

Supporting Information

Alkyne *gem*-Hydrogenation: Formation of Pianostool Ruthenium Carbene Complexes and Analysis of Their Chemical Character

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SUPPORTING CRYSTALLOGRAPHIC INFORMATION

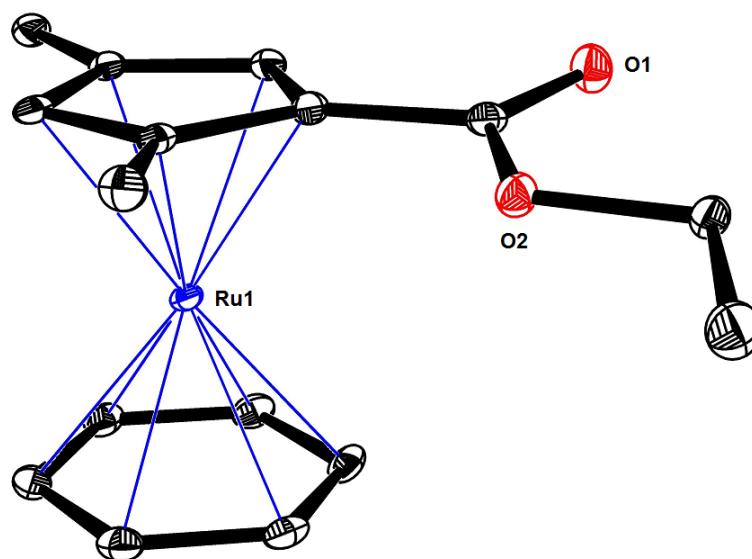


Figure S-1. Structure of complex **S-1** in the solid state; the two PF₆ counterions, one of which is disordered, are not shown for clarity

X-ray Crystal Structure Analysis of Complex S-1: C₁₆ H₁₉ F₆ O₂ P Ru, *Mr* = 489.35 g · mol⁻¹, colorless prism, crystal size 0.13 x 0.05 x 0.04 mm³, triclinic, space group *P*1, *a* = 7.7747(8) Å, *b* = 8.1607(7) Å, *c* = 15.2722(12) Å, α = 94.053(6)°, β = 92.142(5)°, γ = 115.932(6)°, *V* = 866.71(14) Å³, *T* = 100(2) K, *Z* = 2, *D*_{calc} = 1.875 g · cm⁻³, λ = 0.71073 Å, μ (*Mo*-*K*α) = 1.066 mm⁻¹, Gaussian absorption correction (*T*_{min} = 0.89, *T*_{max} = 0.96), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.682 < Θ < 33.128°, 22739 measured reflections, 6550 independent reflections, 5645 reflections with *I* > 2σ(*I*), *R*_{int} = 0.060. The structure was solved by direct methods and refined by full-matrix least-squares against *F*² to *R*₁ = 0.047 [*I* > 2σ(*I*)], *wR*₂ = 0.121, 253 parameters. The H atoms were refined using a riding model, *S* = 1.060, residual electron density 2.14 (0.78 Å from Ru1)/ -2.95 (0.70 Å from Ru1) e · Å⁻³. **CCDC-1905670.**

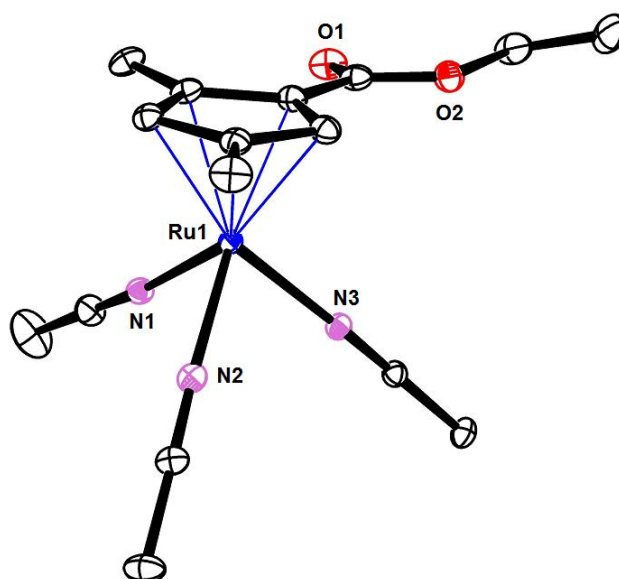


Figure S-2. Structure of complex **7** in the solid state; the disordered PF₆ counterion is now shown for clarity

X-ray Crystal Structure Analysis of Complex 7: C₁₆ H₂₂ F₆ N₃ O₂ P Ru, $M_r = 534.40 \text{ g} \cdot \text{mol}^{-1}$, yellow plate, crystal size 0.15 x 0.10 x 0.06 mm³, orthorhombic, space group $P2_12_12_1$, $a = 11.1167(11) \text{ \AA}$, $b = 12.537(2) \text{ \AA}$, $c = 15.2127(15) \text{ \AA}$, $V = 2120.2(5) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{\text{calc}} = 1.674 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.883 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\text{min}} = 0.72$, $T_{\text{max}} = 1.00$), Bruker AXS Enraf-Nonius KappaCCD diffractometer, $3.133 < \Theta < 33.016^\circ$, 46430 measured reflections, 7985 independent reflections, 7549 reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.069$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.042$ [$I > 2\sigma(I)$], $wR_2 = 0.109$, 280 parameters. The H atoms were refined using a riding model, $S = 1.070$, absolute structure parameter = 0.036(16), residual electron density 1.1 (0.60 \AA from F6A)/ -1.9 (0.74 \AA from Ru1) $\text{e} \cdot \text{\AA}^{-3}$. **CCDC-1905669**.

General. All reactions were carried out under argon in flame-dried glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored and handled under argon: CH₂Cl₂ (CaH₂), MeCN (CaH₂), pentane (Na/K alloy), THF (Na/K alloy). NMR spectra were recorded on Bruker AV400 or AV500 spectrometers at 298 K unless otherwise indicated; chemical shift (δ) given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD₂Cl₂: 5.32 ppm (¹H), 53.8 ppm (¹³C); [D₃]-MeCN: 1.94 ppm (¹H), 118.26 ppm (¹³C); [D₆]-acetone: 2.05 ppm (¹H), 29.8 ppm (¹³C).

PHIP NMR experiments were acquired on an Bruker AVIII 500 MHz (11.7 T) NMR Magnet equipped with a BBFO probe with z-gradient. OPSY spectra were generally acquired using the opsy-d pulse sequence.¹ Typical acquisition parameters were: ¹H offset (ω_{1p}) = -10 ppm, spectral width = 40 ppm, gradient strength = 53.5 g/cm (100%), gradient shape = sine, gp1 = 1 ms, gp2 = 2 ms, gradient recovery delay = 0.2 ms, d1 = 0, fid size = 32.768 data points.

para-Hydrogen enriched to 92% was always freshly generated using a commercially available *pH2 Generator* from *Bruker BioSpin GmbH* with an *F-DGSI* electrolytic hydrogen generator (WM.H2.500.V3) as the hydrogen source.

IR spectra were recorded on Alpha Platinum ATR (Bruker) at room temperature, wavenumbers ($\tilde{\nu}$) are given in cm⁻¹.

Mass spectrometric samples were measured using the following instruments: MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Bruker ESQ3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

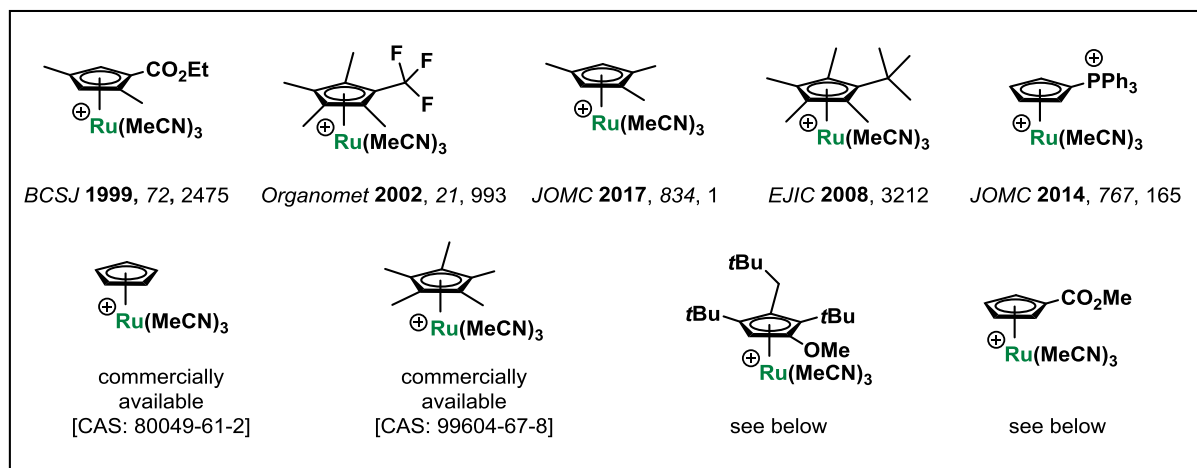
GC-MS was measured on a Shimadzu GCMS-QP2010 Ultra instrument.

Photolysis experiments were performed in a self-made apparatus, consisting of an aluminum box with a circular arrangement of 8 UV-C lamps (Philips Fluorescent lamps TUV PL-S 9W/2P, 100 – 280 nm) at 6 cm distance to the quartz Schlenk tube. The temperature in the apparatus typically rises to 50 °C within 3-4 h.

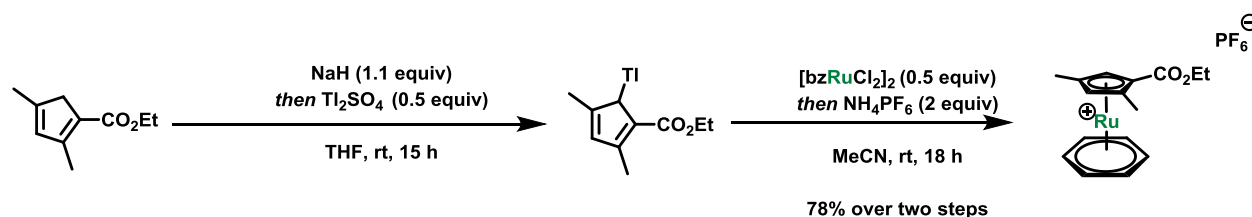
Cyclic voltammetry studies were conducted with a potentiostat SP300 from *BioLogic* in a measuring cell from *BioLogic*. Voltammograms were recorded using solution of the metal complex (0.05 M) and Bu₄NPF₆ (0.2 M) in MeCN (degassed and dried) at sweep rates of ν = 100, 200 and 400 mV/s with a glassy carbon working electrode, a graphite counter electrode and a Ag/AgNO₃ (0.2 M solution of Bu₄NPF₆ in degassed and dried MeCN) pseudoreference electrode. Half-potentials ($E_{1/2}$) were measured relative to the Fc⁺/Fc redox couple.

Catalyst Library

The following complexes were made according to literature,^{2,3,4,5,6} purchased from commercial suppliers, or prepared by the procedures outlined below



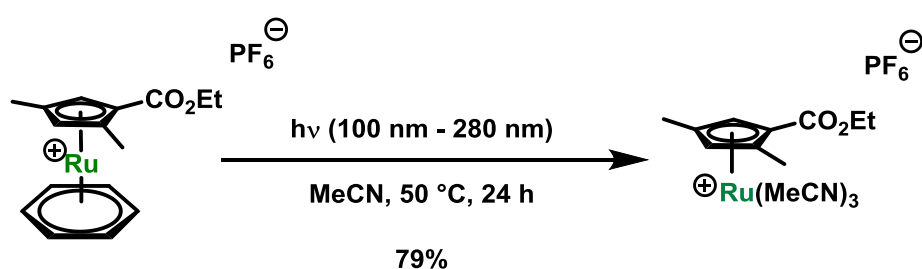
(η^6 -Benzene)(η^5 -1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium Hexafluorophosphate (S-1)



A literature procedure was adapted as follows:⁷ A solution of ethyl-2,4-dimethylcyclopenta-1,3-diene-1-carboxylate (3.32 g, 19.9 mmol, 2 equiv)⁸ in THF (20 mL) was added at 0 °C via canula to a suspension of (oil free) sodium hydride (527 mg, 21.9 mmol, 2.2 equiv) in THF (10 mL). The suspension was stirred for 1 h at room temperature while it gradually turned cherry red. This suspension was then added via canula to a solution of thallium(I) sulfate (5.04 g, 9.98 mmol, 0.5 equiv) in degassed water (150 mL). A pale yellow precipitate crushed out immediately. After stirring overnight at ambient temperature, the precipitate was collected by filtration under argon and was washed with degassed water (30 mL) and THF (5 mL). The remaining solid material (2.88 g, 7.79 mmol, 1 equiv) was thoroughly dried in high vacuum and then suspended in acetonitrile (150 mL) in a Schlenk tube. Solid (benzene)ruthenium dichloride dimer (1.90 g, 3.89 mmol, 0.5 equiv) was added and the suspension was stirred overnight in the dark. The resulting orange suspension was filtered through a pad of Celite and the orange filtrate was concentrated with a rotary evaporator. A solution of ammonium hexafluorophosphate (2.53 g, 15.5 mmol, 2 equiv) in degassed water (120 mL) was added to the red/orange residue causing the precipitation of a pale yellow solid. The suspension was

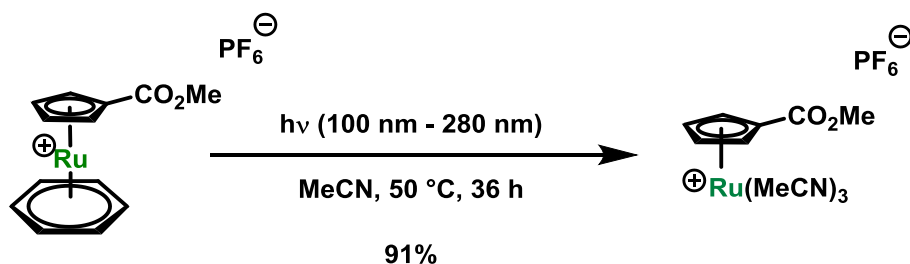
stirred for 30 min at ambient temperature before CH_2Cl_2 (40 mL) was added to dissolve all solid material. The phases were separated, the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL) and the combined organic phases were washed with brine, dried over MgSO_4 and evaporated. The residue was purified by flash chromatography (neutral aluminum oxide, acetone) and the yellow band was collected, yielding a pale yellow solid upon evaporation of the solvent. Recrystallisation of the solid material from ethanol/acetone yielded the title compound as an air-stable, off-white crystalline solid (2.90 g, 78%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 6.05 (s, 6H), 5.74 (d, J = 1.6 Hz, 1H), 5.55 (d, J = 1.6 Hz, 1H), 4.31 (m, 2H), 2.27 (s, 3H), 2.04 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $[\text{D}_6]$ -acetone): δ = 166.3, 101.0, 100.2, 88.9, 86.7, 84.3, 82.6, 62.3, 14.3, 13.6, 13.4. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = -144.4 (hept, J = 706 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ = -72.8 (d, J = 710 Hz). IR (film) = 419, 447, 556, 704, 781, 834, 1240, 1140, 1704 cm^{-1} . HR-MS (ESI+): calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{Ru}$ $[\text{M}]^+$ 345.04255, found: 345.04231.

Tris(acetonitrile)(η^5 -1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium Hexafluorophosphate (7)



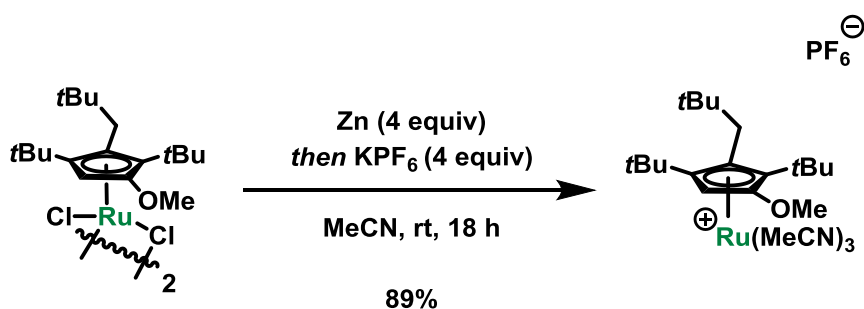
In a quartz Schlenk tube, the ruthenium complex **S-1** (2.30 g, 4.55 mmol, 1 equiv) was dissolved in MeCN (60 mL) and the tube was placed into a photolysis apparatus. The colorless solution was irradiated with UV-C light (100 – 280 nm) for 24 h while slowly turning orange. All volatile materials were removed under vacuum and the remaining orange oil was triturated with pentane (20 mL) and sonicated for 15 min. Solid material was allowed to settle and the supernatant was removed via a filter canula. The remaining orange solid was washed with diethyl ether (10 mL) and pentane (10 mL) and then recrystallized from diethyl ether/acetonitrile to yield the title compound as an air-stable, orange powder (1.93 g, 79%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 4.62 (d, J = 1.5 Hz, 1H), 4.28 – 4.12 (m, 2H), 4.01 (d, J = 1.5 Hz, 1H), 2.40 (s, 9H), 1.96 (s, 3H), 1.75 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 170.4, 125.0, 98.5, 90.1, 72.6, 66.7, 62.2, 60.8, 14.8, 13.1, 12.8, 4.1. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = -144.5 (hept, J = 710.5 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2) δ = -73.2 (d, J = 710.5 Hz). IR (film): 555, 779, 836, 1074, 1216, 1300, 1419, 1709 cm^{-1} . HR-MS (ESI+): calcd. for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}_2\text{Ru}$ $[\text{M}]^+$ 390.07503, found: 390.07500.

Tris(acetonitrile)(η^5 -1-methoxycarbonyl-cyclopentadienyl)ruthenium Hexafluorophosphate (5)



In a quartz Schlenk tube, the ruthenium complex **S-2** (1.13 g, 2.52 mmol, 1 equiv)⁹ was dissolved in MeCN (60 mL) and the tube was placed into a photolysis apparatus. The colorless solution was irradiated with UV-C light (100 – 280 nm) for 36 h, during which time it turned orange. All volatile materials were removed under vacuum and the remaining orange oil was triturated with pentane (20 mL) and sonicated for 15 min. Solid material was allowed to settle and the supernatant was removed via filter canula. The orange residue was washed with diethyl ether (10 mL) and pentane (10 mL) and the dried in vacuo to yield the title compound as an air-stable orange-brown powder (1.13 g, 2.52 mmol, 91%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 5.00 (dd, J = 2.1, 1.6 Hz, 2H), 4.43 (dd, J = 2.1, 1.6 Hz, 2H), 3.76 (s, 3H), 2.40 (s, 9H). ¹³C NMR (101 MHz, CD₂Cl₂): δ = 169.4, 126.2, 77.6, 69.5, 65.1, 52.4, 4.2. ³¹P NMR (162 MHz, CD₂Cl₂): δ = -144.5 (hept, J = 710.5 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂) δ = -73.2 (d, J = 710.5 Hz). IR (film): 486, 509, 556, 771, 836, 1139, 1284, 1468, 1715 cm⁻¹. HR-MS (ESI+): calcd. for C₁₃H₁₆O₂Ru [M]⁺ 348.02809, found: 348.02805.

Tris(acetonitrile)(η^5 -1-methoxy-2-*tert*-butyl-3-neopentyl-4-*tert*-butyl-cyclopentadienyl)ruthenium Hexafluorophosphate (2)

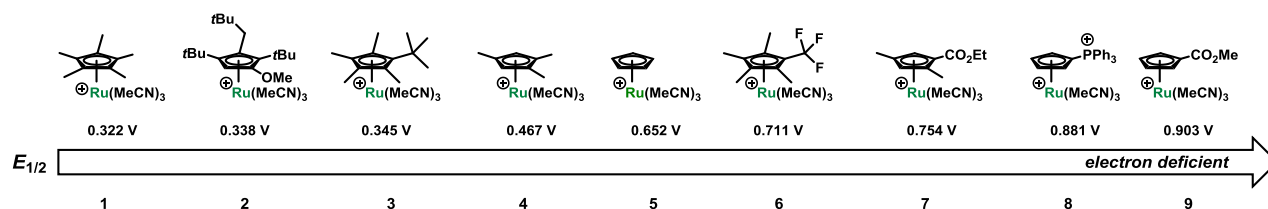


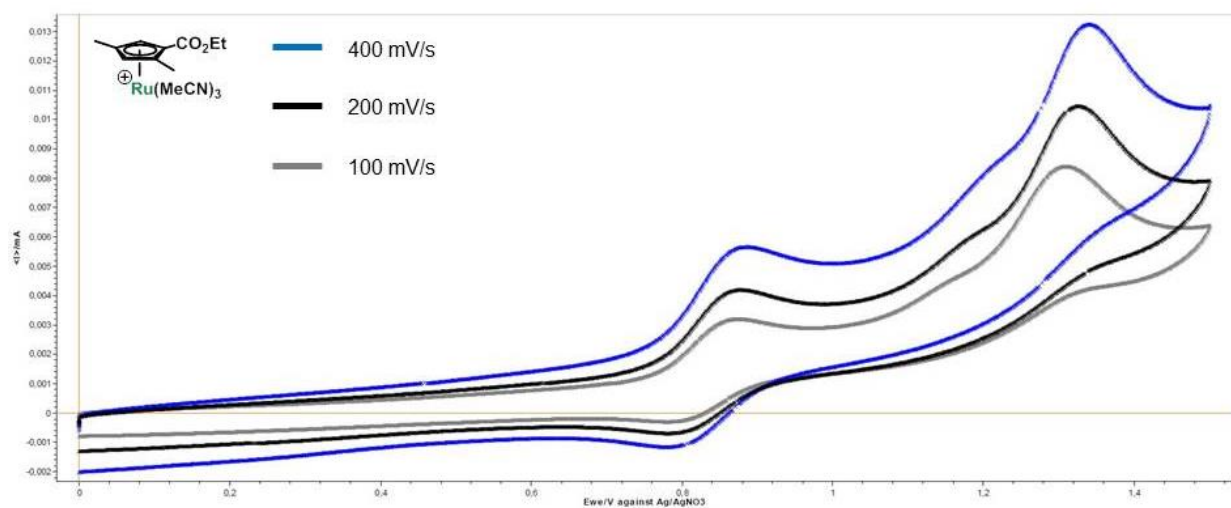
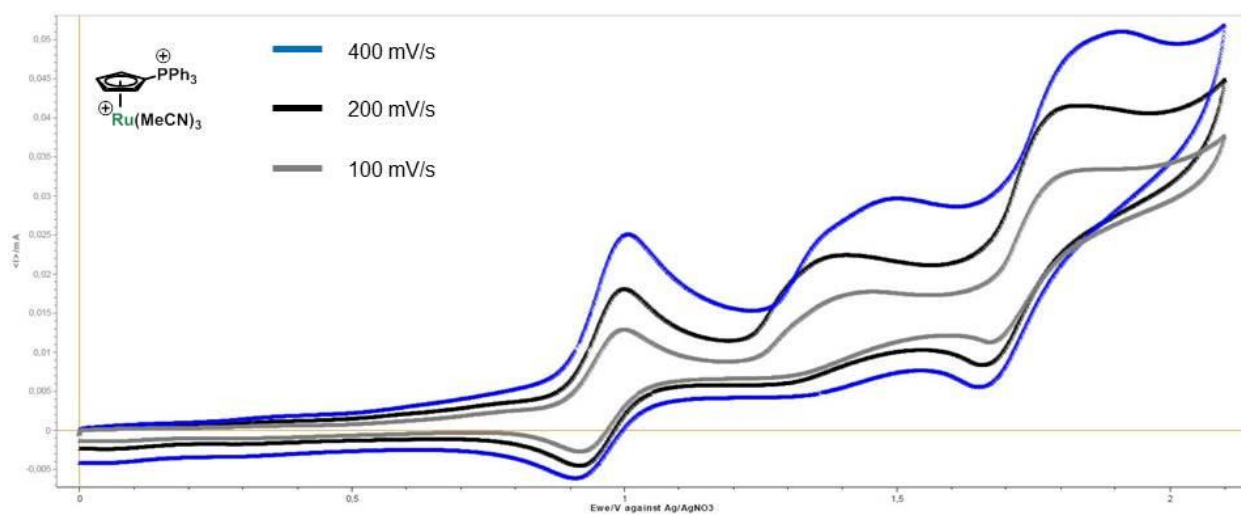
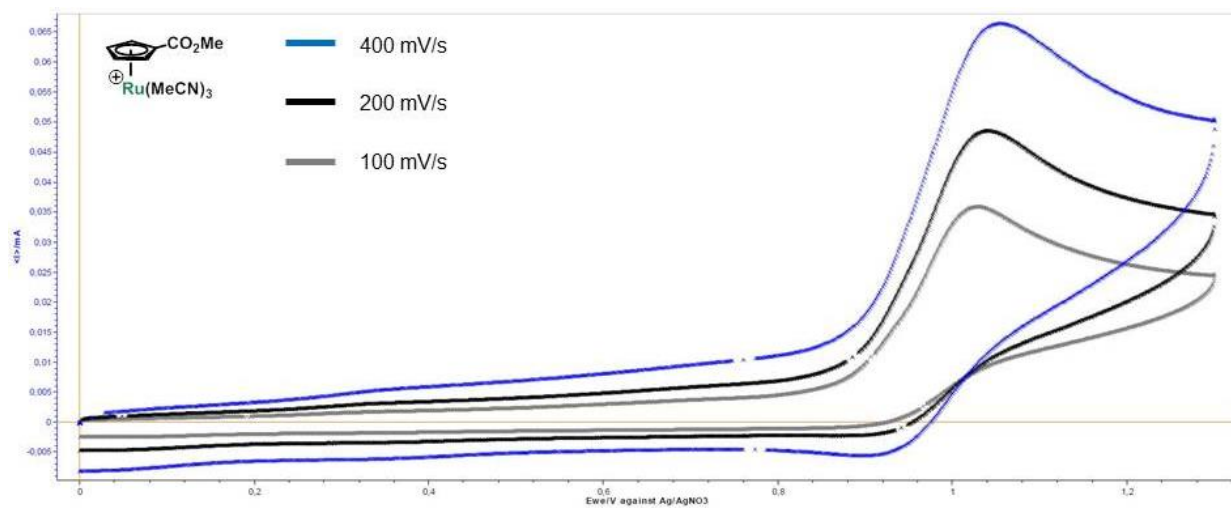
In a Schlenk tube the (freshly prepared) ruthenium complex **S-3** (150 mg, 0.16 mmol, 1 equiv)¹⁰ was dissolved in acetonitrile (10 mL), giving a dark red solution. Zinc powder (43.6 mg, 0.66 mmol, 4 equiv) was added and the suspension was stirred for 2 h while turning bright orange. Potassium hexafluorophosphate (122 mg, 0.66 mmol, 4 equiv) was then added causing a color change of the suspension to bright yellow. The suspension was stirred for 18 h at ambient temperature before it was evaporated to dryness under high vacuum. The residue was dispersed in CH₂Cl₂ (10 mL),

