PPh_2 in $CDCl_3$

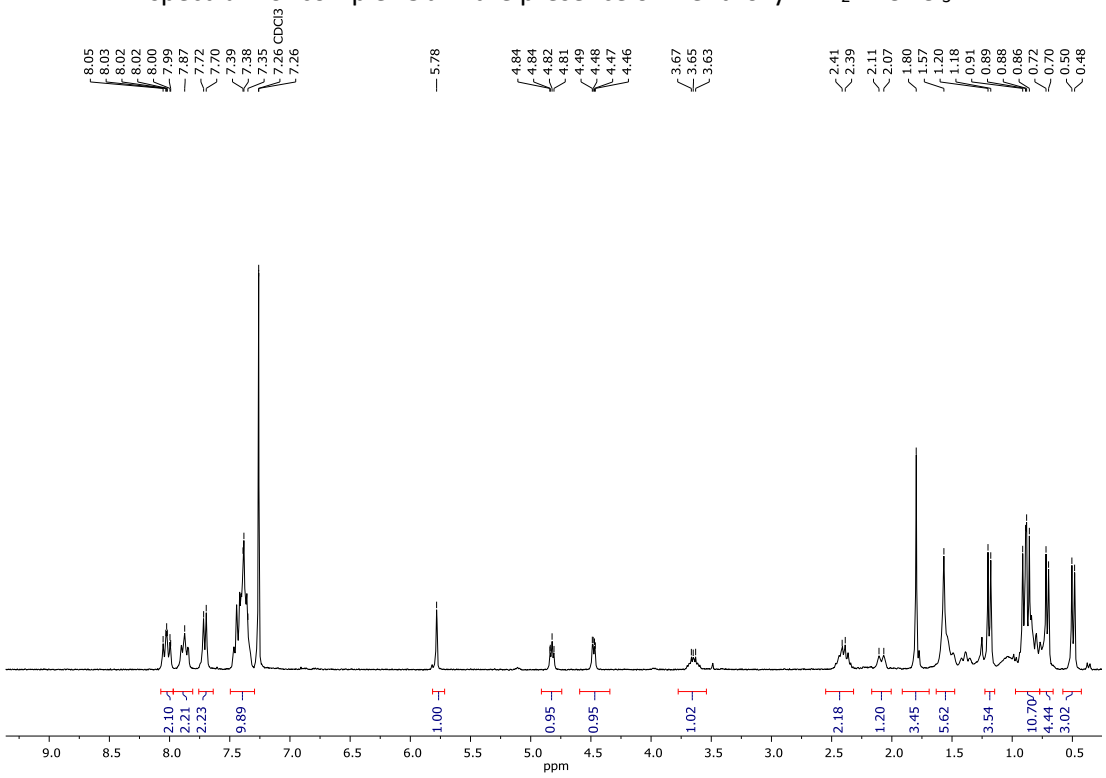


Figure S22. ^{31}P NMR spectrum of complex **5b** in the presence of menthoxy-PPh_2 in $CDCl_3$