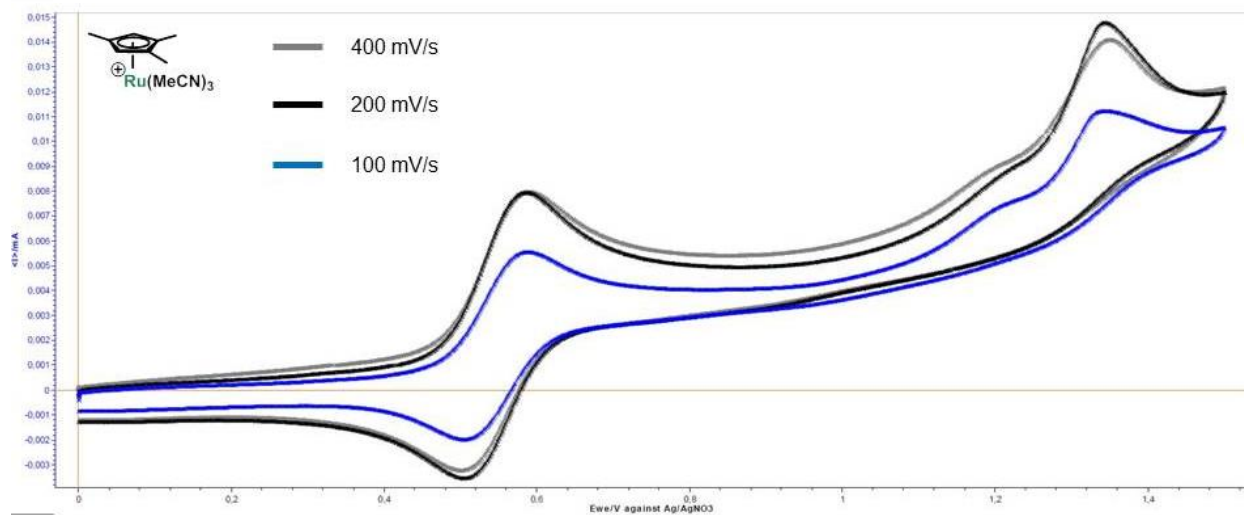
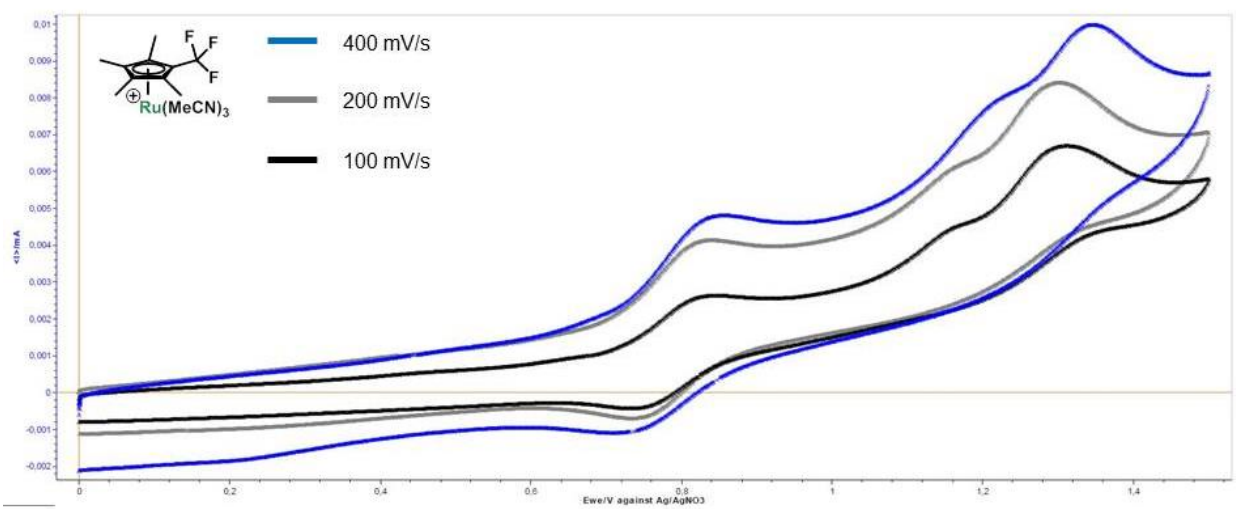
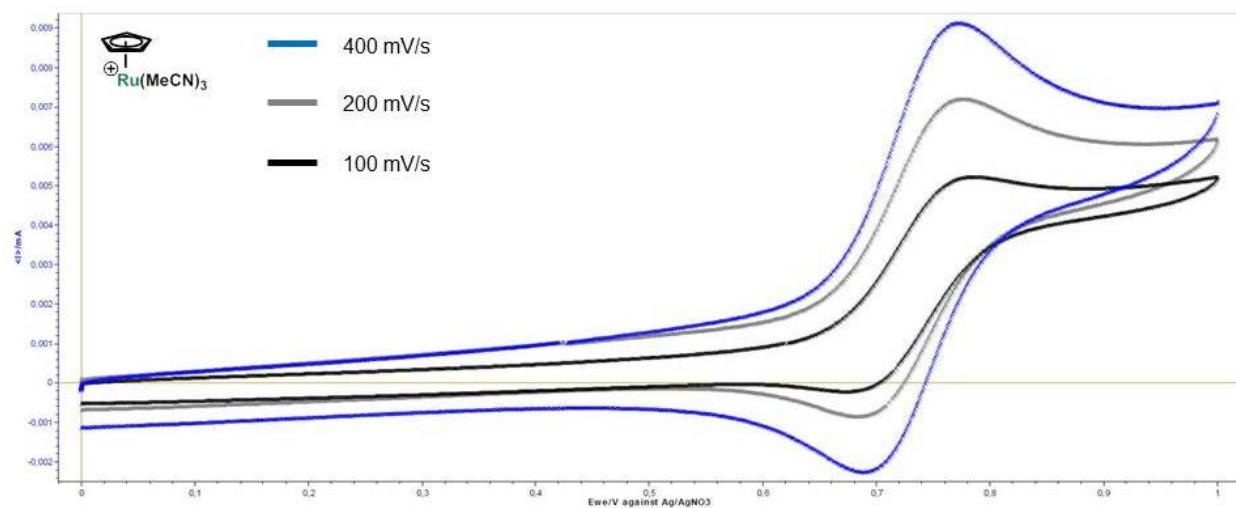
insoluble material was filtered off through a plug of Celite under argon, and the filtrate was evaporated to dryness under high vacuum to give the title compound as an air-sensitive, orange crystalline solid (95 mg, 0.16 mmol, 89%). ^1H NMR (400 MHz, $[\text{D}_3]\text{-MeCN}$): δ = 4.03 (s, 1H), 3.54 (s, 3H), 2.70 (d, J = 16.3 Hz, 1H), 2.35 (d, J = 16.3 Hz, 1H), 1.41 (s, 9H), 1.35 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, $[\text{D}_3]\text{-MeCN}$): δ = 133.7, 94.6, 82.7, 75.1, 57.1, 45.1, 37.9, 33.8, 33.2, 32.4, 32.0, 31.7, 31.5. ^{31}P NMR (162 MHz, $[\text{D}_3]\text{-MeCN}$): δ = -144.6 (hept, J = 706 Hz). ^{19}F NMR (282 MHz, $[\text{D}_3]\text{-MeCN}$) δ = -73.2 (d, J = 706 Hz). IR (film): 557, 680, 840, 1082, 1363, 1489, 2958 cm^{-1} .

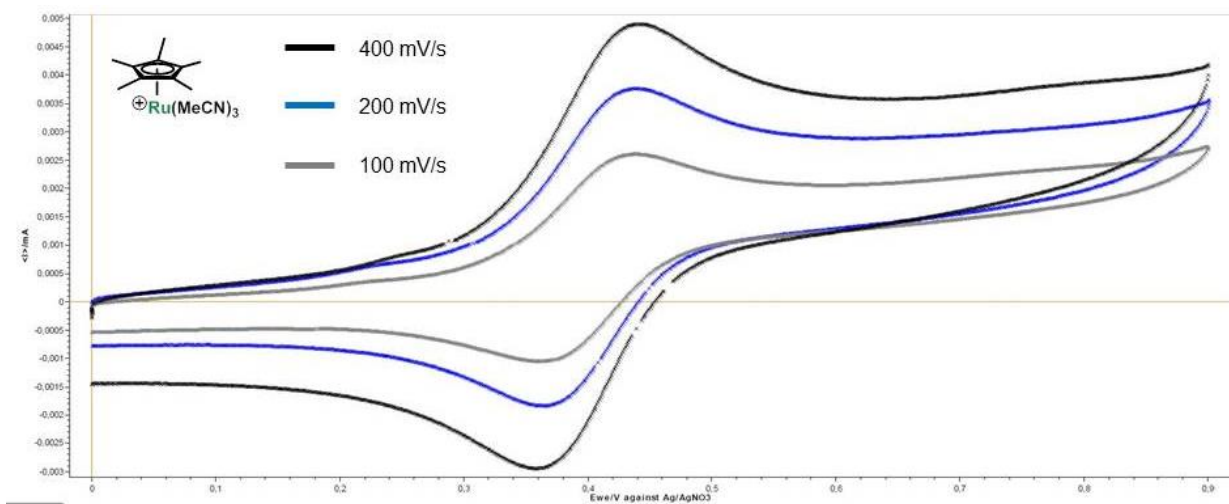
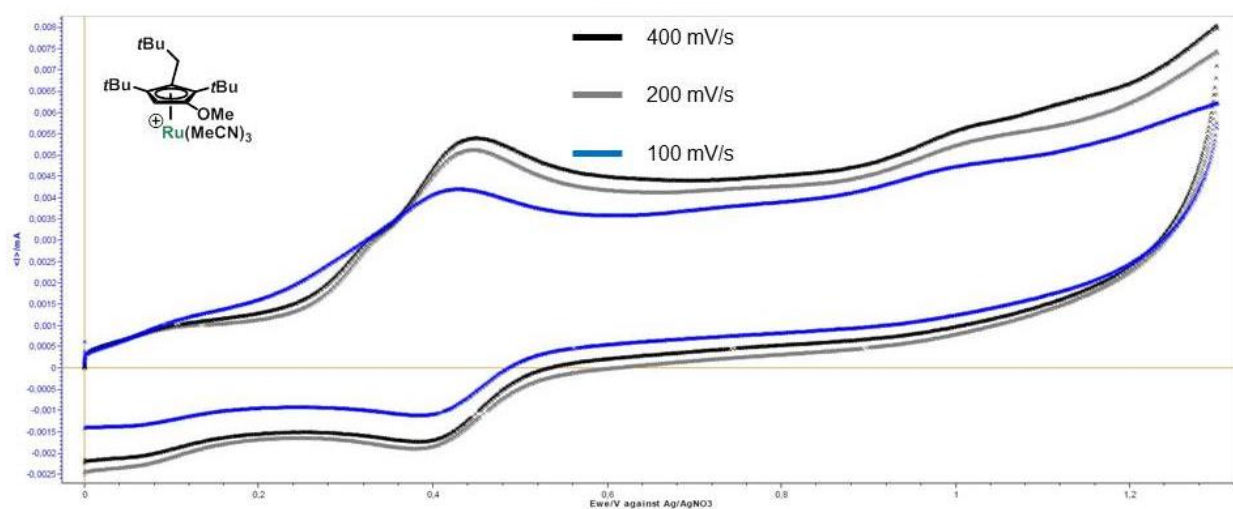
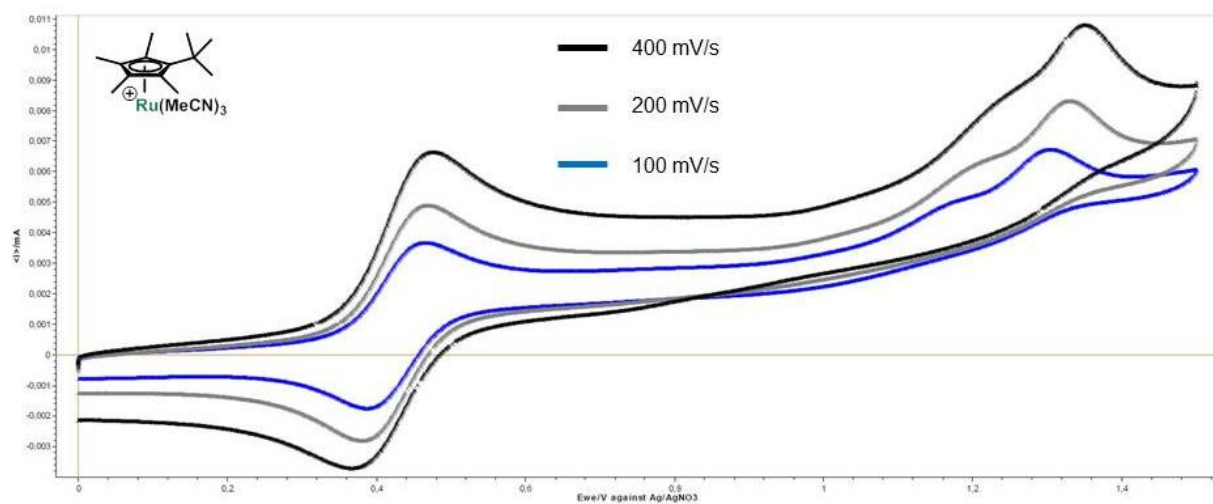
Cyclic Voltammetry Studies of Cationic $[\text{Cp}^x\text{Ru}(\text{MeCN})_3]\text{PF}_6$ Complexes

Initially, a potential window from 2 to -2 V was applied to study the complete electrochemical behavior of the chosen $[\text{Cp}^x\text{Ru}(\text{MeCN})_3]\text{PF}_6$ complex. Reduction events were not detected for any of the studied complexes. Hence, all shown CV spectra show scans from 0 V in direction to anodic potentials. All complexes showed one-electron oxidations in the range between 0.322 – 0.903 V. These oxidations were fully reversible for complexes **1-6** and **8** but only quasi reversible for **7** and **9**; for the sake of comparison, only the 400 mV sweep was used to determine a " $E_{1/2}$ " for **7** and **9**. Some complexes showed further oxidation peaks, which, however, appeared to be mostly irreversible.

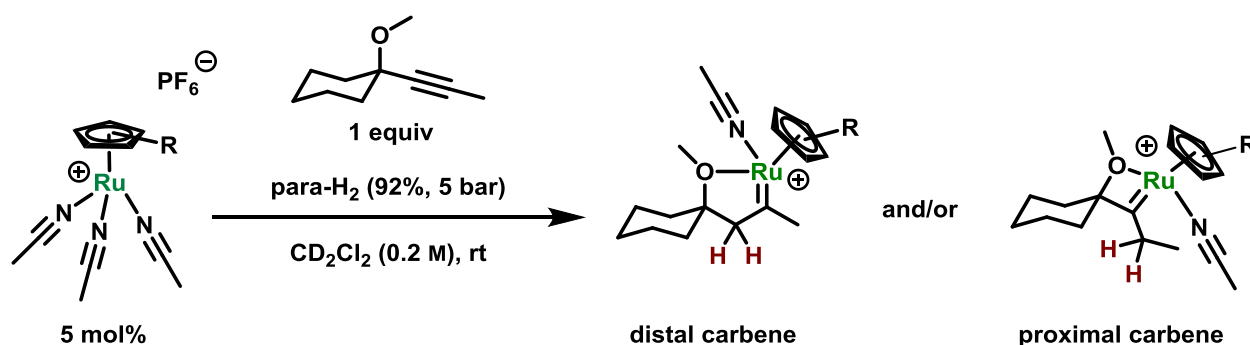




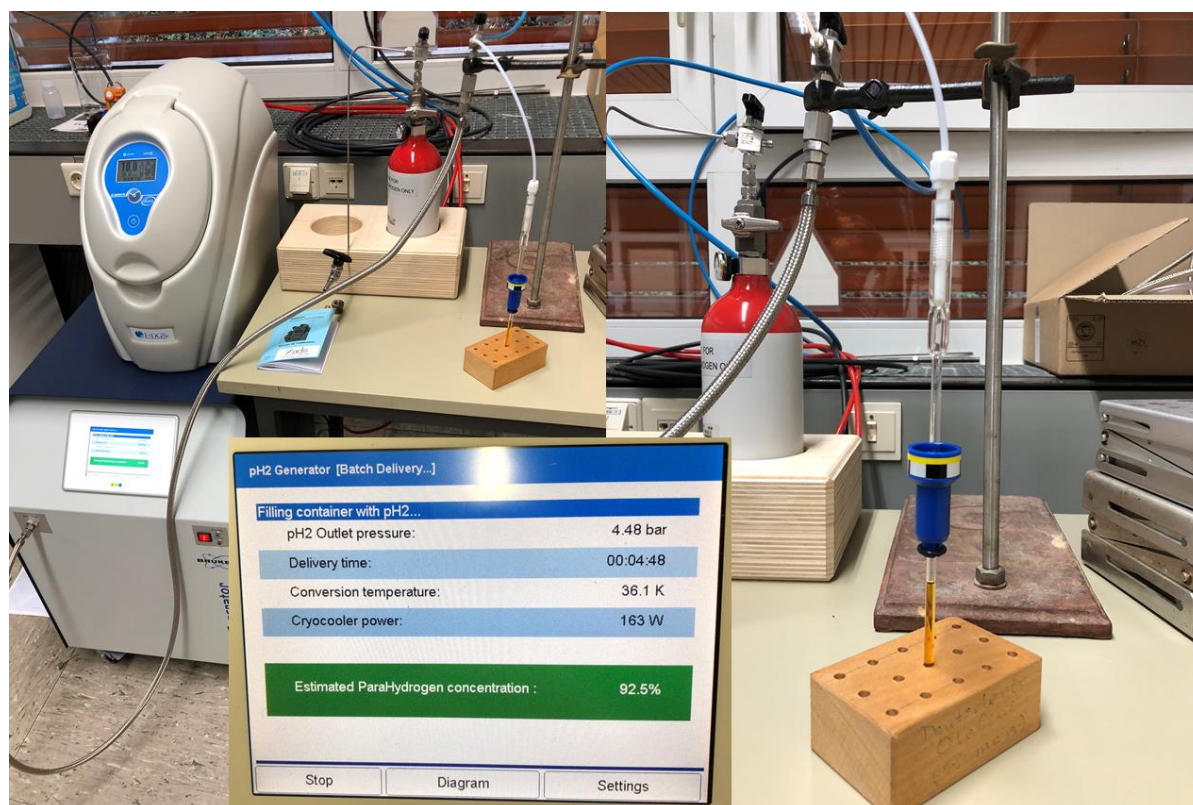




PHIP NMR Experiments with Cationic [Cp^xRu] Complexes

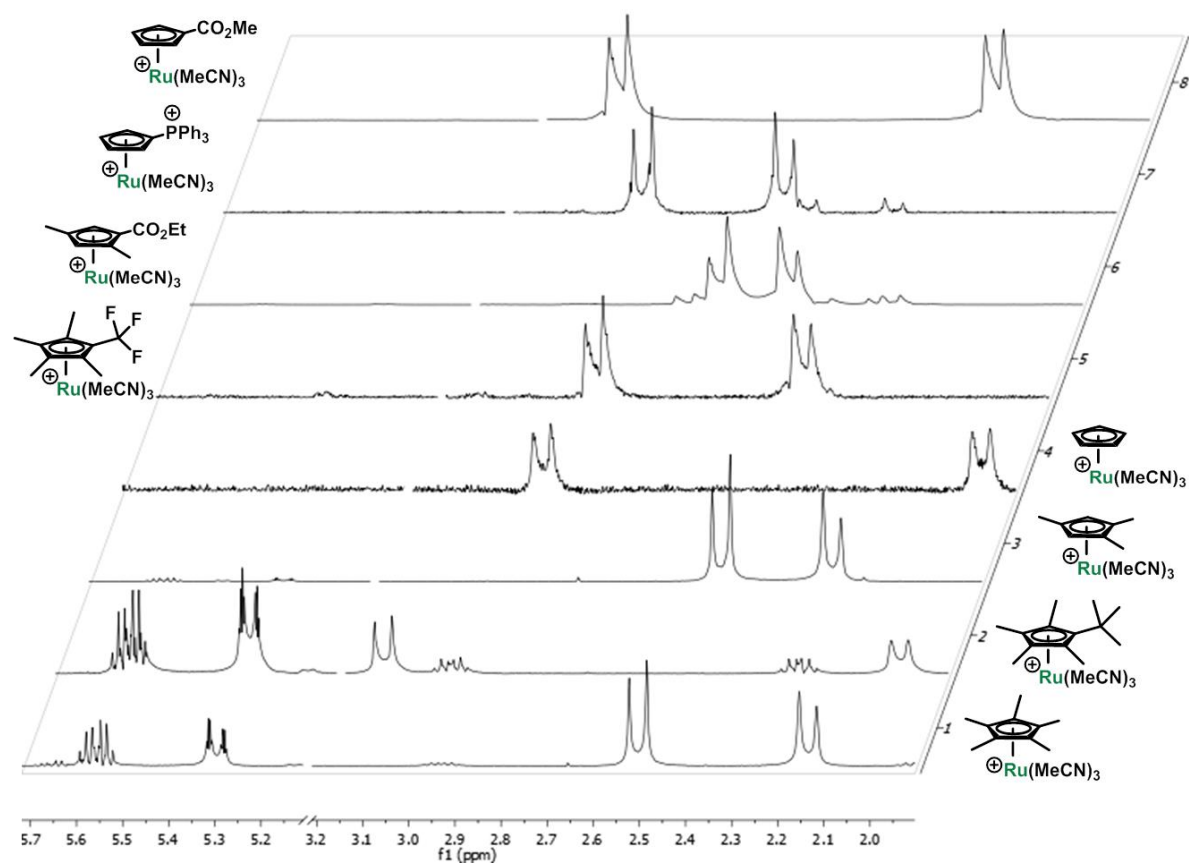


In a glovebox, 1-methoxy-1-(prop-1-yn-1-yl)cyclohexane **10** (15 mg, 0.098 mmol, 1 equiv) was added to a solution of the corresponding [Cp^xRu] complex (5 mol%) in CD₂Cl₂ (0.2 M). The solution was transferred into a pressure NMR tube (5 mm medium wall precision pressure/vacuum valve NMR sample tube, *Wilmad-LabGlass*), which was tightly closed and then taken out from the glovebox. The tube was connected to the *p*-H₂ generator and all tubings were evacuated and backfilled with *para*-hydrogen (*p*-H₂) three times. Then, the pressure was increased to 5 bar and the valve was opened to fill the tube with *para*-hydrogen to a total pressure of \approx 6 bar [the insert of the monitor of the *para*-hydrogen generator shows the pressure in barg (pressure above atmosphere)]. After closing the valve, the tube was shaken and inserted into the NMR magnet.

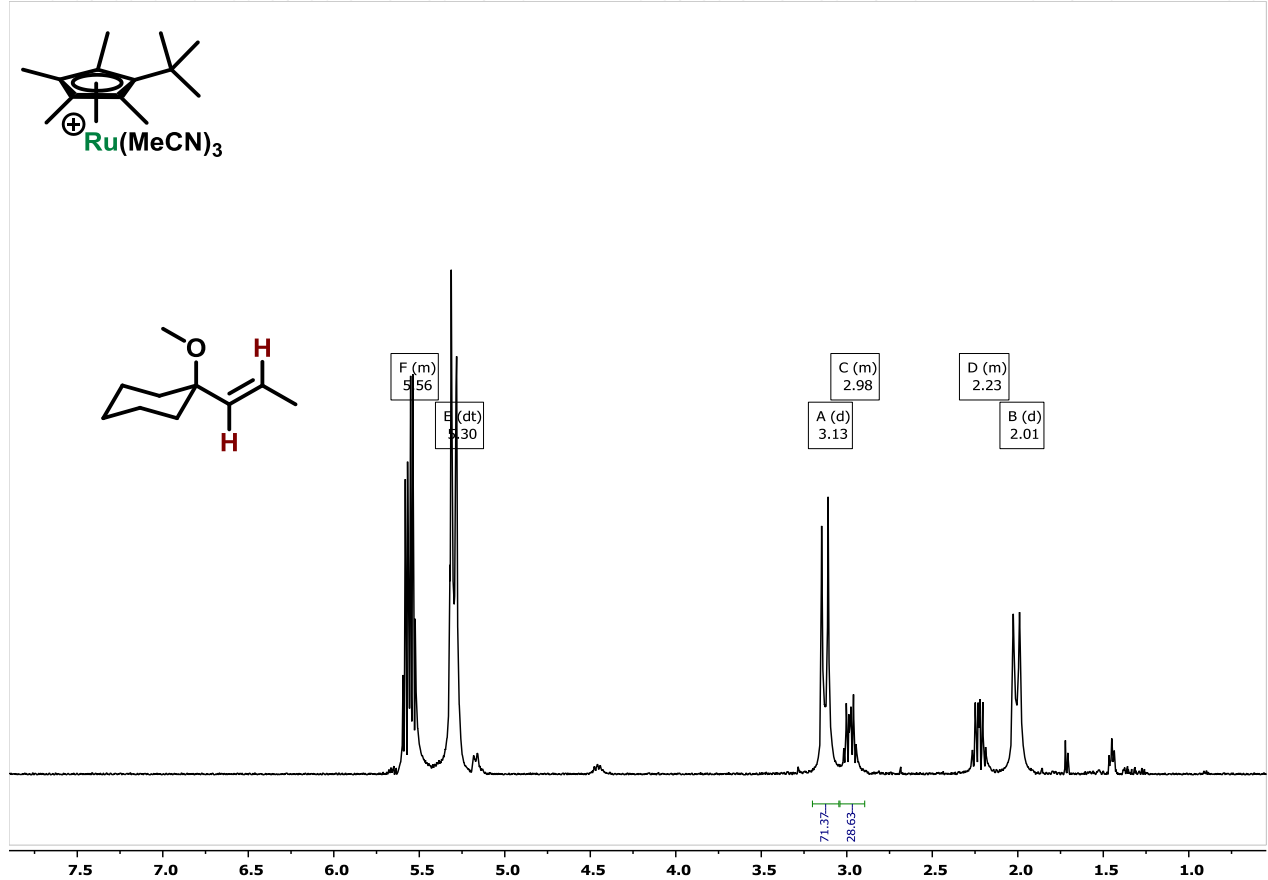
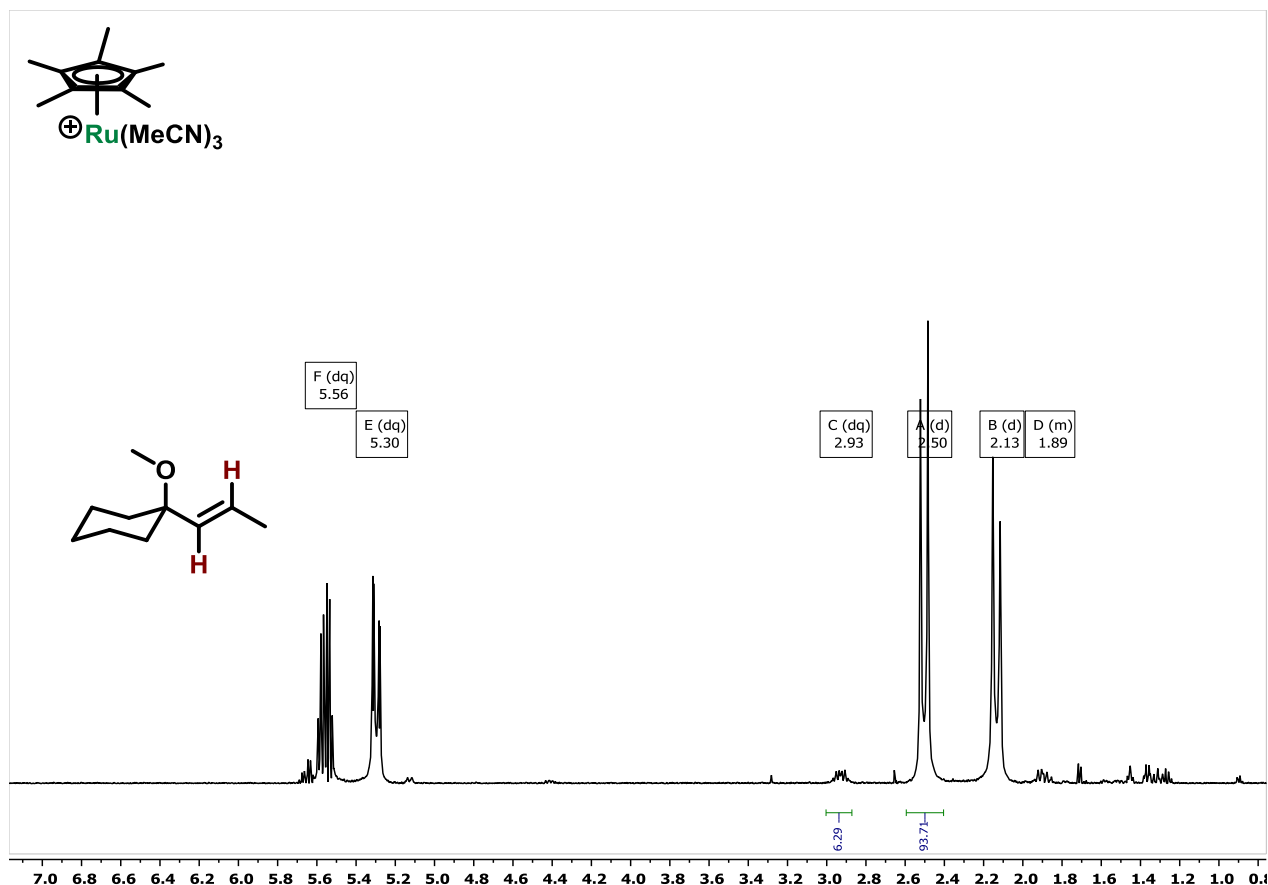


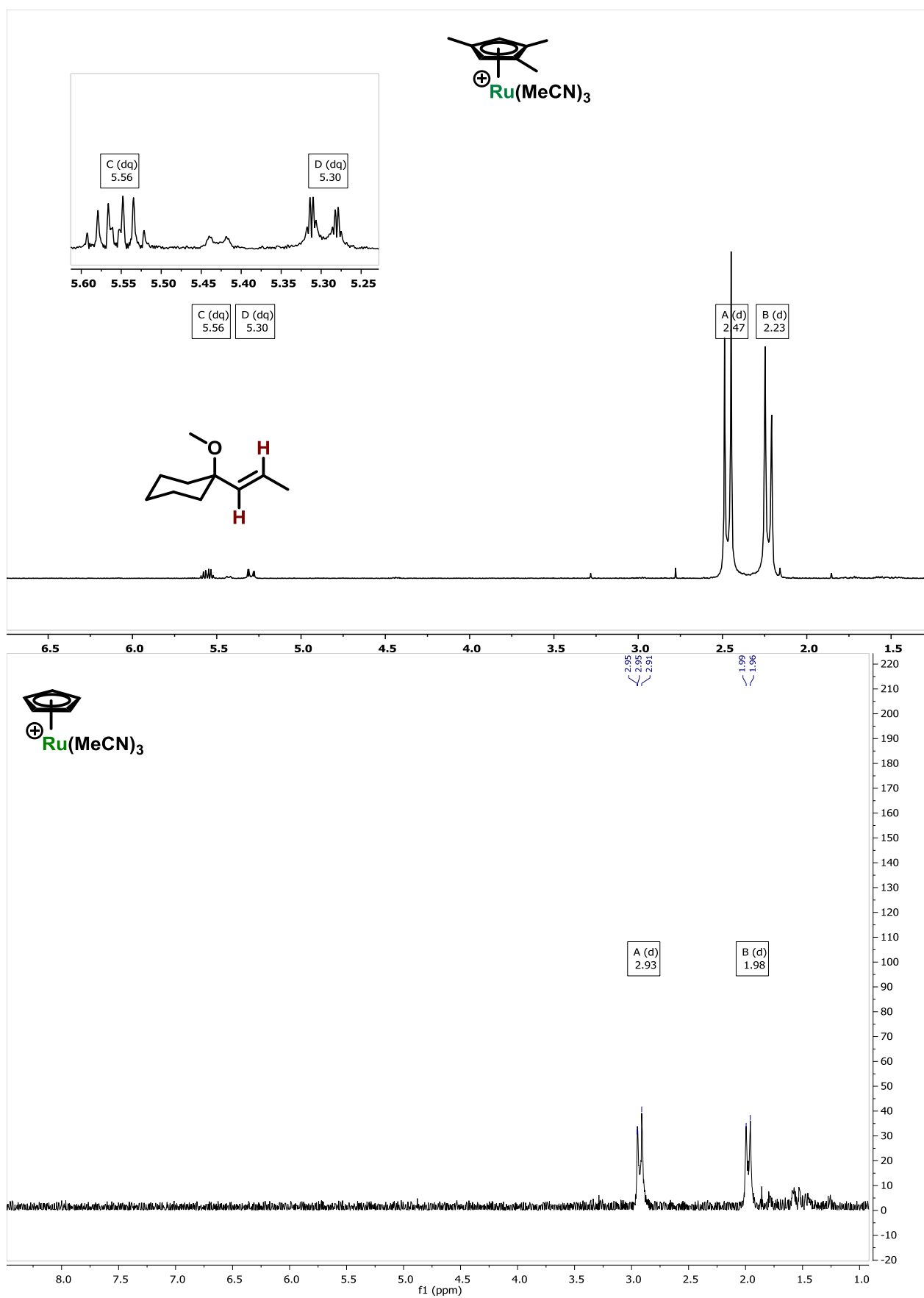
PHIP NMR (^1H OPSY) Spectra of Reactions Generating Cationic Ruthenium Carbenes from 1-Methoxy-1-(prop-1-yn-1-yl)cyclohexane (10) as the Substrate

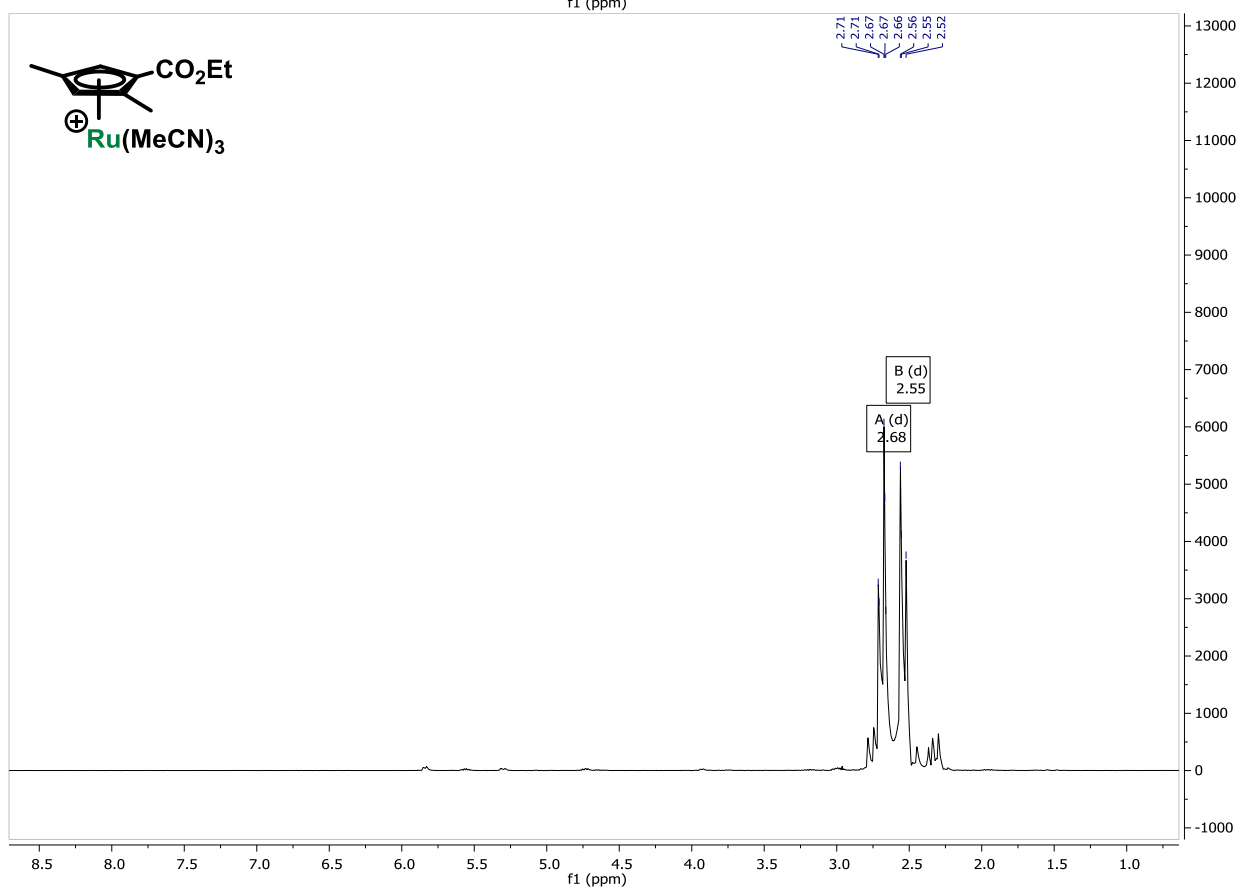
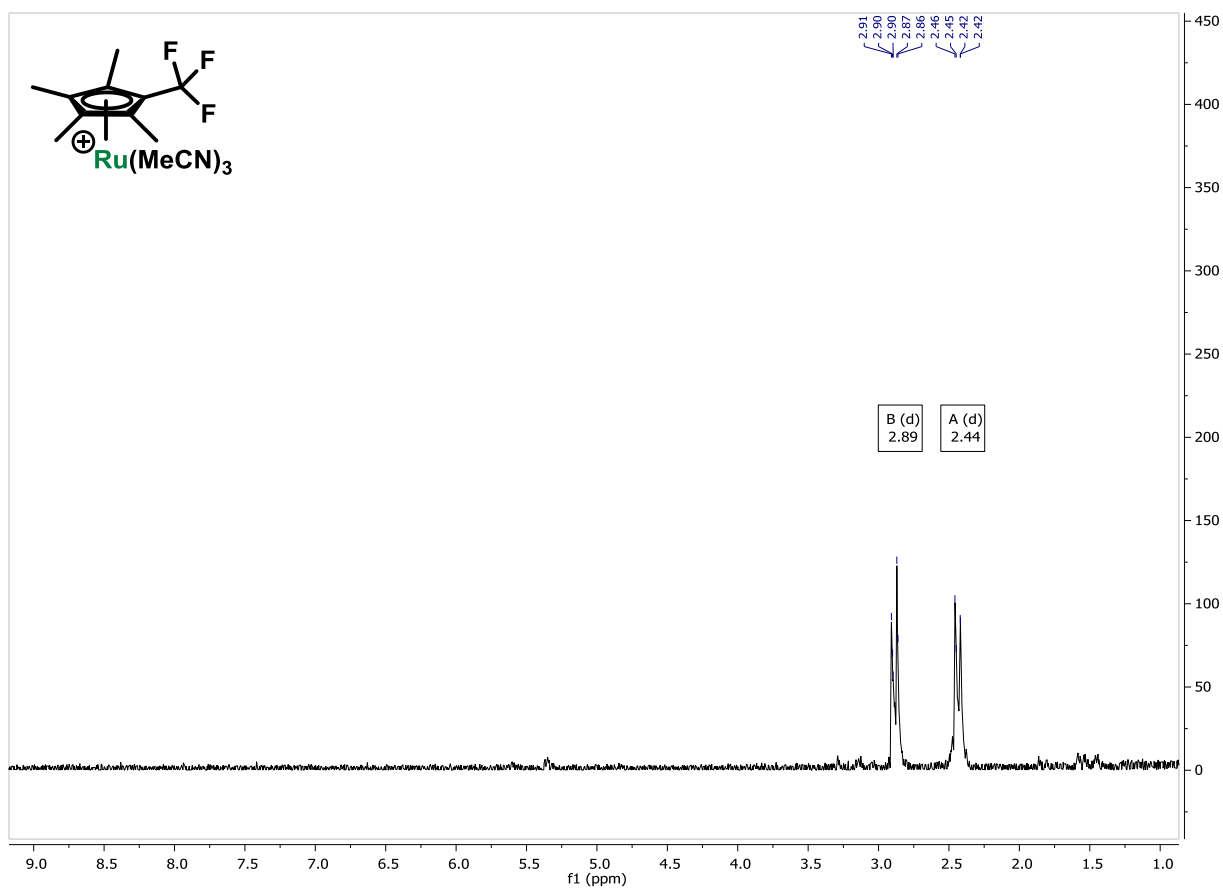
Overview

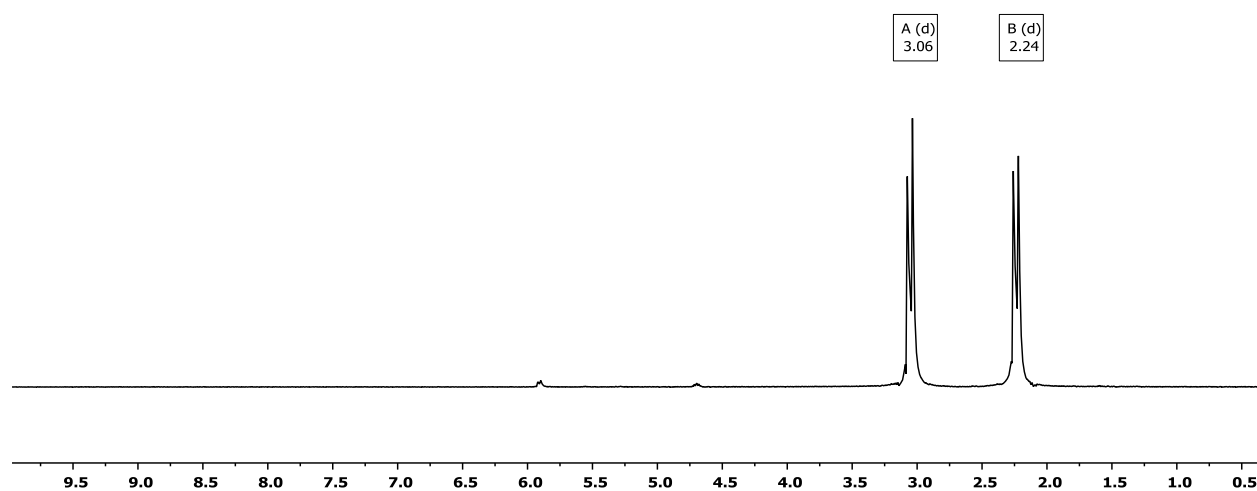
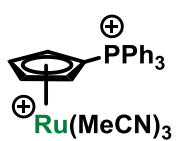
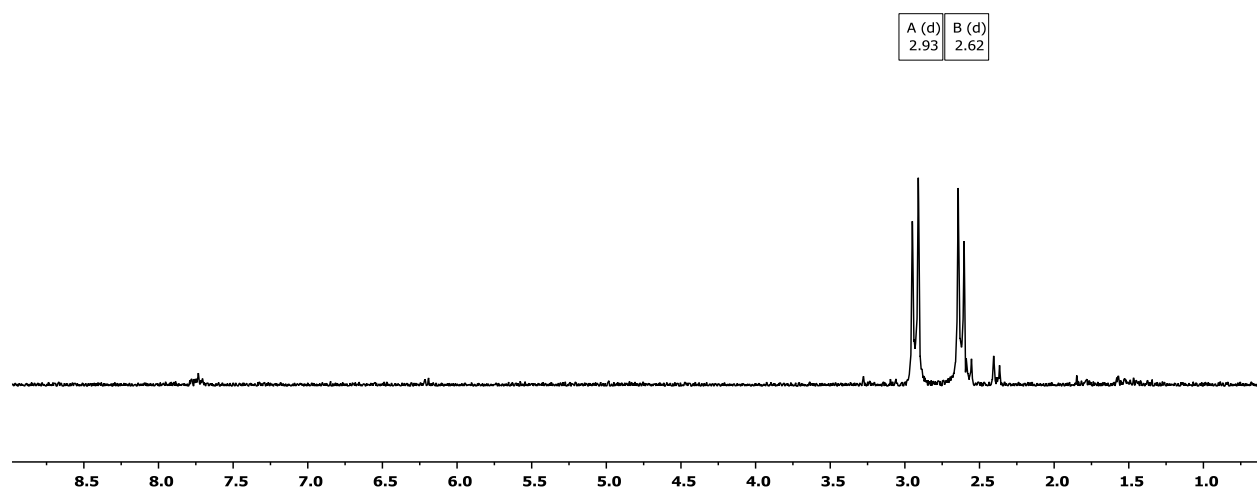
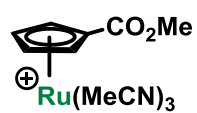


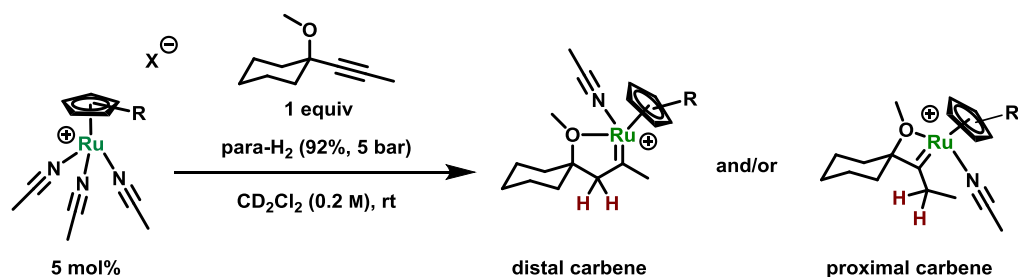
The individual spectra obtained with the indicted complexes are compiled below







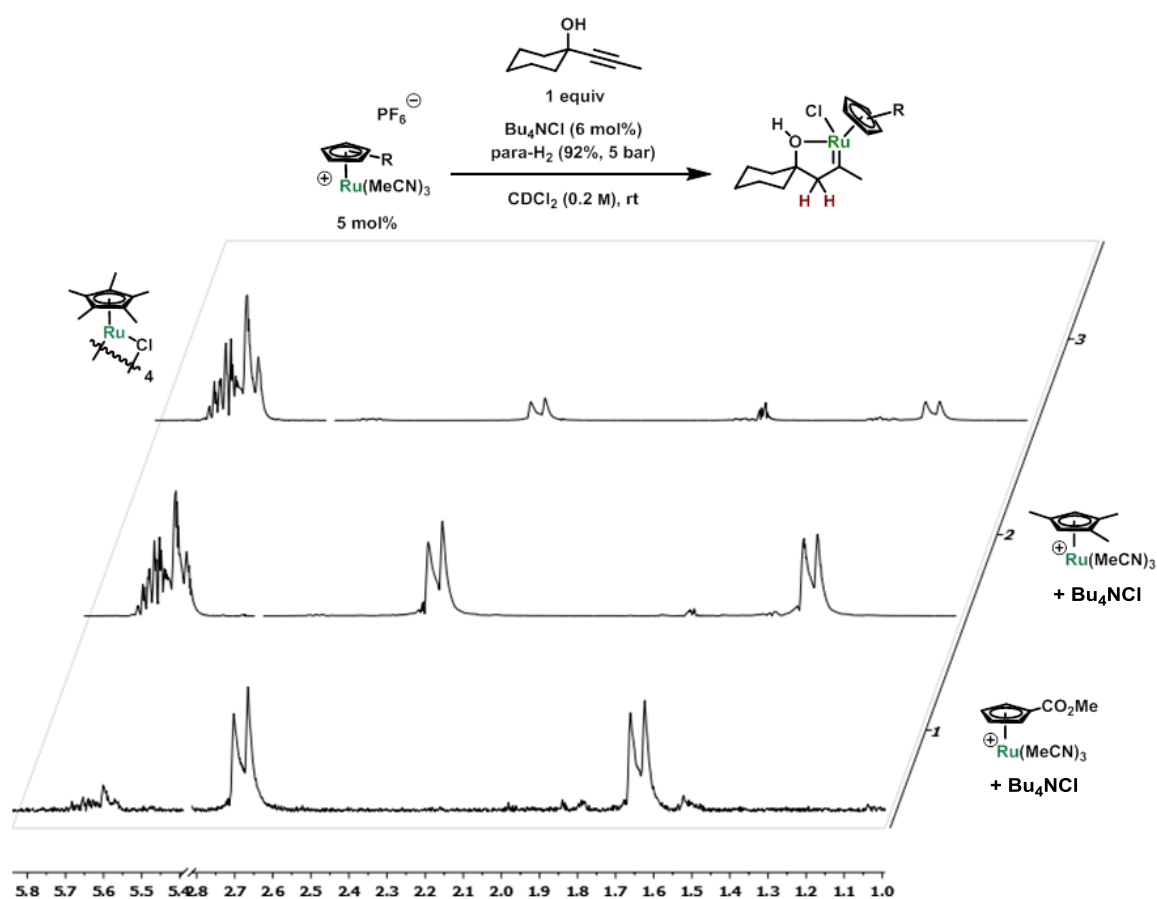




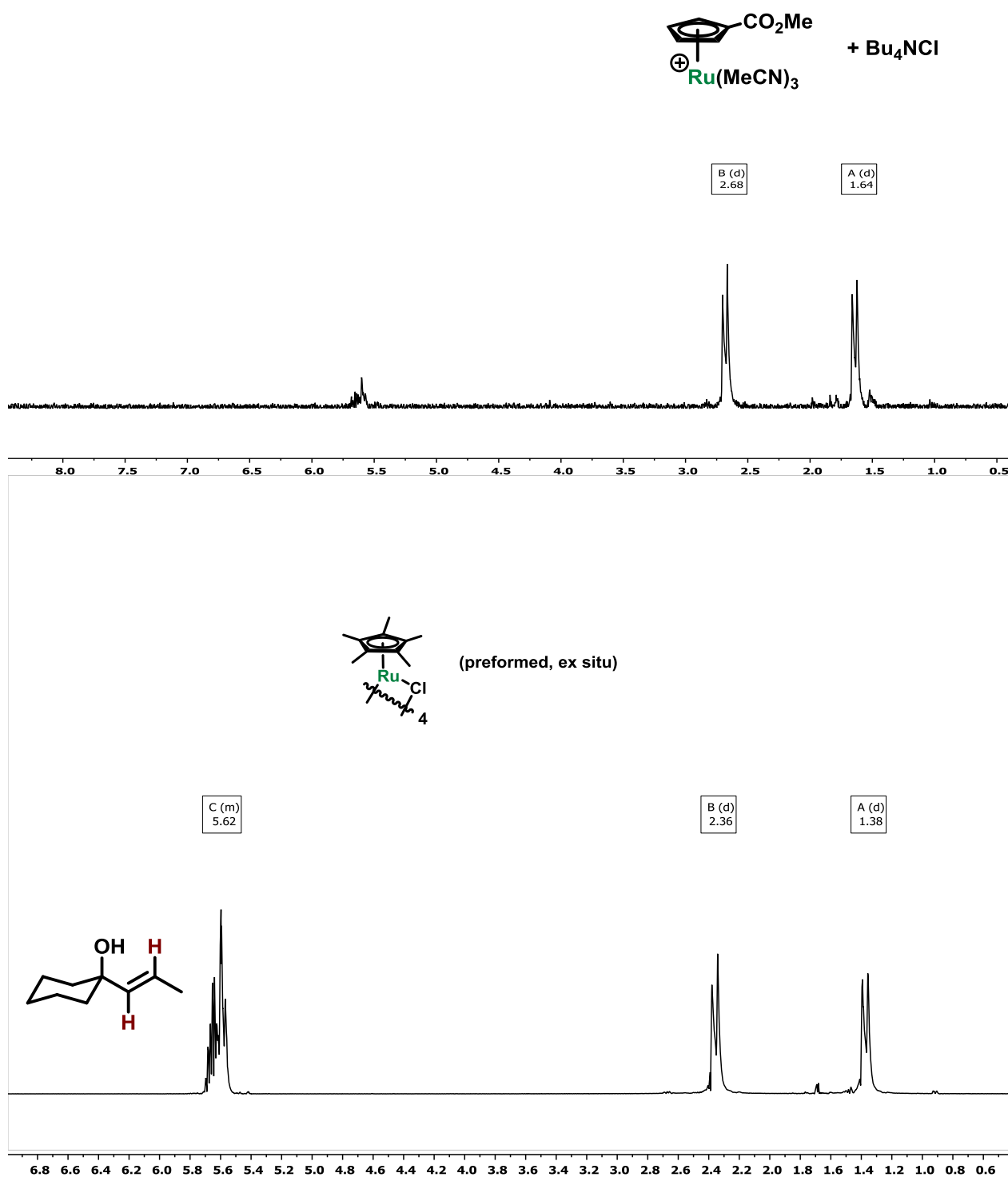
catalyst	distal carbene:proximal carbene	$\delta^1\text{H/ppm}$	$^2\text{J/Hz}$
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	100:0	3.06, 2.24	20.0
	100:0	2.68, 2.55	19.5
	100:0	2.89, 2.44	19.3
	100:0	2.93, 1.98	18.0
	100:0	2.47, 2.23	19.5
	71:29	3.13, 2.01 (proximal) 2.98, 2.23 (distal)	19.5
	<i>no conversion</i>		
	94:6	2.50, 2.13 (proximal) 2.93, 1.89 (distal)	19.0

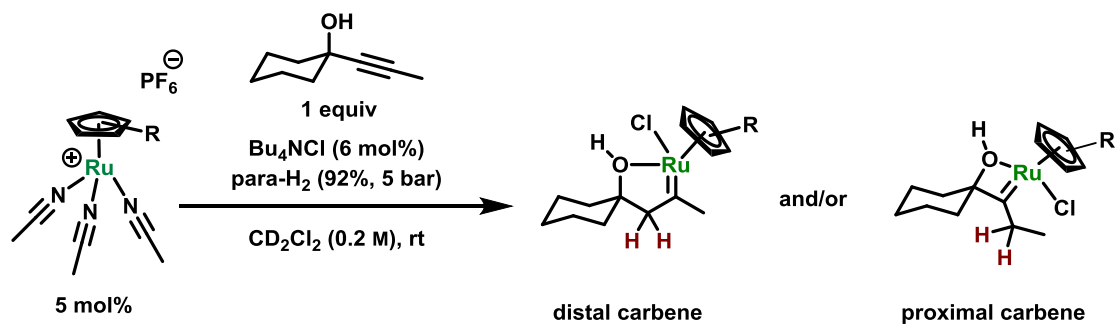
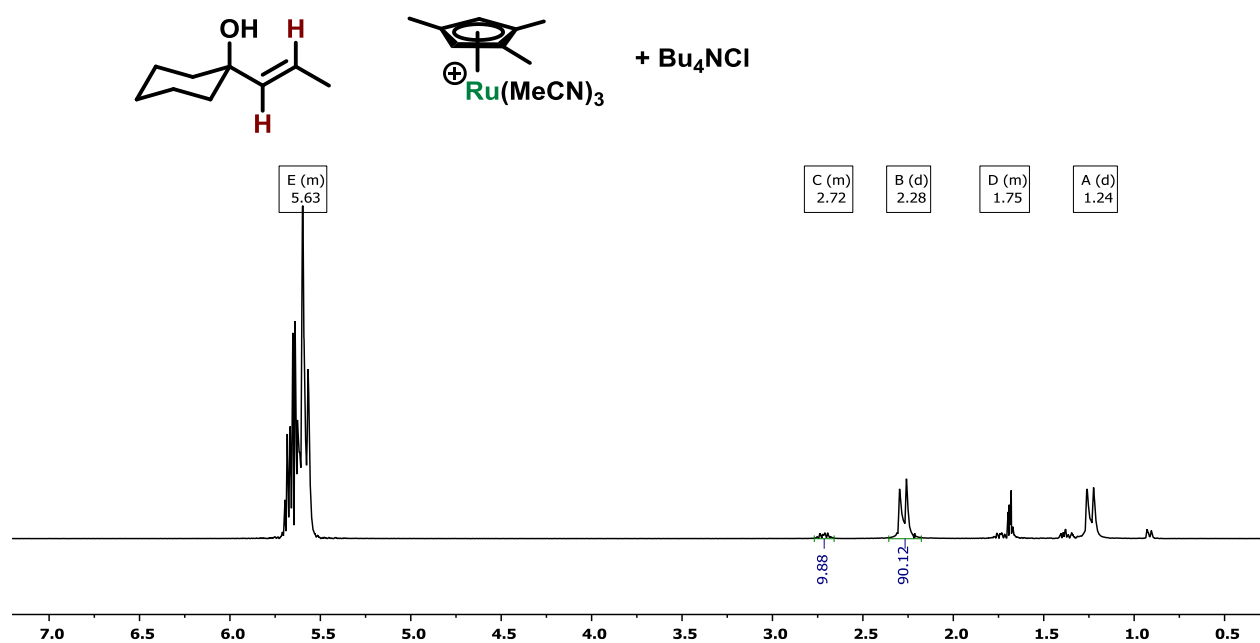
PHIP NMR Experiments with Neutral $[\text{Cp}^*\text{RuCl}]$ Complexes Generated In Situ. In a glovebox, the corresponding alkyne (0.098 mmol, 1 equiv) was added to a solution of the corresponding $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ complex (5 mol%) and tetra-*n*-butylammonium chloride (6 mol%) in CD_2Cl_2 (0.2 M). The solution was transferred into a pressure NMR tube (5 mm medium wall precision pressure/vacuum valve NMR sample tube, *Wilmad-LabGlass*), which was tightly closed and then taken out from the glovebox. The tube was connected to the *p*- H_2 generator and all tubings were evacuated and backfilled with *para*-hydrogen (*p*- H_2) three times. Then, the pressure was increased to 5 bar and the valve was opened to fill the tube with *para*-hydrogen to a total pressure of ≈ 6 bar. After closing the valve, the tube was shaken and inserted into the NMR magnet.

Overview: PHIP NMR (^1H OPSY) data of neutral ruthenium carbenes generated from 1-(prop-1-yn-1-yl)cyclohexan-1-ol as the alkyne substrate:



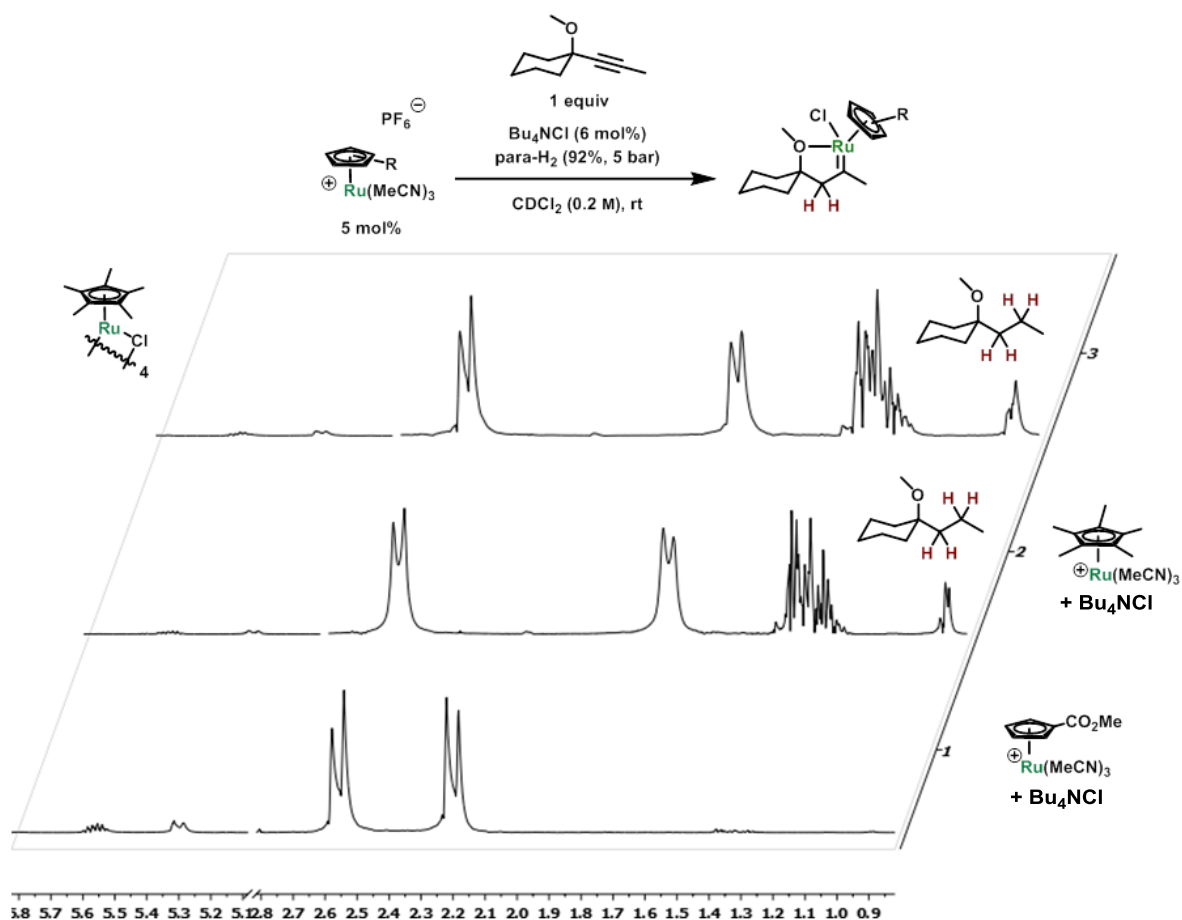
The individual spectra obtained with the indicated complexes are compiled below



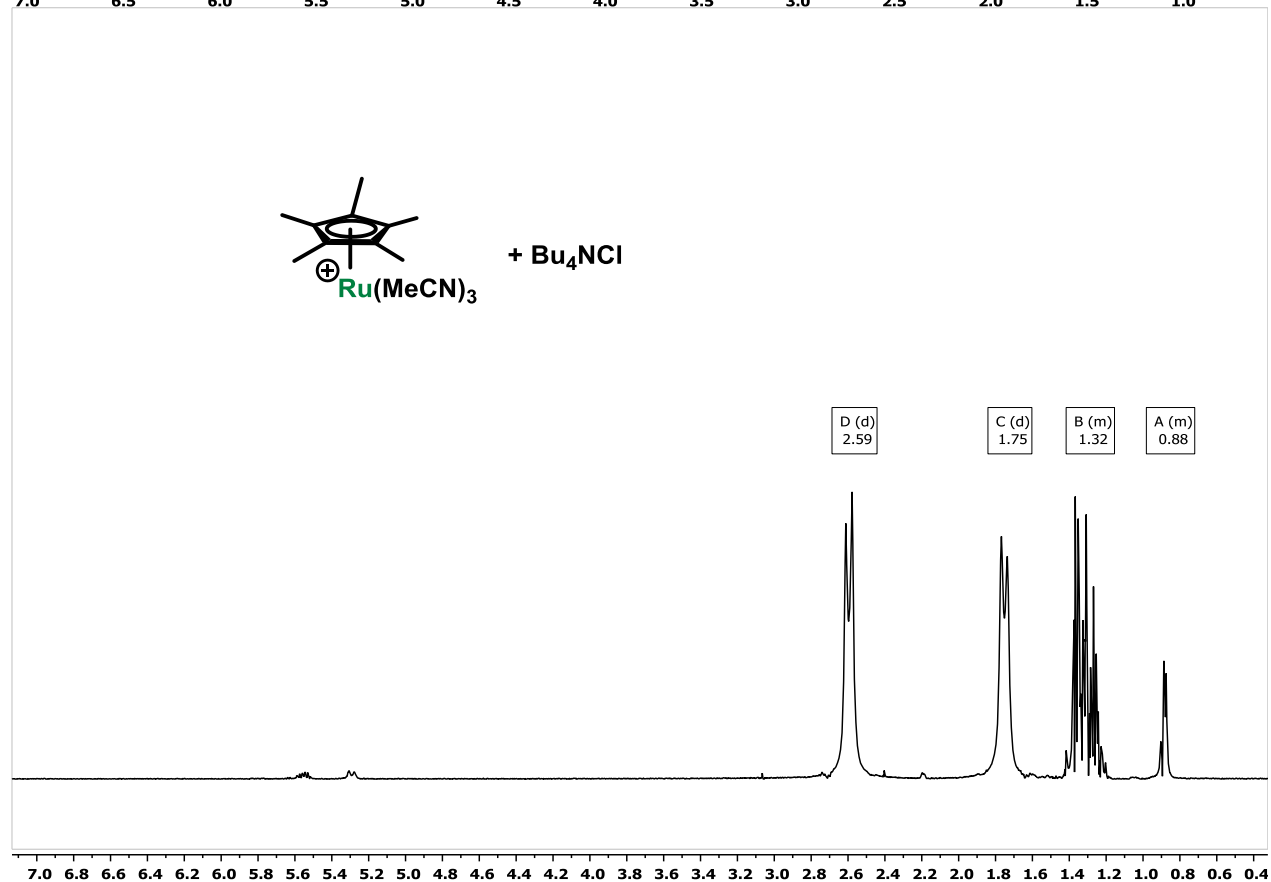
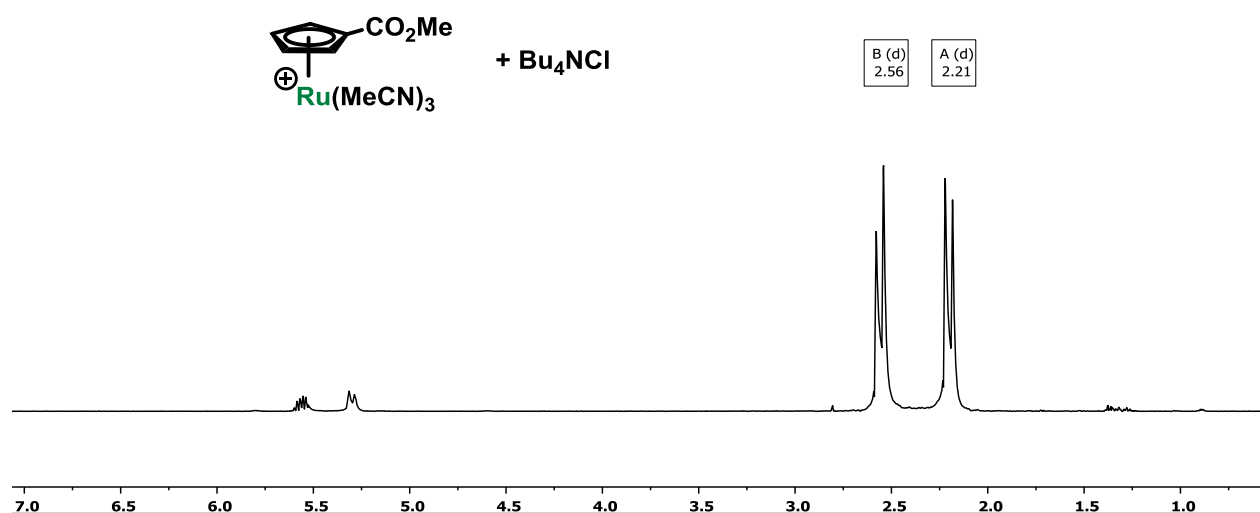


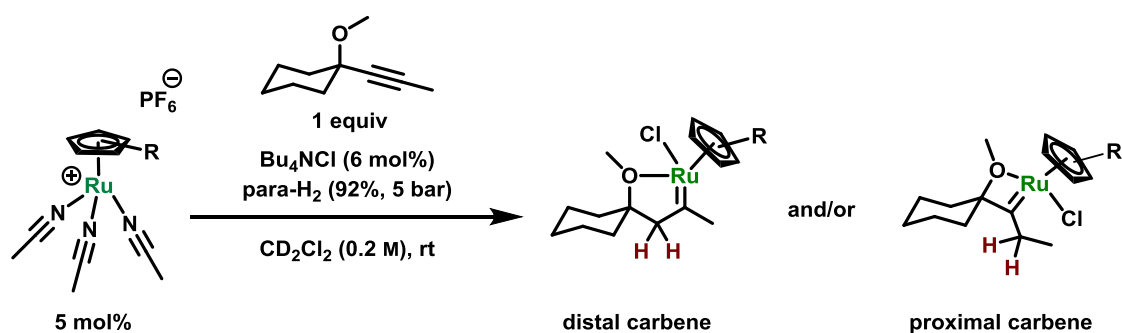
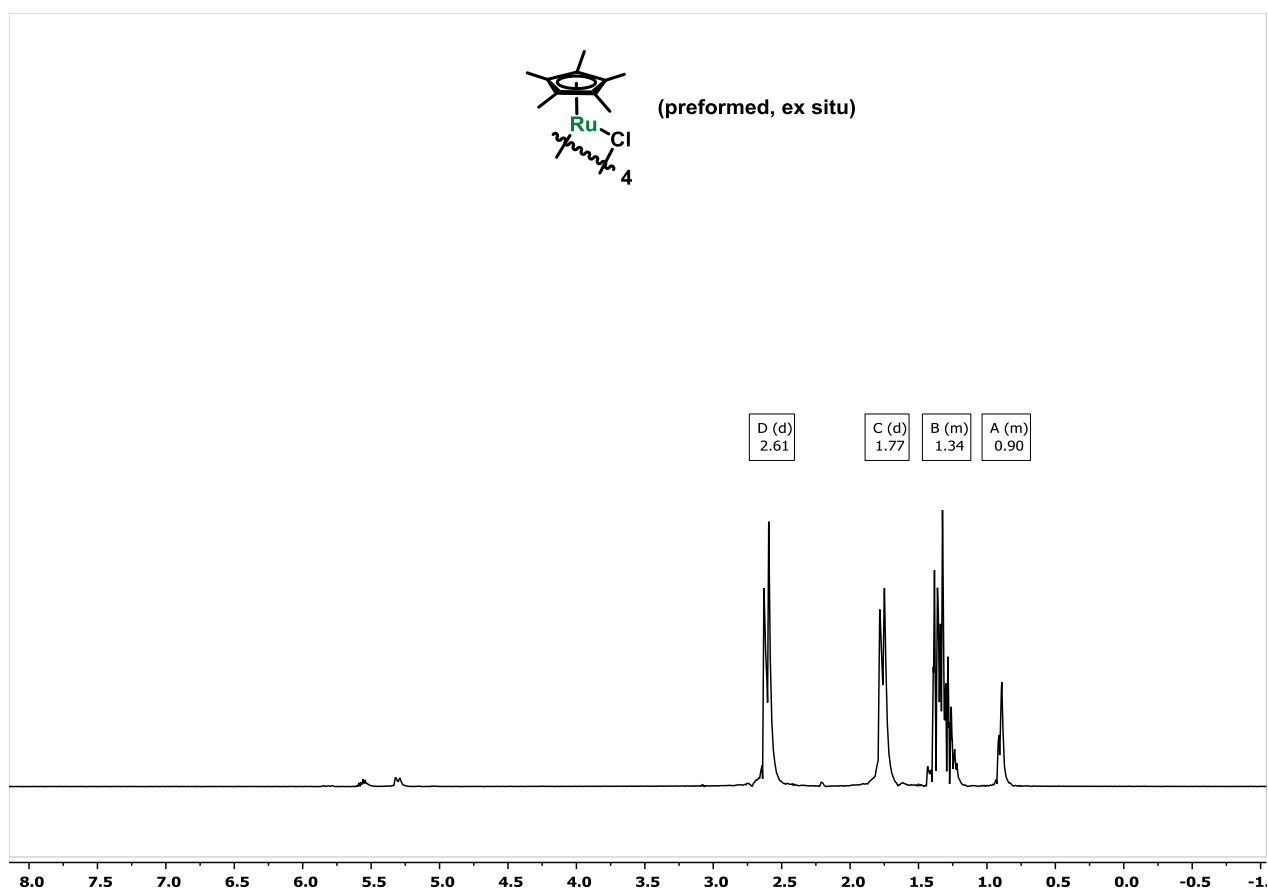
catalyst	distal carbene:proximal carbene	$\delta^1\text{H/ppm}$	$^2J/\text{Hz}$
	100:0	1.64, 2.68	18.5
	100:0	1.38, 2.36	18.7
	90:10	1.24, 2.28	19.4

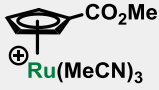

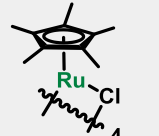
Overview: PHIP NMR (^1H OPsy) data of neutral ruthenium carbenes generated from 1-methoxy-1-(prop-1-yn-1-yl)cyclohexane (**10**) as the alkyne substrate



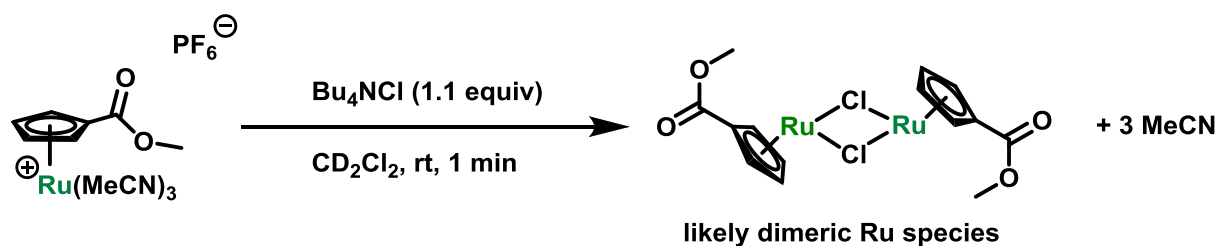
The individual spectra obtained with the indicated complexes are compiled below



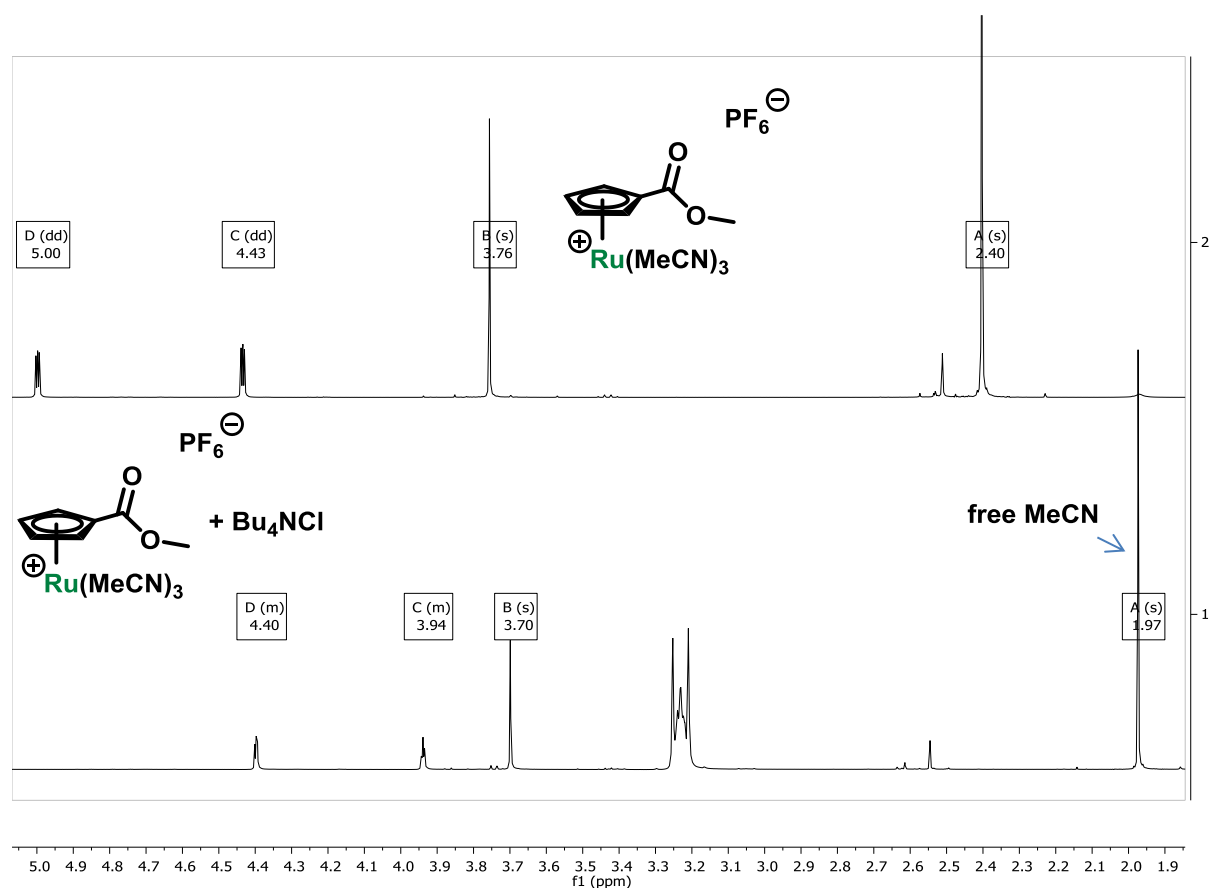


catalyst	distal carbene:proximal carbene	δ ¹ H/ppm	² J/Hz
 ⁺ Ru(MeCN) ₃	100:0	2.21, 2.56	19.2
 ⁺ Ru(MeCN) ₃	100:0	1.75, 2.59	17.3
 ⁺ Ru-Cl	100:0	1.77, 2.61	17.3

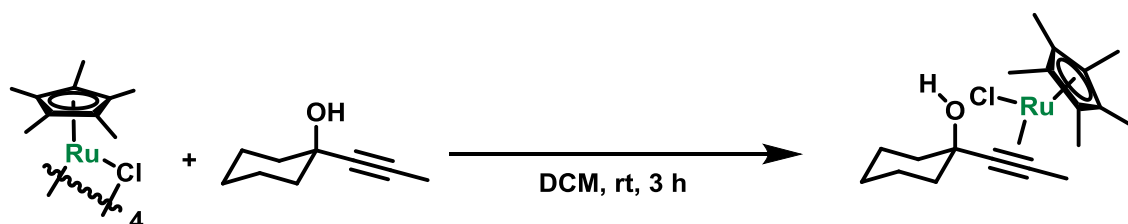
in situ Generation of a Neutral [Cp^xRuCl] Complex



A flame dried NMR tube was charged with tris(acetonitrile)(η^5 -1-methoxycarbonyl-cyclopentadienyl)ruthenium hexafluorophosphate **9** (7.1 mg, 0.014 mmol, 1 equiv) and tetrabutylammonium chloride (4.4 mg, 0.015 mmol, 1.1 equiv). CD_2Cl_2 was added and the bright red solution was analyzed by means of NMR. As expected for a neutral [Cp^xRuCl] complex, all signals shifted towards higher field. Additionally, no coordinated acetonitrile was observed, which is suggestive of a dimeric (or higher oligomeric) structure of the resulting complex. Attempted isolation in pure form was to no avail.

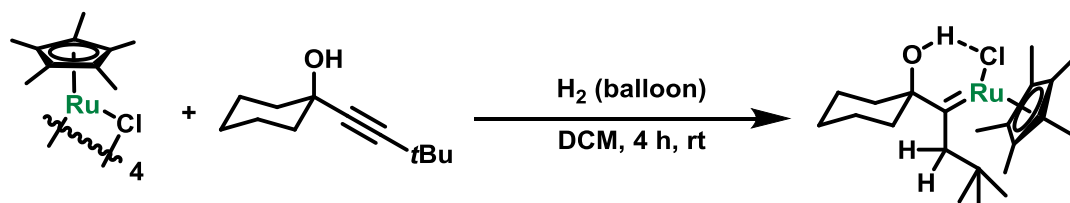


Synthesis of the Ruthenium Alkyne Complex (14)



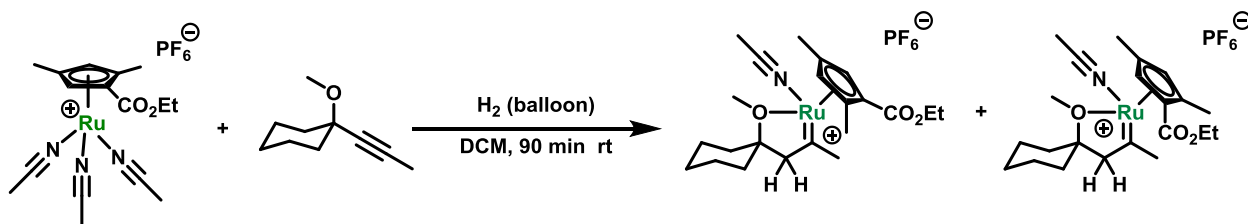
1-(Prop-1-yn-1-yl)cyclohexan-1-ol (43.1 mg, 0.31 mmol, 1 equiv) was added to a solution of $[\text{Cp}^*\text{RuCl}]_4$ (84.7 mg, 0.078 mmol, 0.25 equiv) in CH_2Cl_2 (3 mL) and the resulting mixture was stirred for 3 h at ambient temperature. Full conversion was noted by NMR spectroscopy. All volatile materials were removed under high vacuum to afford the title compound as a dark red solid which was used for solid state NMR measurements. The spectroscopic data match those previously reported.¹¹ ^1H NMR (400 MHz, CD_2Cl_2): δ = 5.07 (s, 1H), 2.77 (s, 3H), 1.72 (s, 15H), 1.71 – 1.11 (m, 11H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 154.7, 130.1, 89.5, 74.2, 39.2, 26.1, 14.9, 10.4.

Synthesis of the Neutral Ruthenium Carbene (17)



1-(3,3-Dimethylbut-1-yn-1-yl)cyclohexan-1-ol (32 mg, 0.045 mmol, 1 equiv) was added via syringe to a solution of $[\text{Cp}^*\text{RuCl}]_4$ (49.6 mg, 0.045 mmol, 0.25 equiv) in CH_2Cl_2 (4 mL). The Schlenk tube was then closed with a septum and hydrogen gas was flushed through the solution via canula for 3 min. The resulting solution was stirred for 4 h at ambient temperature before all volatile materials were removed under high vacuum to afford the title compound as a dark red solid that was used for solid state NMR measurements. The spectroscopic data match those previously reported.¹² ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.69 (d, J = 13.2 Hz, 1H), 2.12 – 2.03 (m, 1H), 1.74 – 1.68 (m, 1H), 1.60 – 1.54 (m, 3H), 1.50 (s, 15H), 1.47 – 1.41 (m, 3H), 1.36 – 1.26 (m, 1H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 306.7, 116.2, 92.6, 57.5, 41.0, 32.1, 29.0, 27.7, 25.6, 21.0, 19.5, 10.8.

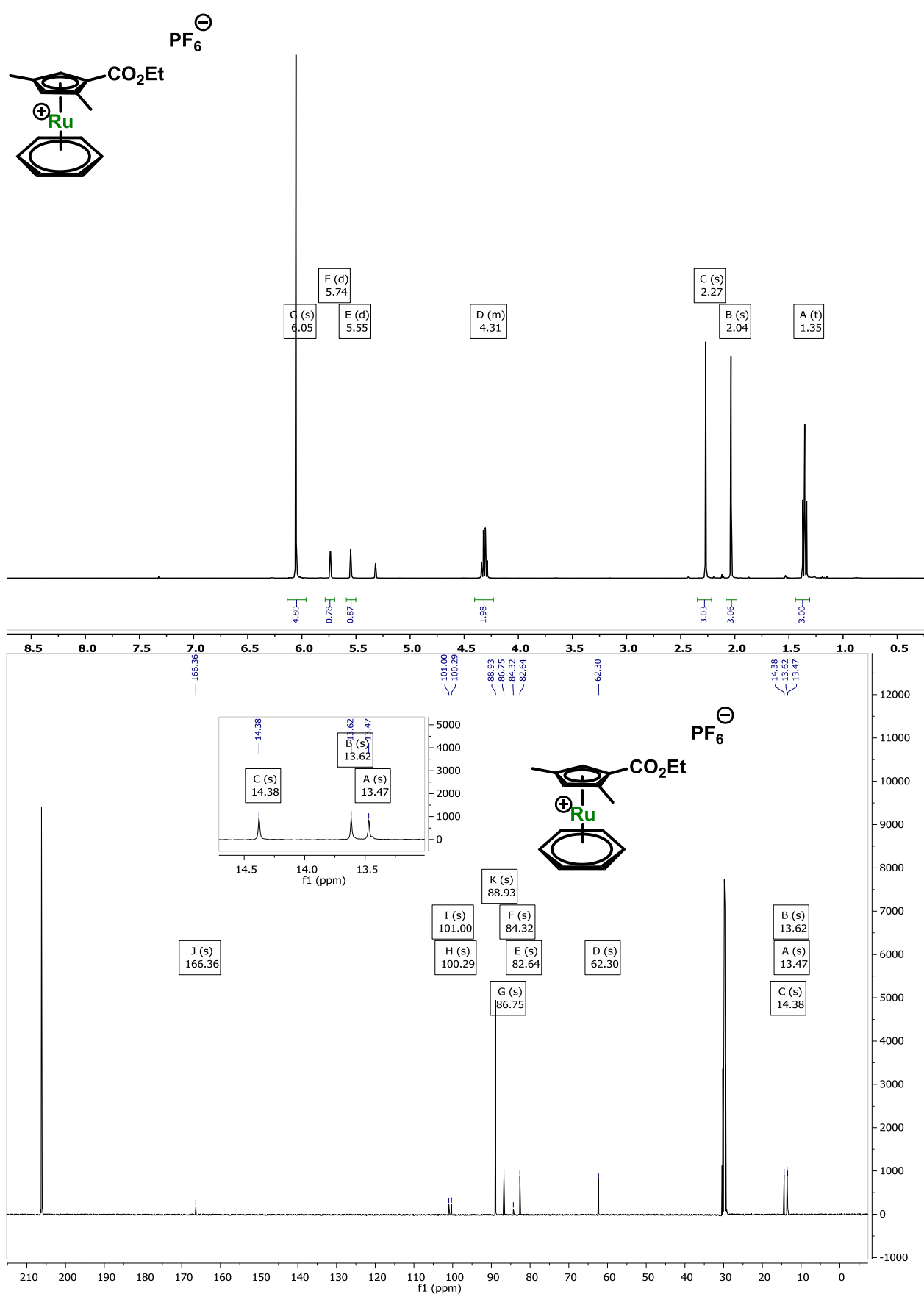
Preparation of the (Diastereomeric) Cationic Ruthenium Carbenes (18)

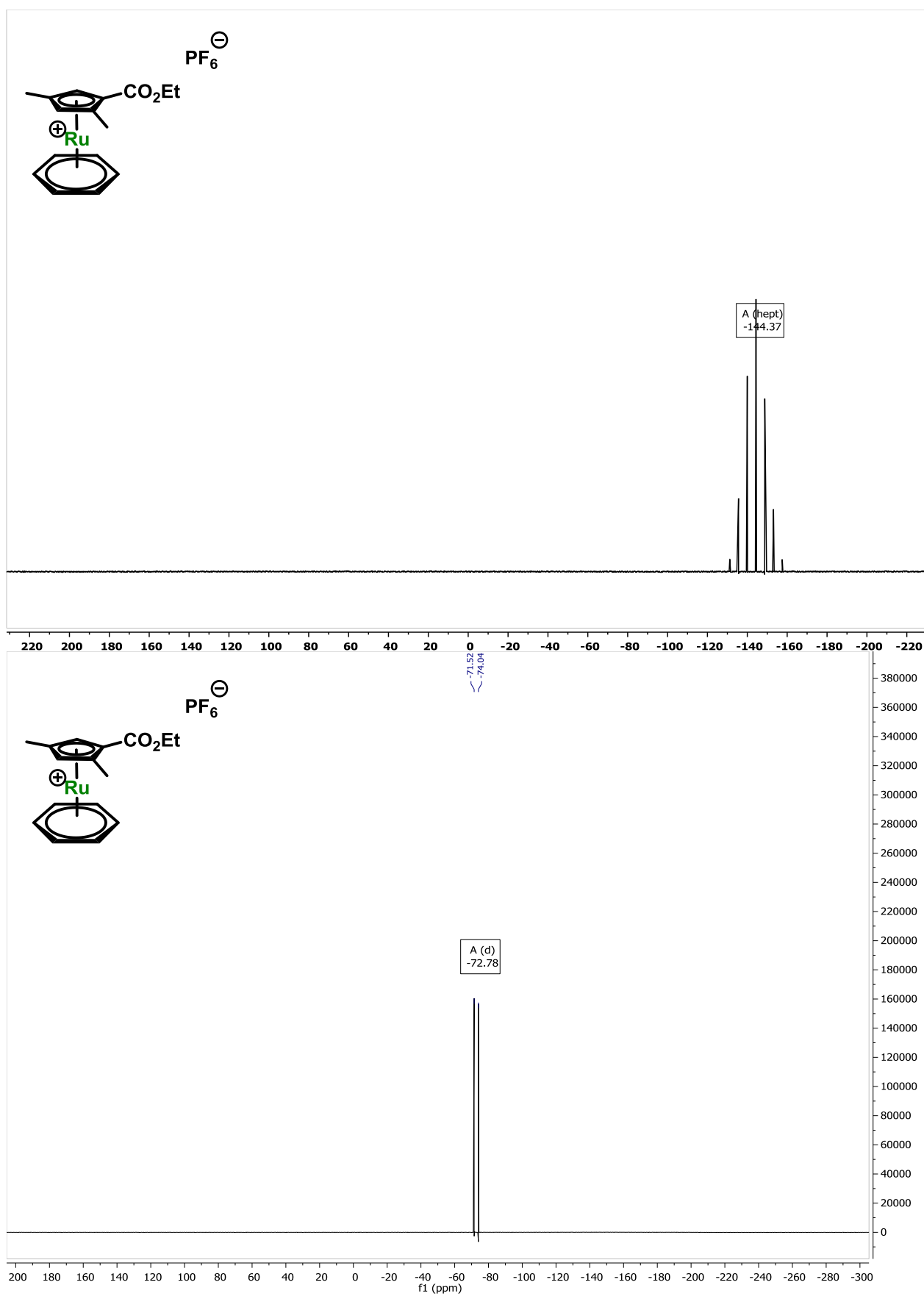


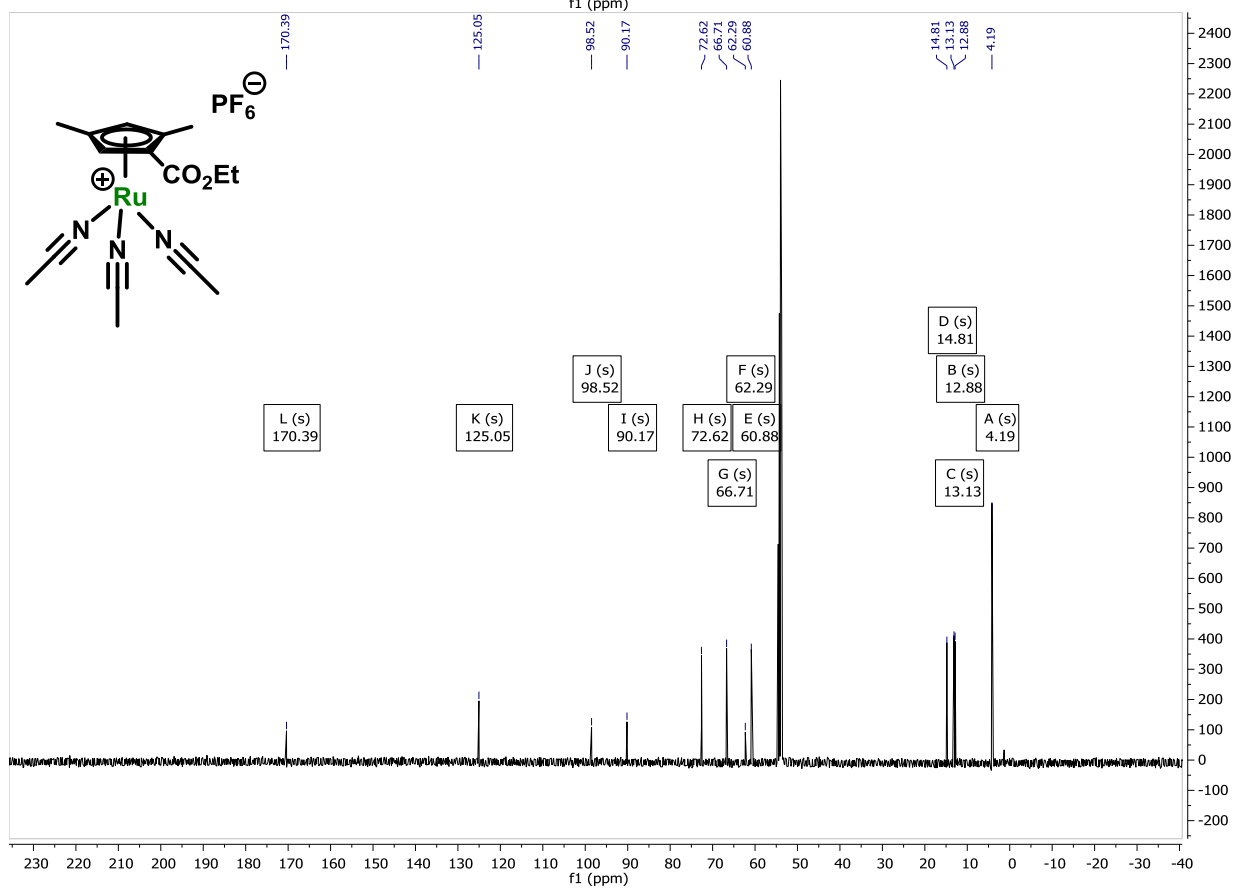
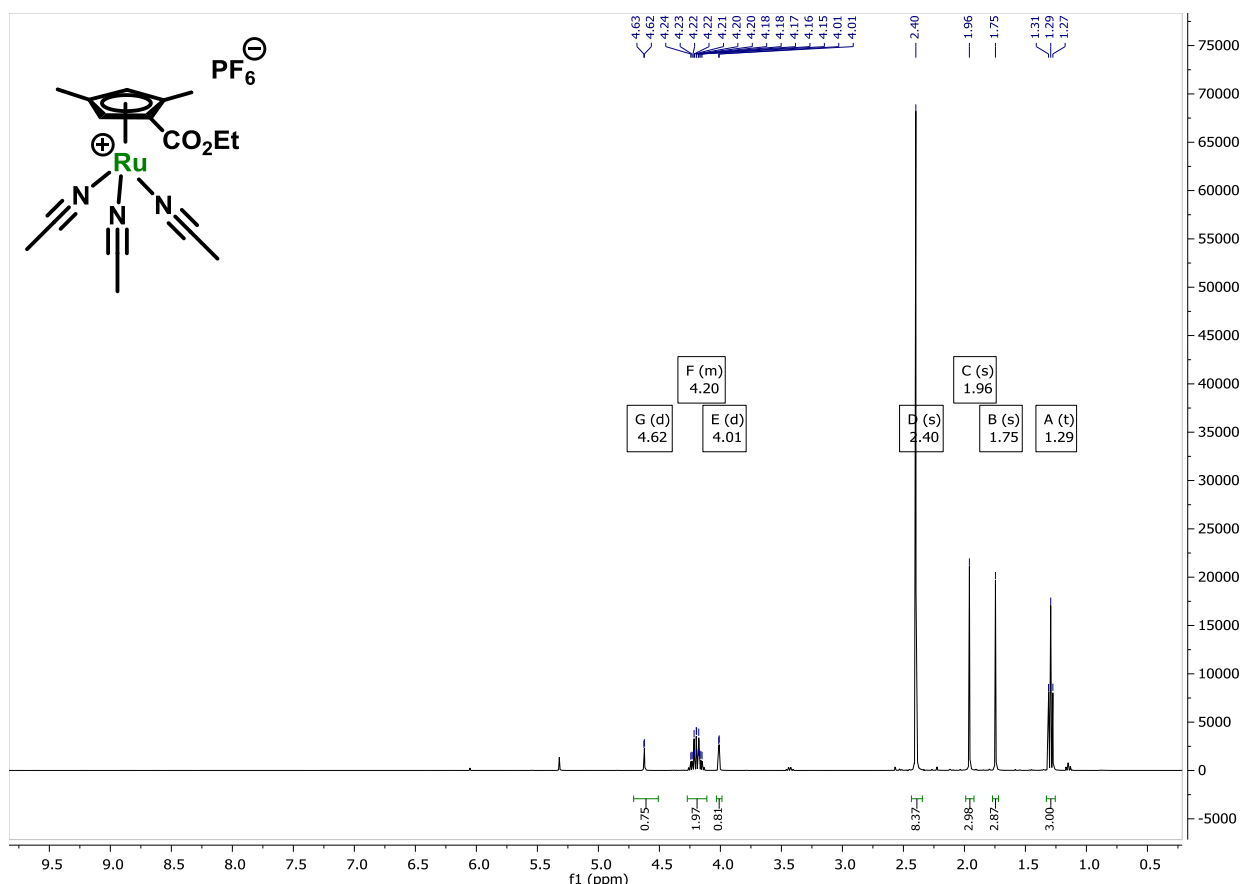
1-Methoxy-1-(prop-1-yn-1-yl)cyclohexane **10** (288 mg, 1.89 mmol, 6 equiv) was added via syringe to a solution of tris(acetonitrile)(η^5 -1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium hexafluorophosphate (**7**) (169 mg, 0.316 mmol, 1 equiv) in CH₂Cl₂ (10 mL). The Schlenk tube was closed with a septum and hydrogen gas was flushed through the solution via canula for 3 min, causing a color change from orange to cherry red. The mixture was stirred for 90 min before it was concentrated to a volume of about 1 mL under high vacuum. Pentane (10 mL) was added quickly to the mixture causing the formation of a dark red oil. The supernatant was removed via a filter canula and the residue was washed pentane (3 x 10 mL) and dried under high vacuum to provide the cationic ruthenium carbene as a dark red foamy, waxy solid that was used for solid-state NMR measurements. *Note: the complex is chiral-at-metal and carries a planar chiral Cp ligand; therefore this ruthenium carbene complex was obtained as a 1.8:1 mixture of diastereomer; their interconversion was confirmed by EXSY (cf. copy of spectrum).*

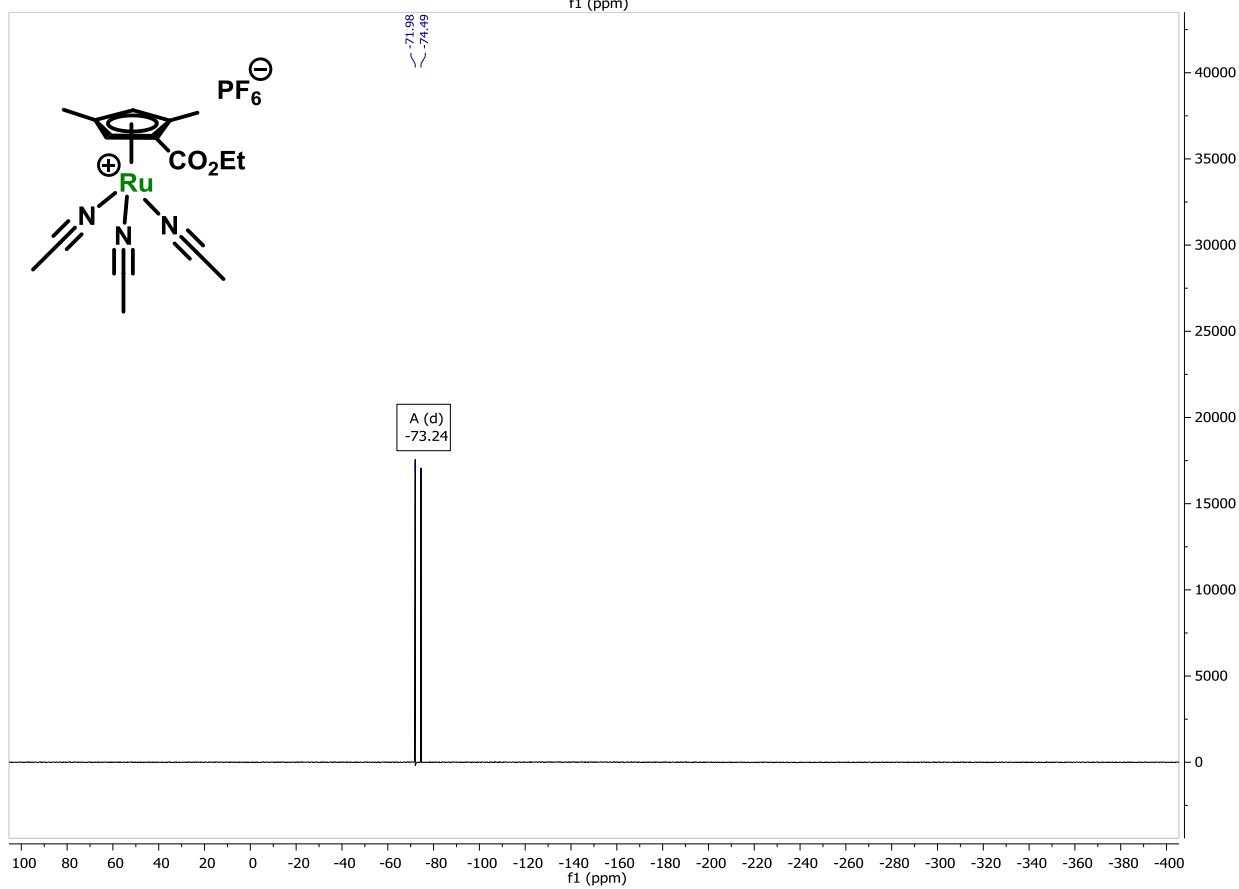
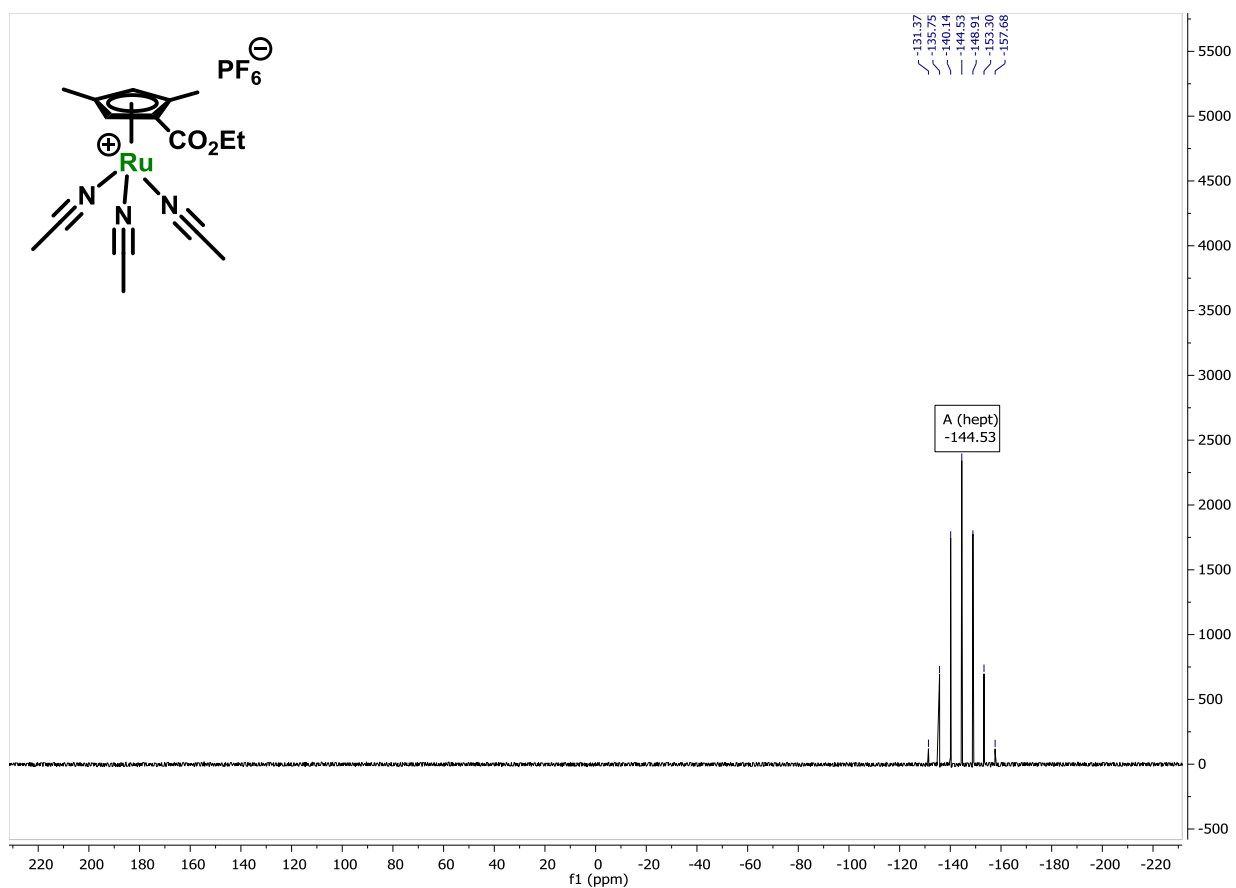
¹H NMR (400 MHz, CD₂Cl₂): δ (major diastereomer) = 5.37 (d, J = 1.7 Hz, 1H), 4.50 (d, J = 1.7 Hz, 1H), 4.26 – 4.17 (m, 2H), 3.61 (s, 3H), 3.02 (s, 3H), 2.75 (d, J = 20.0 Hz, 1H), 2.40 (s, 3H), 2.32 (d, J = 20.0 Hz, 1H), 1.92 (s, 3H), 1.85 – 1.69 (m, 6H), 1.65 (s, 3H), 1.56 – 1.41 (m, 3H), 1.30 – 1.22 (m, 3H), 1.18 – 1.06 (m, 1H). ¹³C NMR (101 MHz, CD₂Cl₂): δ (major diastereomer) = 358.8, 166.8, 133.3, 114.5, 91.5, 85.2, 81.4, 77.0, 72.5, 70.6, 61.0, 58.4, 52.2, 32.9, 32.6, 32.0, 31.5, 25.5, 14.8, 14.0, 13.1, 4.5. ³¹P NMR (162 MHz CD₂Cl₂): δ = –144.63 (hept, J = 706 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = –73.16 (d, J = 711 Hz). HR-MS (ESI+): calcd. for C₁₂H₃₄NO₃Ru [M]⁺ 462.157720, found: 462.15767.

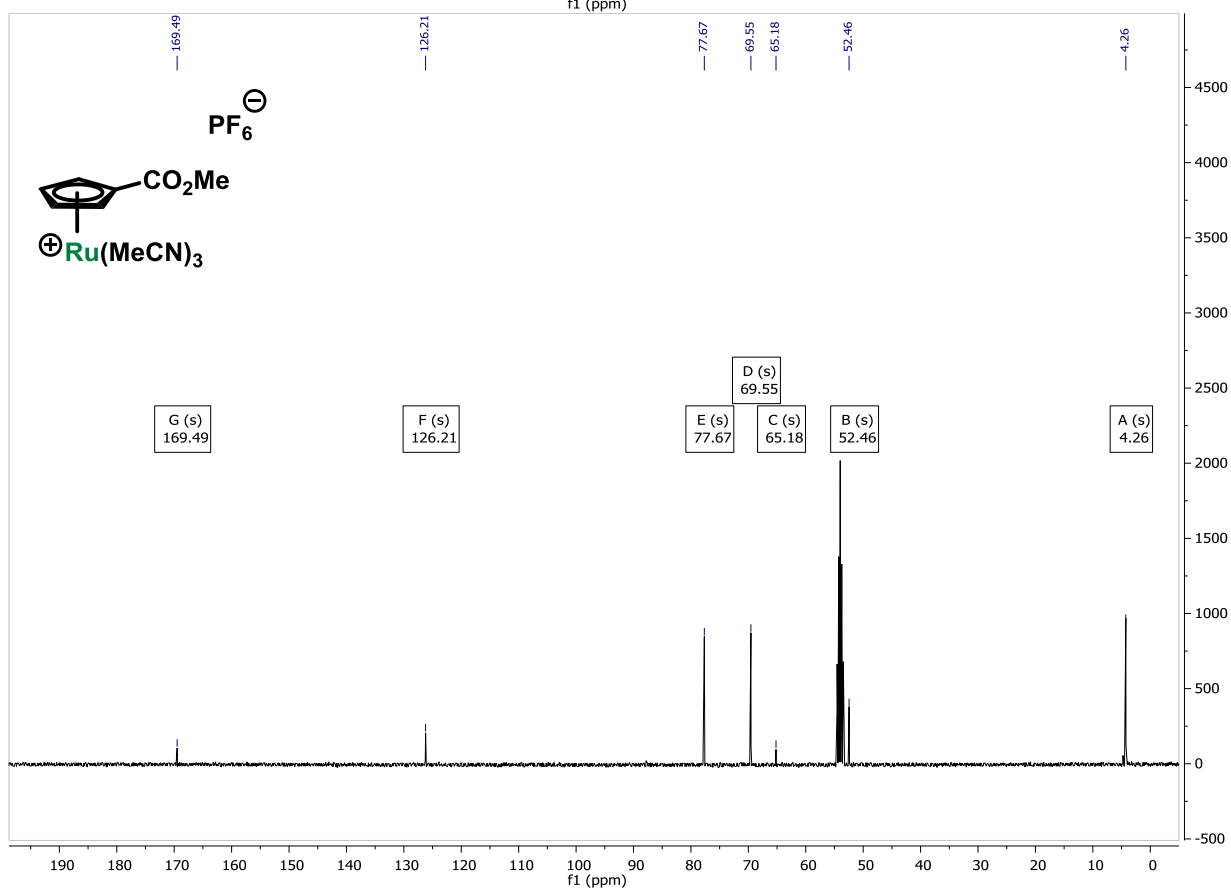
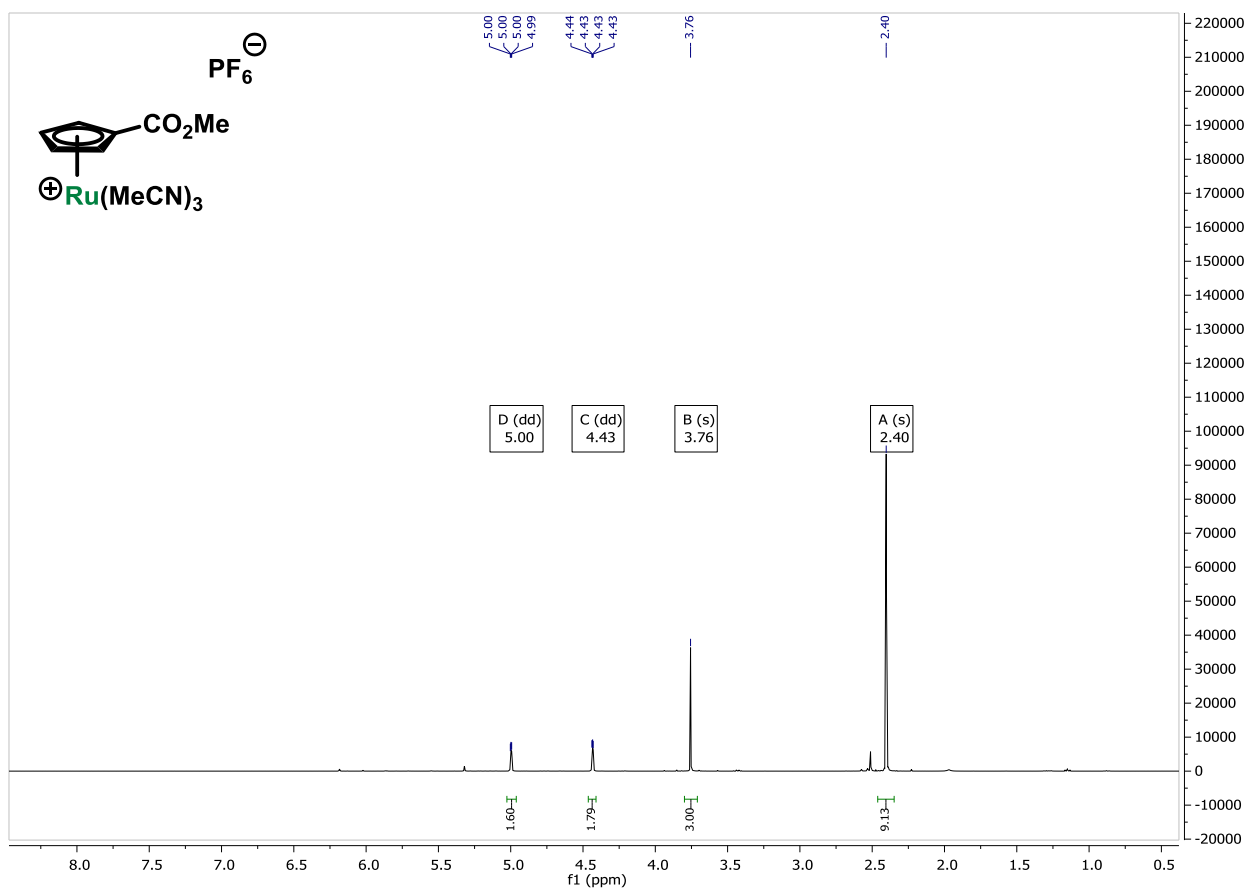
Characteristic signal of the minor diastereomer: δ_c = 351.9 ppm

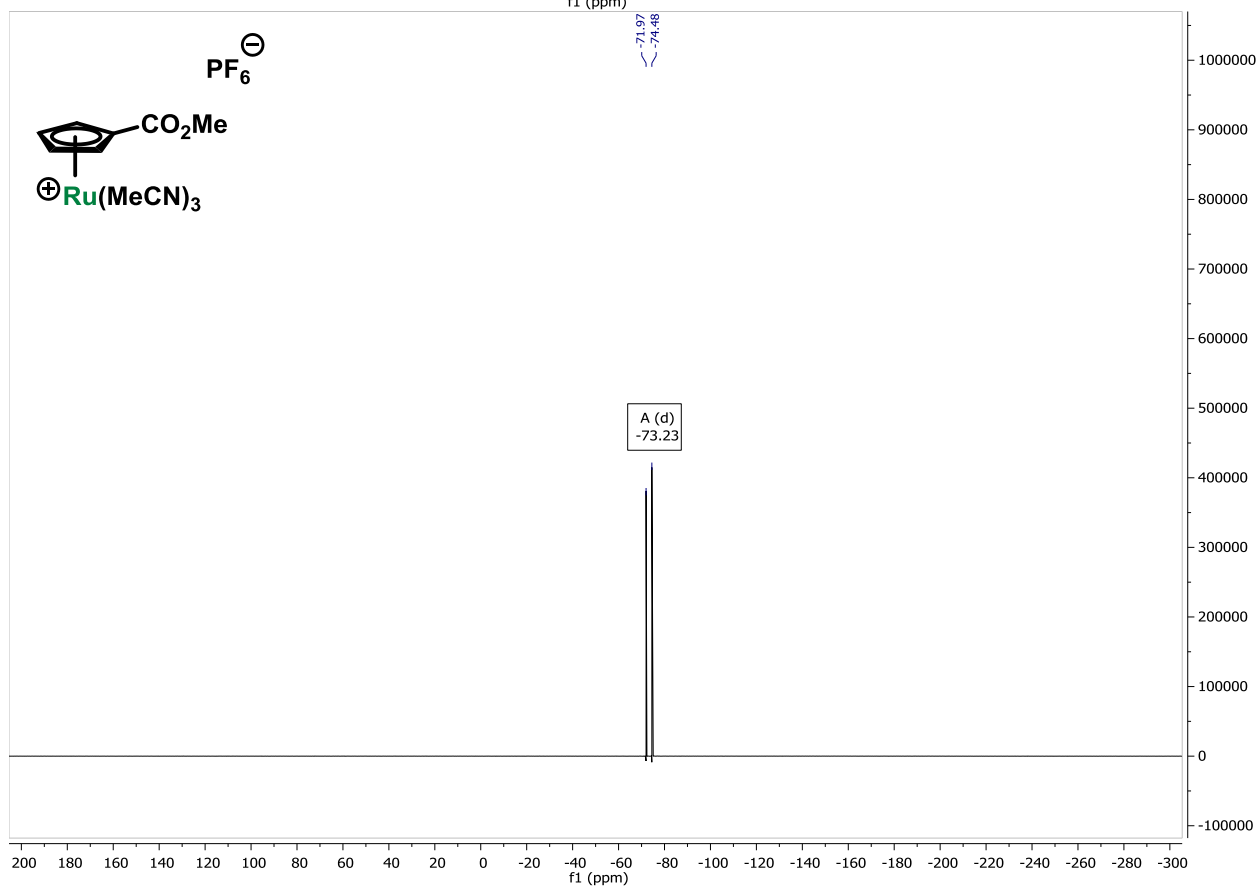
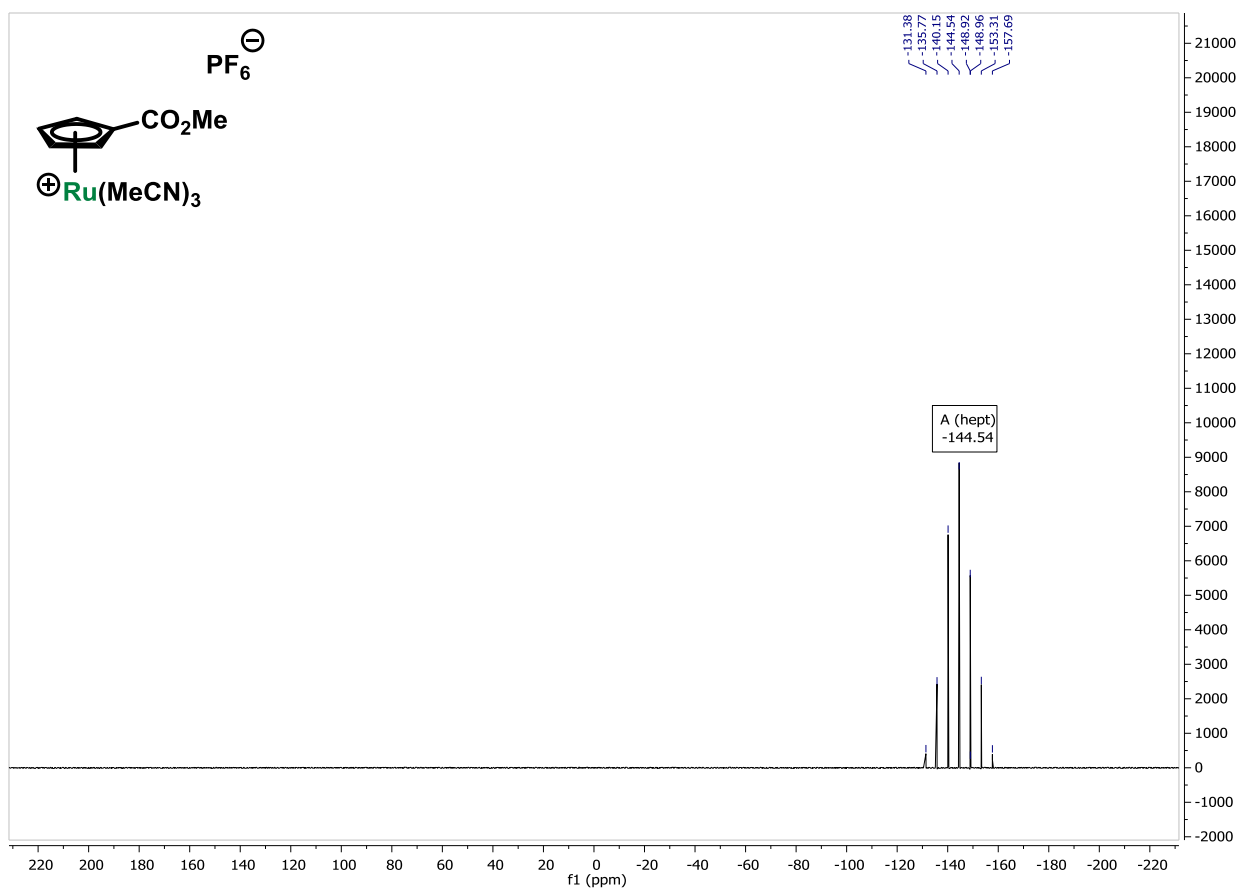


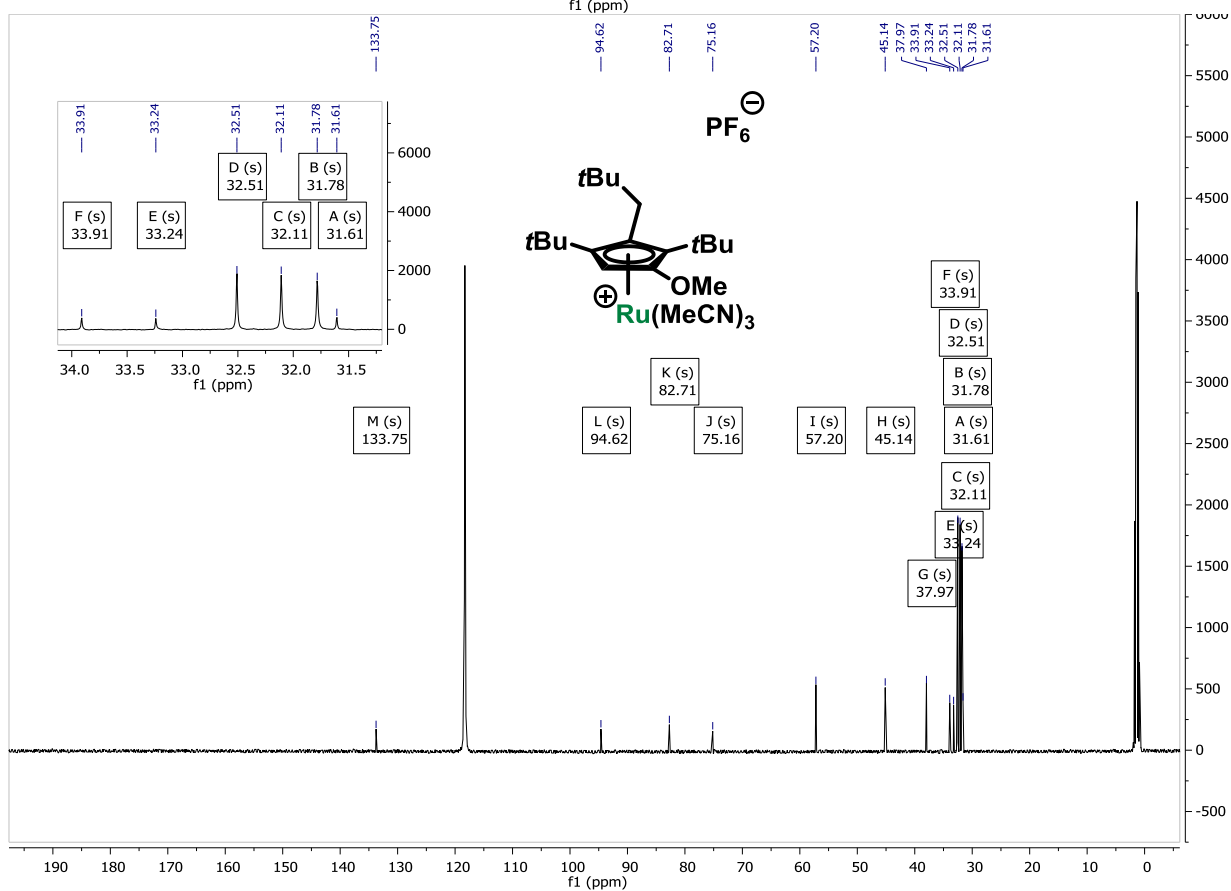
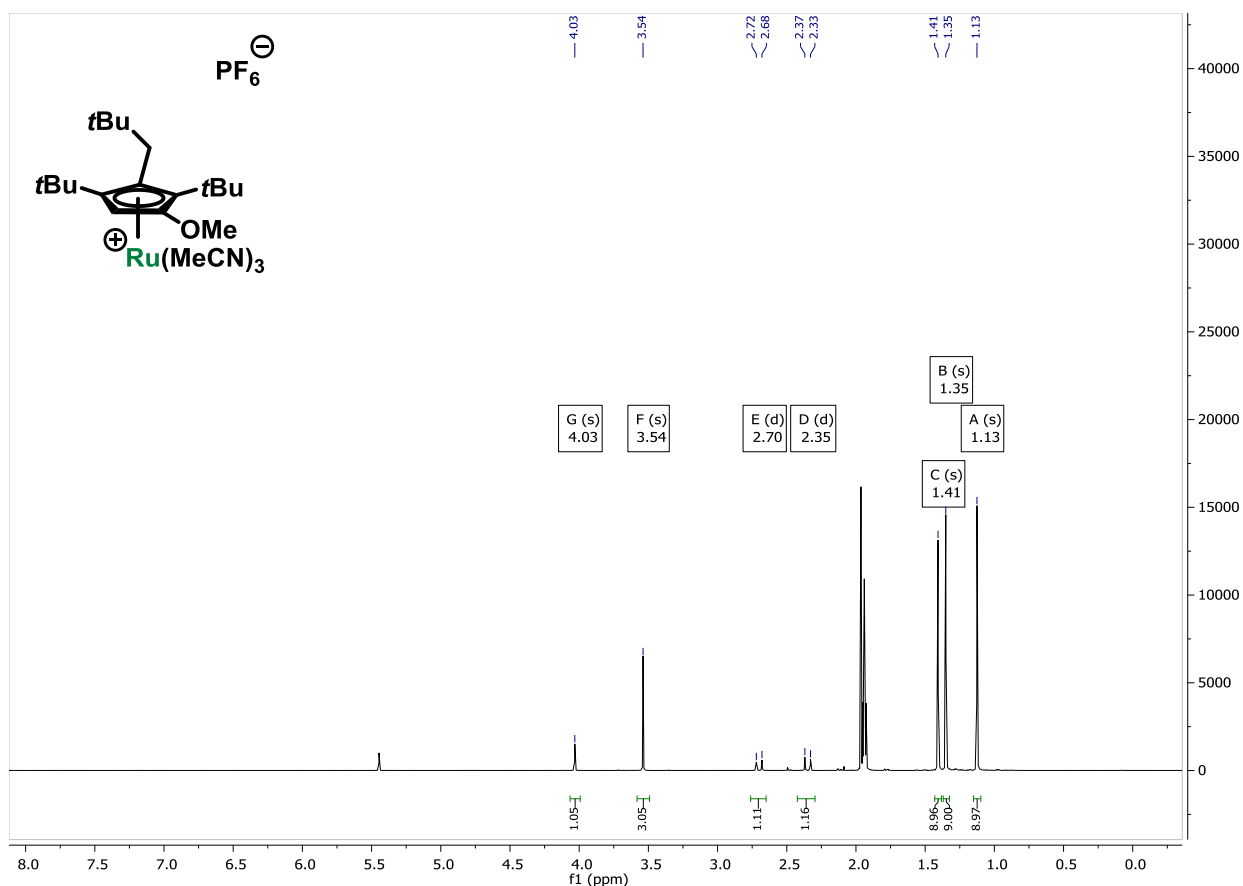


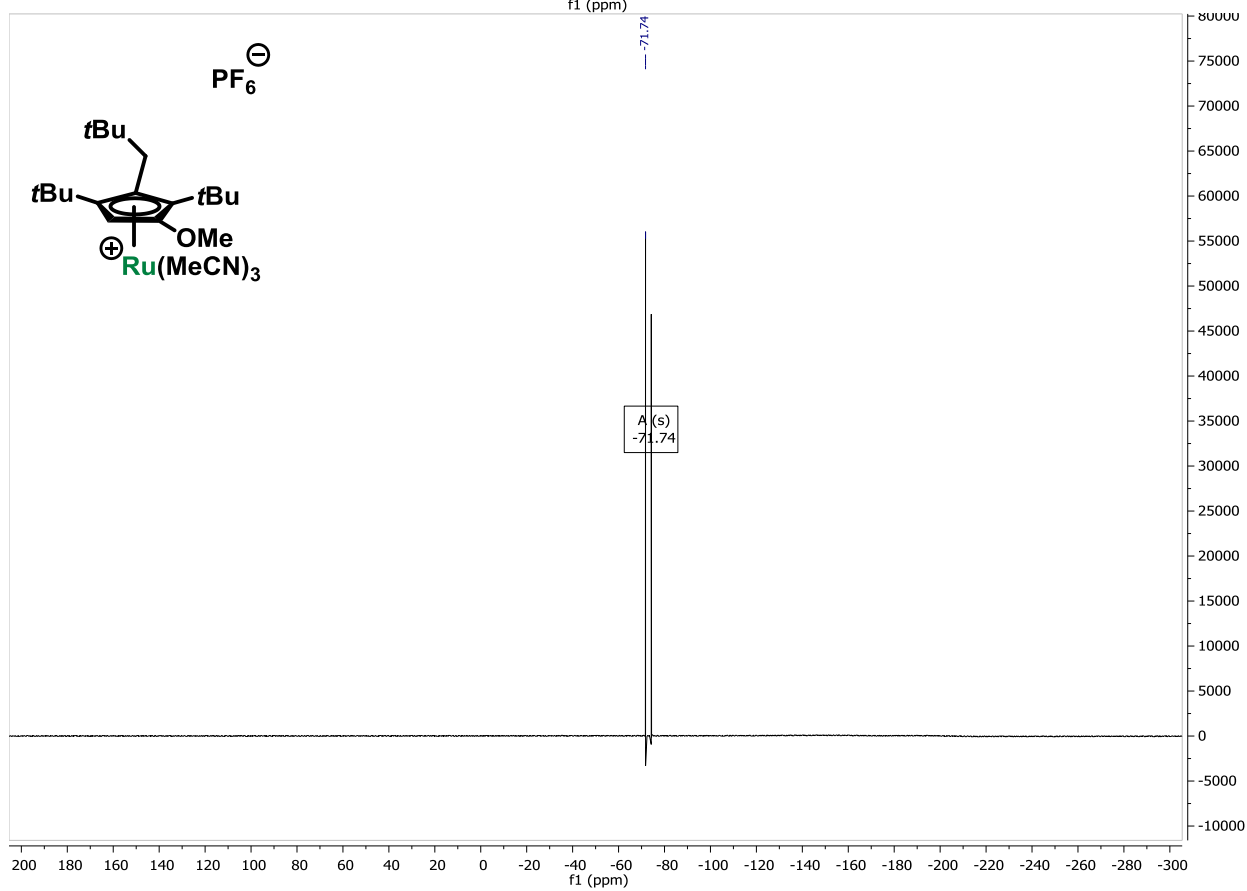
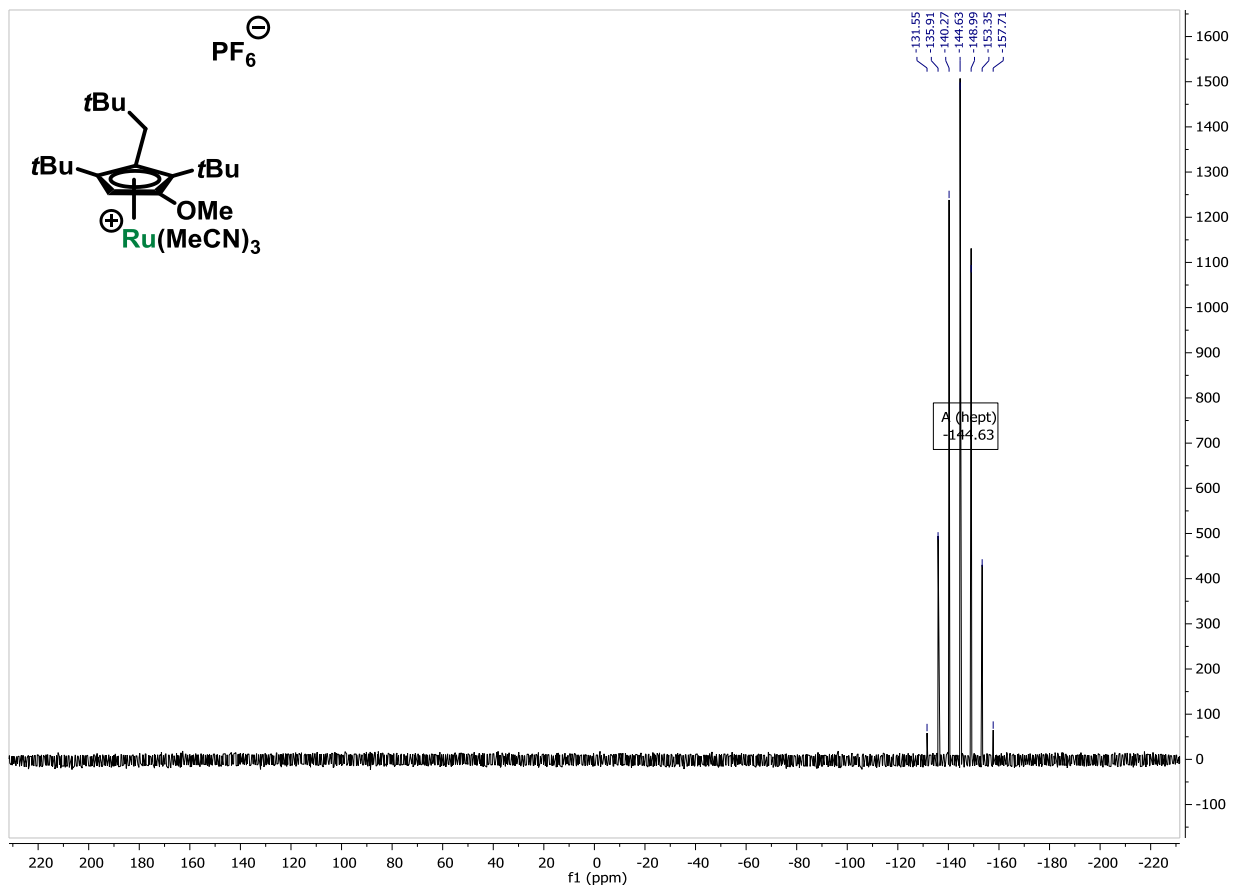


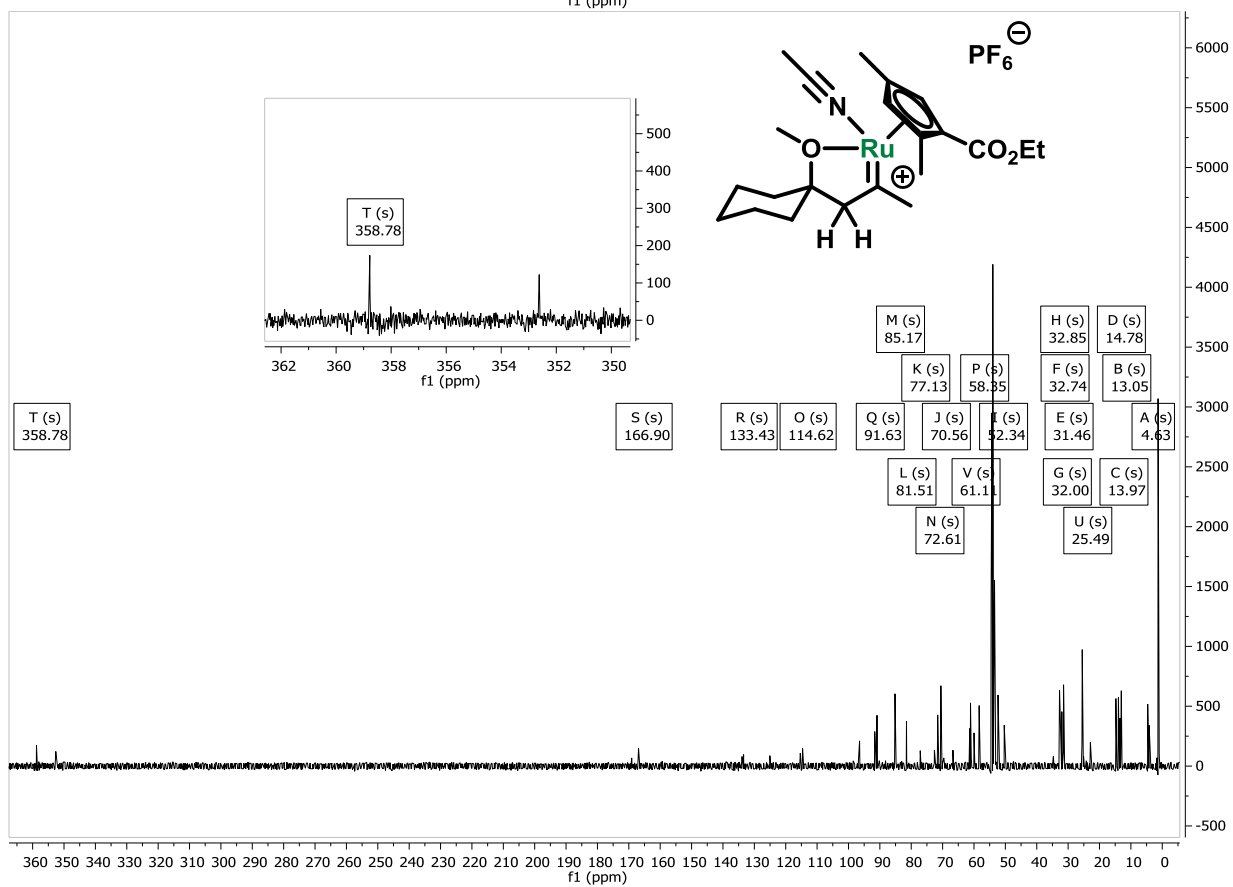
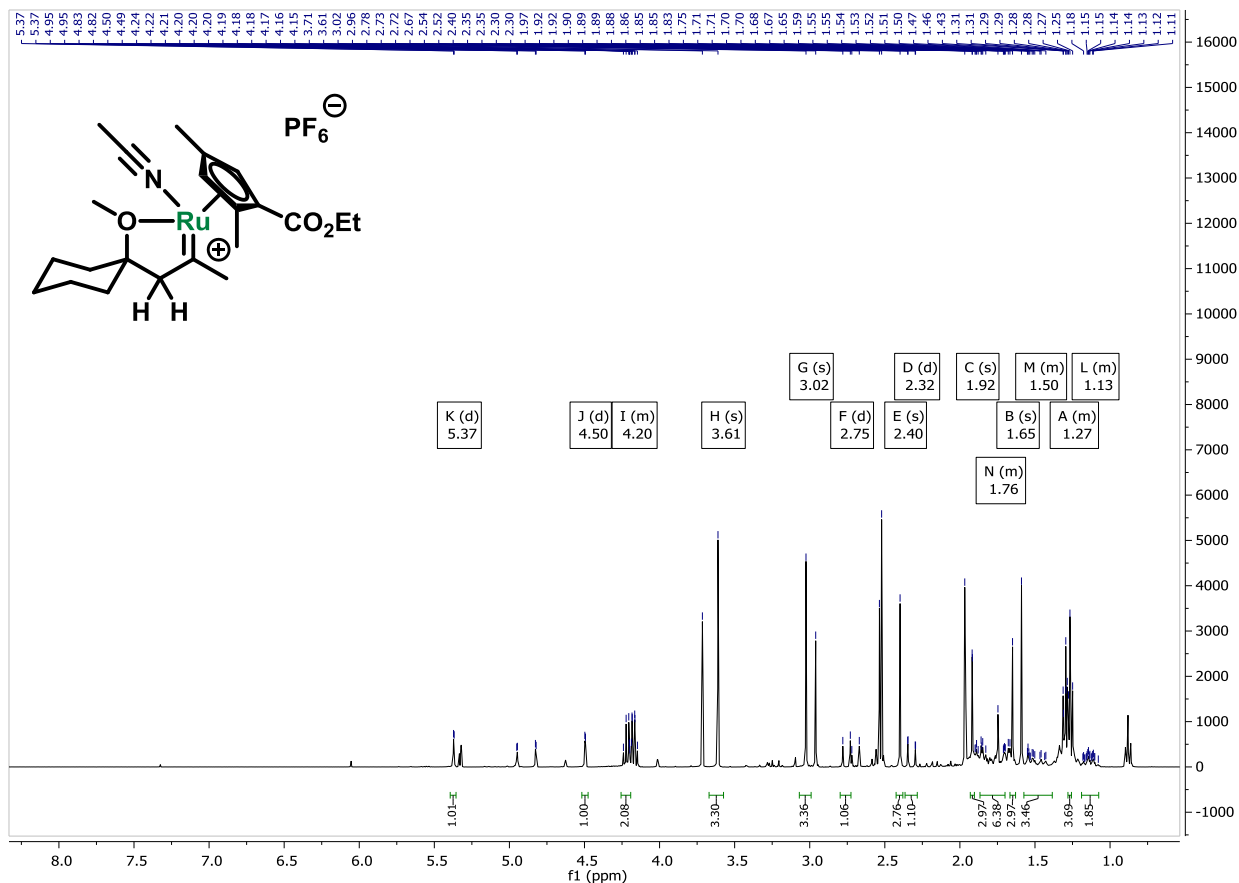


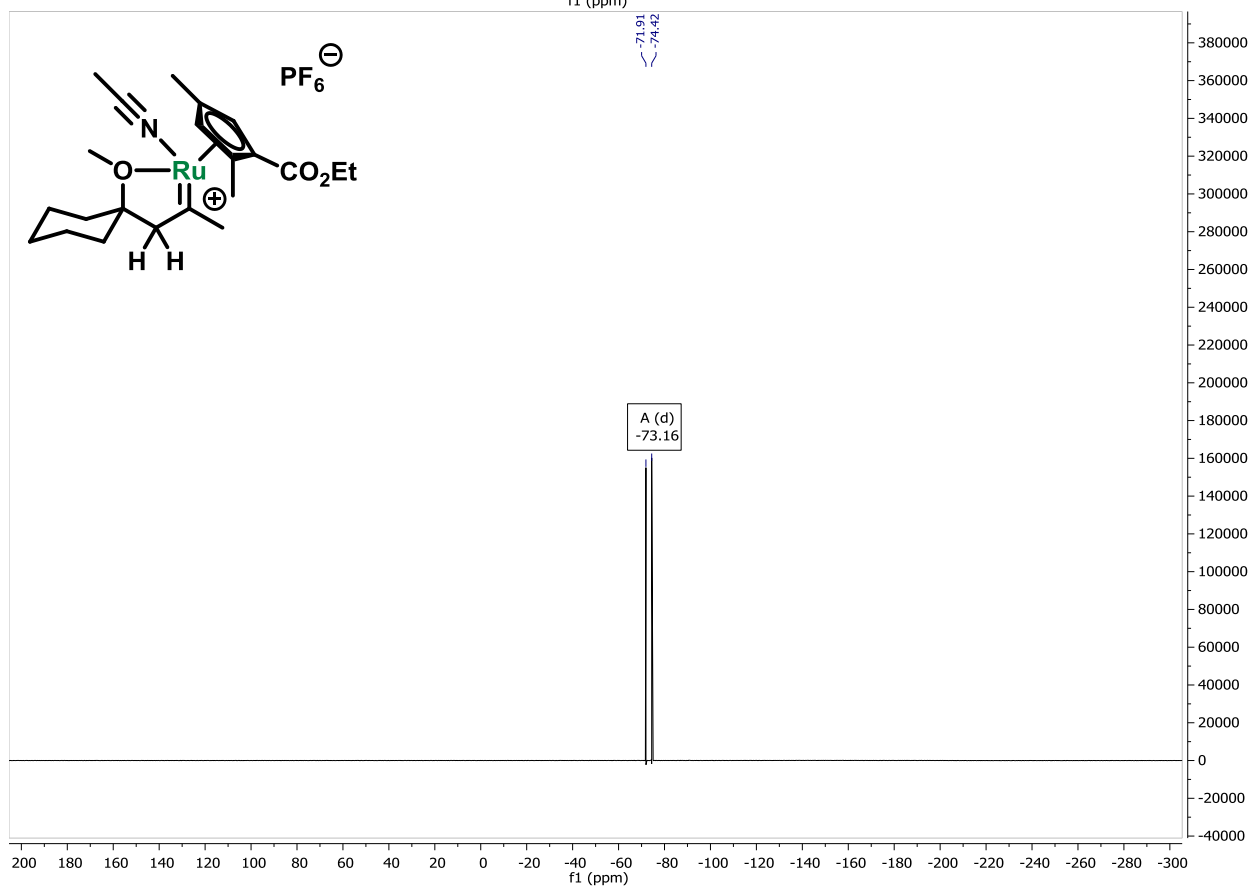
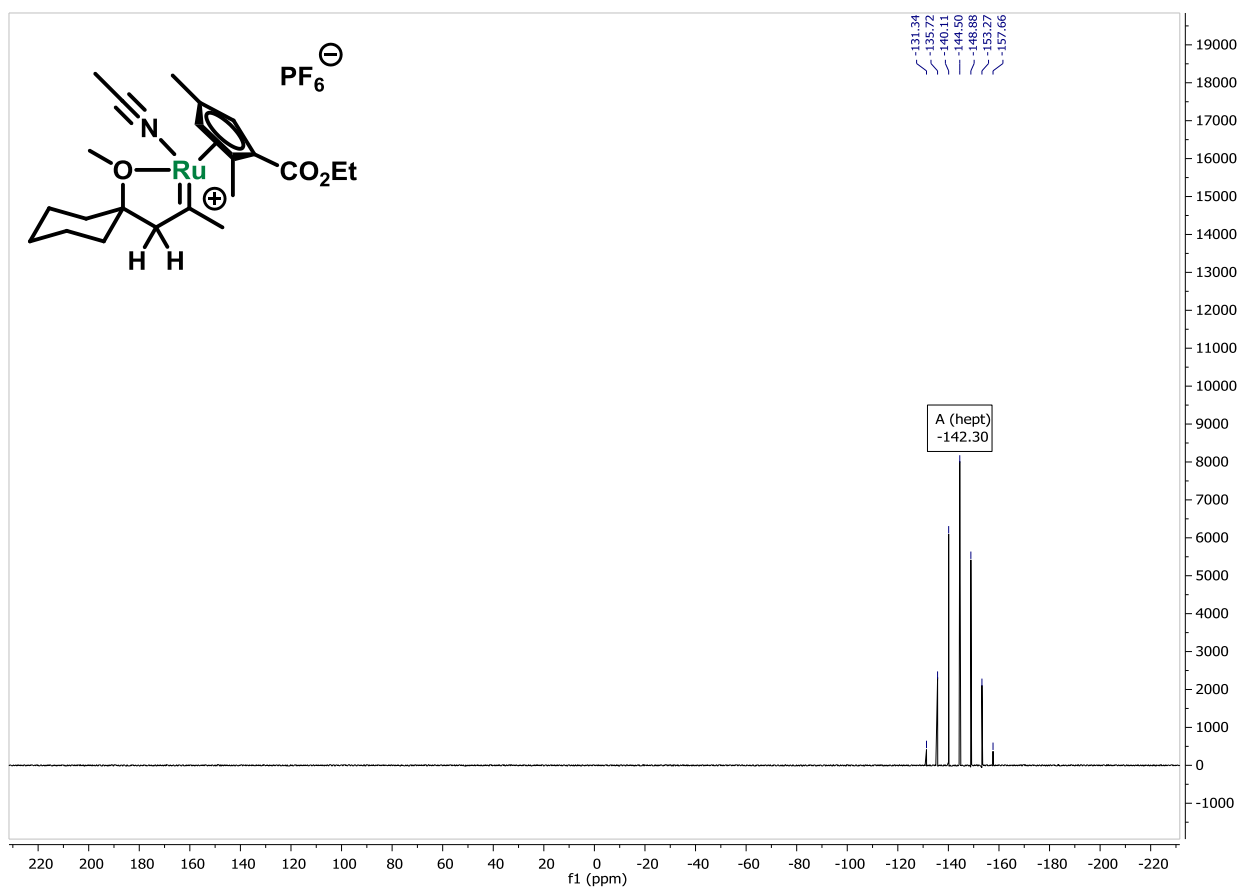


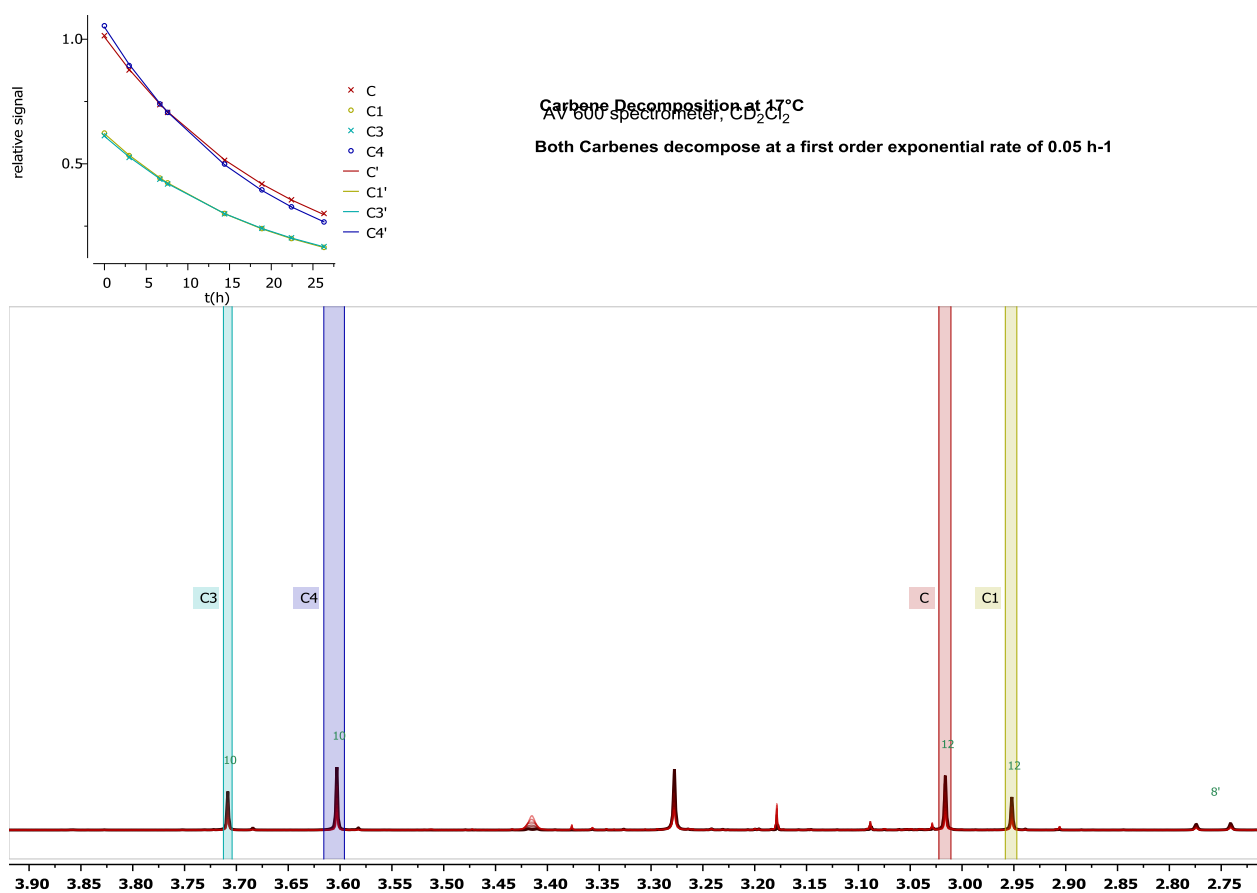




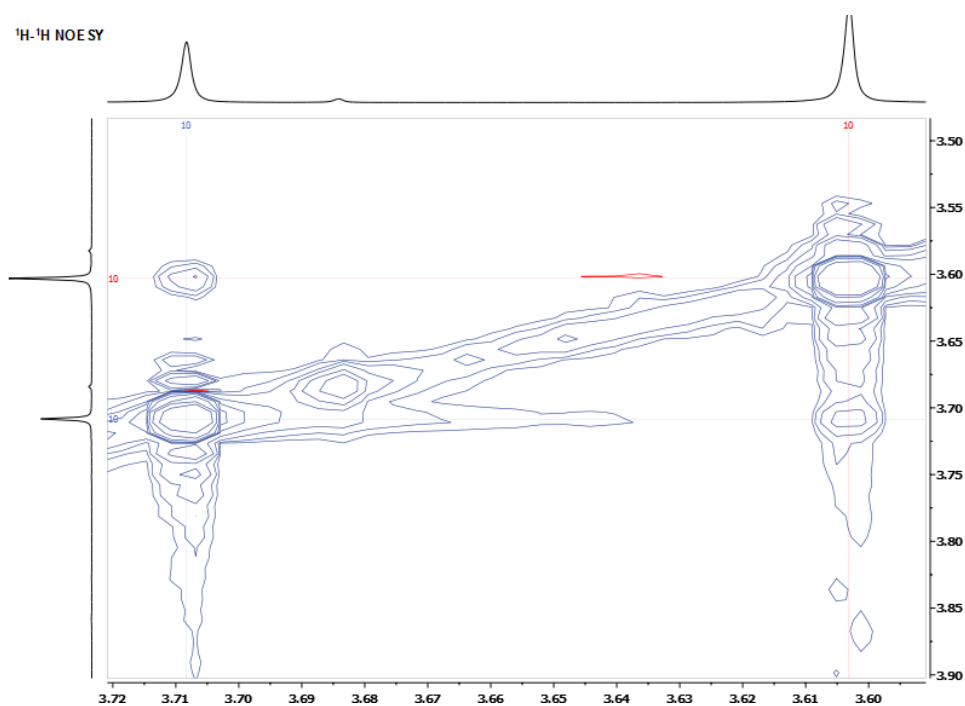








the diastereomeric carbenes interconvert as evident from EXSY cross peaks:



Solid-State NMR Measurements

The solid-state ^1H and ^{13}C NMR spectra were obtained on Bruker Avance III 600 MHz spectrometer at 100 K, using a 3.2 mm probe, and the magnetic fields were externally referenced by setting the downfield ^{13}C signal of adamantane to 38.4 ppm. The samples were loaded in a 3.2 mm sapphire rotor closed with a zirconia cap with a Teflon insert placed between the sample and the cap.

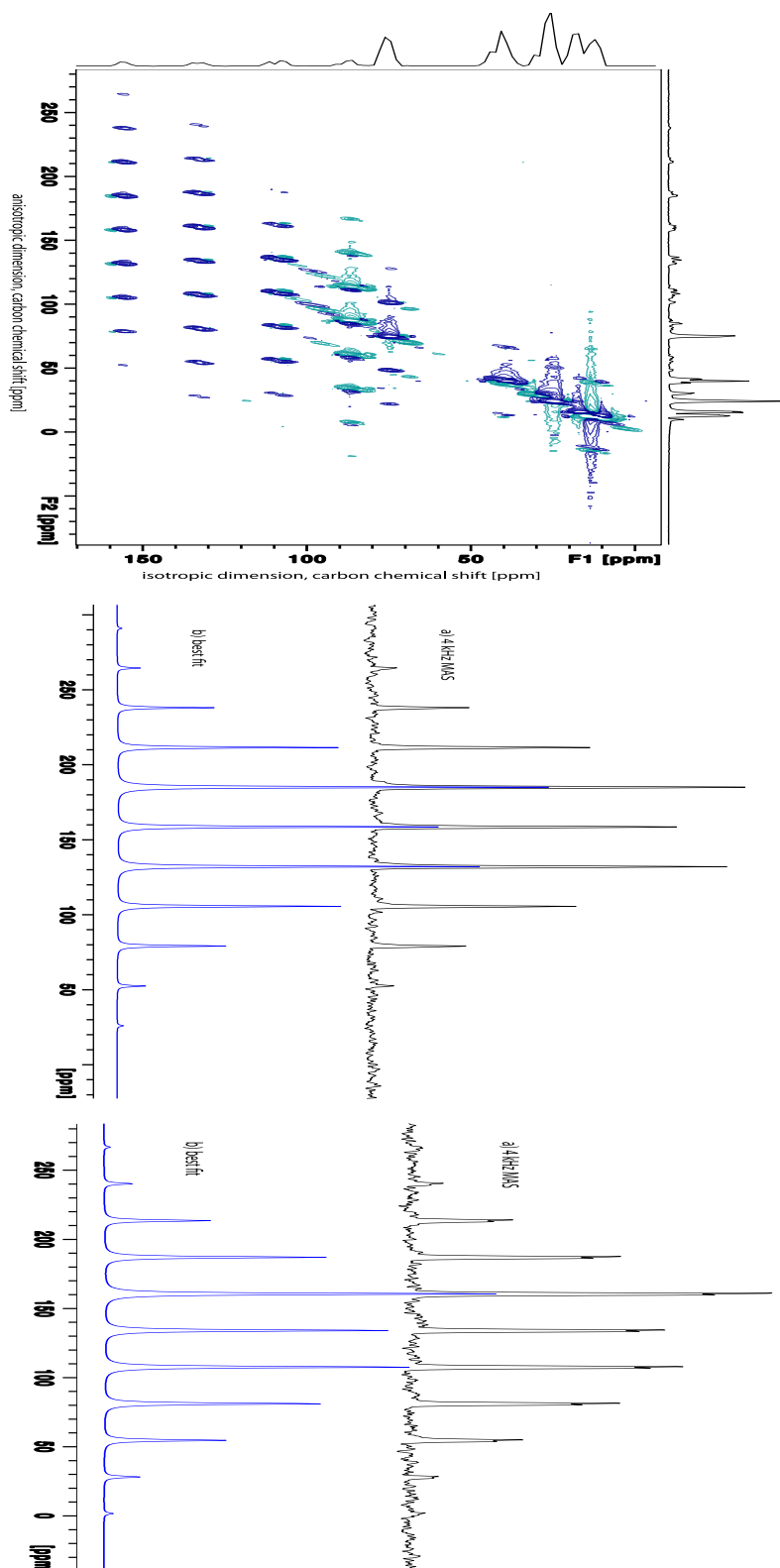
Cross polarization magic angle spinning (CPMAS) and spin echo type experiments were used to measure ^{13}C and ^1H spectra, respectively. The ^1H excitation and decoupling radiofrequency (rf) fields were set to 100 kHz. For CPMAS measurements, the CP condition was optimized to match the Hartmann-Hahn condition under MAS with minor adjustments to reach the best CP efficiency experimentally. For measurements of the chemical shift anisotropy, CP-MAT (magic angle turning) experiments were used.¹³

Computational Details

All geometry optimizations were performed with the Gaussian09 package¹⁴ with the PBE0 functional¹⁵. Ru represented by the quasi-relativistic effective core potential (RECP) from the Stuttgart group and the associated basis sets.^{16,17,18} The remaining atoms (H, C, O, Cl) were represented by a triple- ζ pcseg-2 basis set.¹⁹ NMR calculations were performed within the GIAO framework using ADF 2014²⁰ with the PBE0 functional and Slater-type basis sets of triple- ζ quality (TZ2P), with the exception of carbene species, for which a basis set of double- ζ quality was used (DZ). Relativistic effects were treated by the 2 component zeroth order regular approximation (ZORA).²¹ Analysis of scalar-relativistic natural localized molecular orbitals were done with the NBO 6.0 program.²² Calculated NMR shielding tensors were analyzed using these scalar-relativistic NLMO.^{23,24} The 3D representation of the calculated shielding tensors were obtained as polar plots²⁵ of functions $\sum_{ij} r_i \sigma_{ij} r_j$.

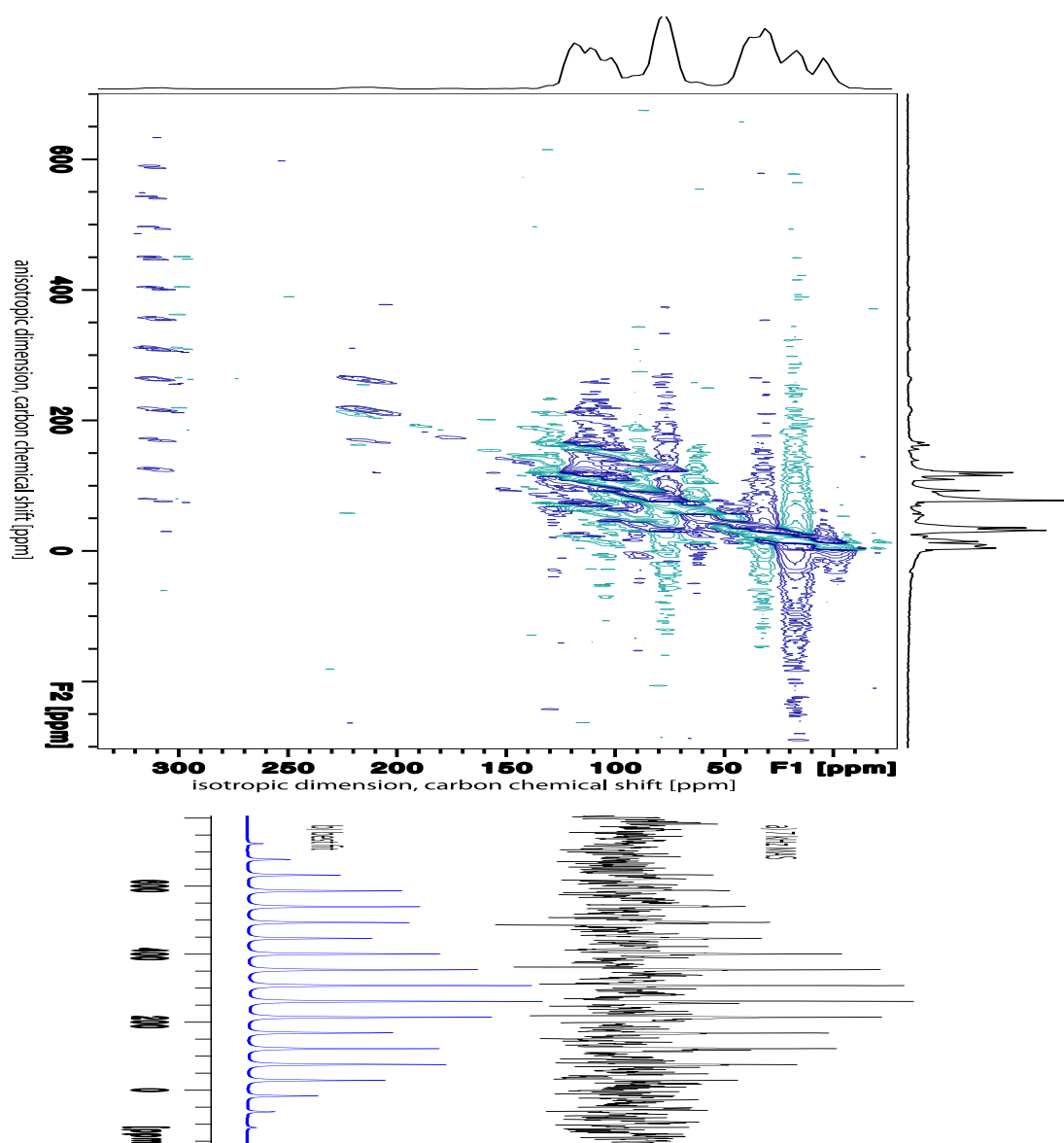
Solid-State NMR Spectra

Ru-Alkyne Complex **14**



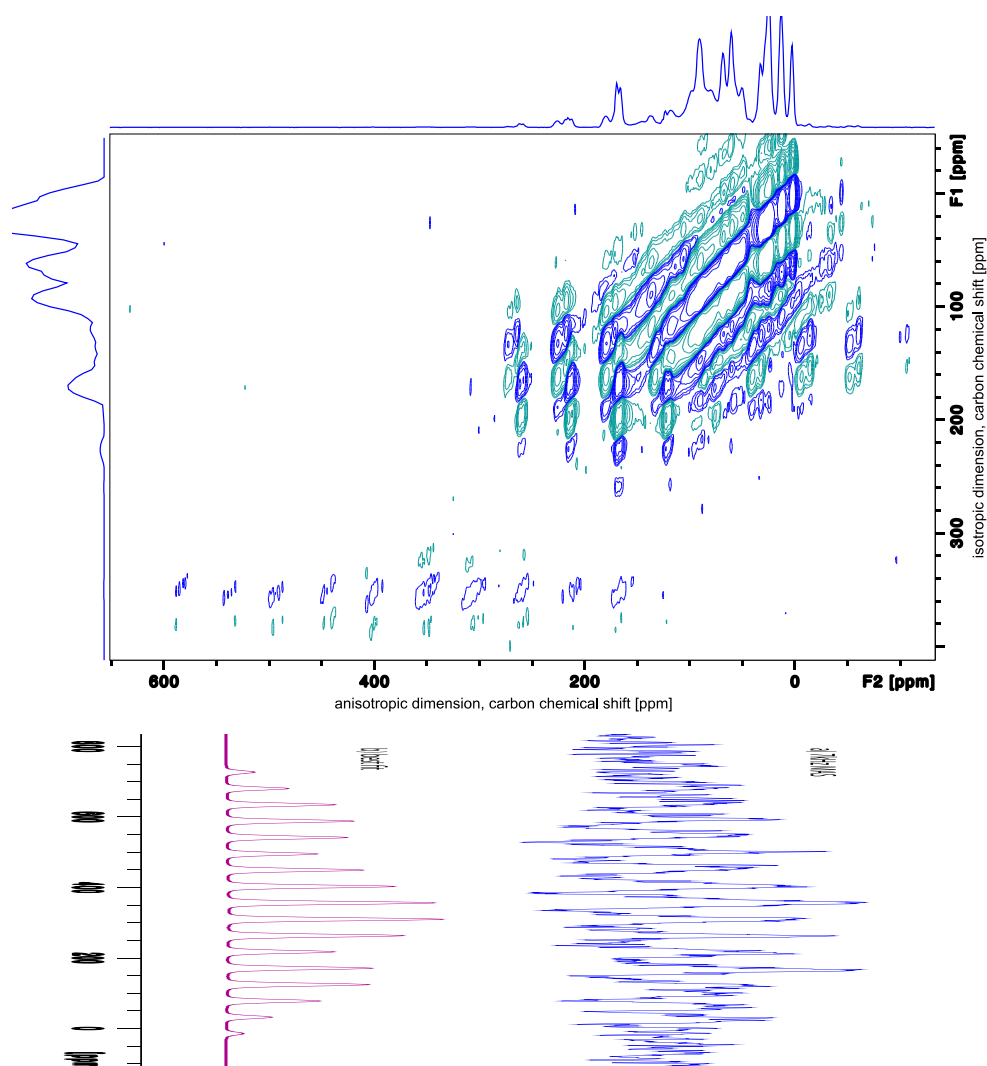
(Top) CP-MAT (14.1 T, 100 K) spectrum of Ru-alkyne complex **14** measured at a spinning rate of 4 kHz (128 scans per t_1 increment, 357 t_1 increments, 1.4 s recycle delay, 2000 ms CP contact time). (Middle) Slice of C1-carbon atom and best fit. (Bottom) Slice of C2-carbon atom and best fit.

Ru-Carbene Complex 17



(Top) CP-MAT (14.1 T, 100 K) spectrum of the neutral Ru-carbene complex **17** measured at a spinning rate of 7 kHz (1024 scans per t_1 increment, 119 t_1 increments, 1.4 s recycle delay, 2500 ms CP contact time). (Bottom) Slice of carbene-carbon atom and best fit.

Cationic Ru-Carbene Complex 18



(Top) CP-MAT (14.1 T, 100 K) spectrum of the neutral Ru-carbene complex **17** measured at a spinning rate of 7 kHz (1024 scans per t_1 increment, 55 t_1 increments, 1 s recycle delay, 2000 ms CP contact time). (Bottom) Slice of carbene-carbon atom and best fit. The very low intensity of this signal renders an accurate fitting difficult. However, the measured spectrum allows to probe the highly anisotropic nature of the carbene-carbon atom and hence to at least in part validate the results obtained from DFT calculations.

Measured and Calculated Chemical Shift Values

The following table gives all calculated isotropic chemical shift values, as well as the principal components of the corresponding chemical shift tensors. Experimentally obtained values are given in parenthesis. All values are reported in ppm.

compound – site	δ_{iso}	δ_{11}	δ_{22}	δ_{33}
alkyne 10 – C1	94 (84)	189	181	-89
alkyne 10 – C2	91 (80)	168	162	-57
Ru-alkyne 14 – C1	170 (159)	264 (246)	172 (163)	75 (66)
Ru-alkyne 14 – C2	145 (130)	249 (227)	145 (141)	40 (35)
Ru-alkyne-H ₂ 15 – C1	91	237	114	-77
Ru-alkyne-H ₂ 15 – C2	73	209	86	-75
Ru-cyclopropene 16 – C1	332	645	263	88
Ru-cyclopropene 16 – C2	44	91	25	16
Ru-carbene 17	307 (307)	697 (683)	273 (281)	-49 (-42)
Ru-carbene cation 18	367 (357)	750 (727)	334 (329)	13 (15)

Results of Natural Chemical Shielding (NCS) Analysis

All values in the following tables are reported in ppm.

	σ_{xx}	σ_{dia}	σ_{para}	$\sigma(\text{C-C})$	components of σ_{para}		
					$\pi(\text{C-C})$	$\pi(\text{C-C})'$	$\sigma(\text{C-C}')$
alkyne 10 – C1 (σ_{11})	12	259	-247	-121	-17	0	-84
alkyne 10 – C2 (σ_{11})	26	248	-222	-120	0	9	-94
alkyne 10 – C1 (σ_{22})	19	259	-240	-116	0	-22	-79
alkyne 10 – C2 (σ_{22})	34	249	-215	-117	8	0	-91
alkyne 10 – C1 (σ_{33})	272	280	-8	1	0	-9	0
alkyne 10 – C2 (σ_{33})	241	280	-39	0	-24	-12	0

	σ_{xx}	σ_{dia}	σ_{para}	$\sigma(\text{C-C})$	components of σ_{para}		
					$\pi(\text{C-C})$	$\sigma(\text{C-C})'$	$\sigma(\text{Ru-C})$
Ru-alkyne 14 – C1 (σ_{11})	-73	252	-325	-163	-40	-52	-46
Ru-alkyne 14 – C2 (σ_{11})	-58	249	-307	-170	-17	-96	0
Ru-alkyne 14 – C1 (σ_{22})	19	263	-244	-3	-38	-76	-122
Ru-alkyne 14 – C2 (σ_{22})	46	263	-217	-7	-4	-35	-155
Ru-alkyne 14 – C1 (σ_{33})	116	241	-125	-57	0	-39	-1
Ru-alkyne 14 – C2 (σ_{33})	151	237	-87	-43	3	-41	4

	σ_{xx}	σ_{dia}	σ_{para}		components of σ_{para}		
				$\sigma(C-C)$	$\pi(C-C)$	$\pi(C-C)'$	$\sigma(C-C')$
Ru-alkyne- H_2 15 – C1 (σ_{11})	-46	251	-297	-153	-26	-4	-82
Ru-alkyne- H_2 15 – C2 (σ_{11})	-18	251	-269	-140	-19	-5	-80
Ru-alkyne- H_2 15 – C1 (σ_{22})	77	238	-161	-64	-3	-16	-69
Ru-alkyne- H_2 15 – C2 (σ_{22})	105	237	-132	-71	-8	-5	-51
Ru-alkyne- H_2 15 – C1 (σ_{33})	268	265	3	2	10	-1	-21
Ru-alkyne- H_2 15 – C2 (σ_{33})	266	264	2	0	4	8	-21

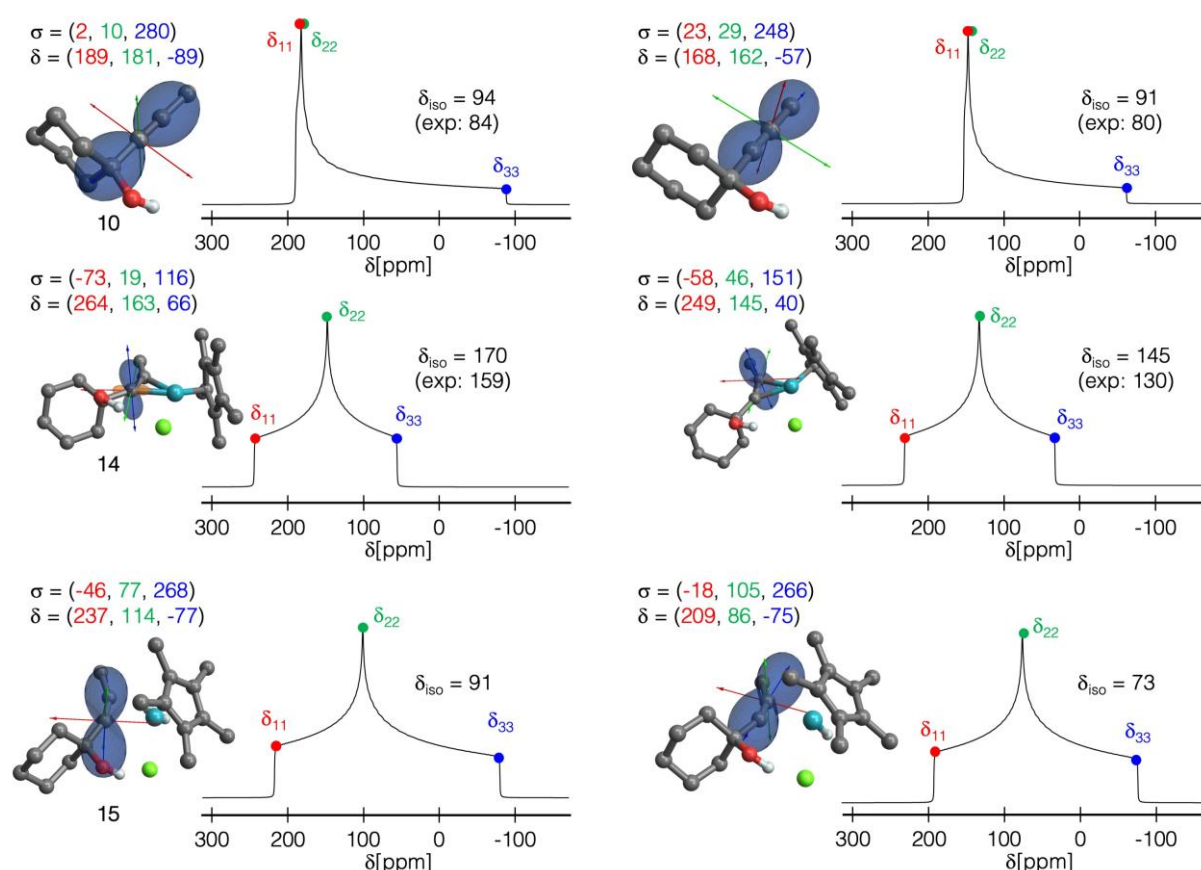
	σ_{xx}	σ_{dia}	σ_{para}		components of σ_{para}		
				$\sigma(M-C)$	$\pi(M-C)$	$\sigma(C-C)'$	$\sigma(C-C')$
Ru-cyclopropene 16 – C1 (σ_{11})	-454	256	-710	-274	-233	-57	-53
Ru-cyclopropene 16 – C1 (σ_{22})	-72	246	-317	21	3	-200	-134
Ru-cyclopropene 16 – C1 (σ_{33})	103	237	-134	7	-11	-35	-51

	σ_{xx}	σ_{dia}	σ_{para}		components of σ_{para}		
				$\sigma(C-C)$	$\pi(C-C')$	$\sigma(C-H)$	LP(C)
Ru-cyclopropene 16 – C2 (σ_{11})	100	241	-141	-14	-54	-44	-3
Ru-cyclopropene 16 – C2 (σ_{22})	166	228	-62	-27	-19	-12	-2
Ru-cyclopropene 16 – C2 (σ_{33})	175	220	-45	-10	1	-13	-22

	σ_{xx}	σ_{dia}	σ_{para}		components of σ_{para}		
				$\sigma(M-C)$	$\pi(M-C)$	$\sigma(C-C)'$	$\sigma(C-C')$
Ru-carbene 17 (σ_{11})	-487	251	-737	-410	-159	-63	-63
Ru-carbene 17 (σ_{22})	-63	241	-304	20	-18	-141	-167
Ru-carbene 17 (σ_{33})	259	219	40	13	20	-23	-17

	σ_{xx}	σ_{dia}	σ_{para}		components of σ_{para}		
				$\sigma(M-C)$	$\pi(M-C)$	$\sigma(C-C)'$	$\sigma(C-C')$
Ru-carbene cation 18 (σ_{11})	-540	250	-790	-504	-100	-82	-68
Ru-carbene cation 18 (σ_{22})	-124	243	-367	6	0	-177	-181
Ru-carbene cation 18 (σ_{33})	197	223	-27	-3	12	-36	-28

Graphical Representation of Chemical Shift Tensors in the Free Alkyne, **14** and **15**



The figure above shows the calculated chemical shift and shielding tensors and simulated static NMR spectra (powder pattern) of the C1 (left) and C2 (right) atom in the free alkyne **10** (top), the Ru-alkyne complex **14** (middle) and the “loaded” catalyst **15** (bottom). The free alkyne (top) shows almost axially symmetric tensors with deshielded δ_{11} and δ_{22} components, and a shielded δ_{33} component which is oriented along the C-C axis as expected for this type of molecule. Upon coordination to Ru (complex **14**, middle), the tensor orientation and the principal components change. Most notably, the direction along the C-C axis (now δ_{22}) is no longer strongly deshielded. As seen by the NCS analysis, this direction is now significantly deshielded by a contribution from the $\sigma(\text{Ru-C})$ bond, illustrative of the metal-alkyne interaction. Upon coordination of H_2 (complex **15**, bottom), the strong shielding along the C-C axis is restored (δ_{33}), reminiscent of the free alkyne. However, the chemical shift tensor of **15** is not axially symmetric: The δ_{11} component is more deshielded than in the free alkyne **10**, while the δ_{22} component is less deshielded, leading to a similar isotropic chemical shift in **10** and **15**. Hence, even though the alkyne ligand in **15** is somewhat reminiscent of a free alkyne, a significant perturbation of its electronic structure by the metal can be evidenced in the principal components of the chemical shift tensor

References

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