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Electronic Supporting Information

Second-coordination sphere effects on reactivities of Hoveyda–Grubbs-type catalysts: A ligand exchange study using phenolic moiety-functionalized ligands

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CONTENTS

1. Experimental details

Materials and Instruments. Hoveyda-Grubbs 2nd generation catalyst (HG-II(**1**)) Grubbs 2nd catalyst (**24**) were purchased from Sigma-Aldrich. 2-Alkoxybenzylidene ligands and the corresponding Ru complexes were synthesized by the methods described below. Substrate compounds for the evaluation of metathesis activities (compounds **25**,[1] **27**,[2] and **29**[3]) and ligand **^{i}Pr-L**[4] were synthesized by previously reported methods. For purification of Ru complexes, silica gel-60N (particle size: 63–210 μm; Kanto Chemical Co., Inc, Japan) was used. Other chemicals and column supports were obtained from conventional vendors and used as received unless noted.

NMR spectra were recorded on a JEOL ECP-400 MHz NMR spectrophotometer. Chemical shifts are reported with relative to tetramethylsilane (TMS, δ = 0 ppm) or residual unlabeled solvent in chloroform (δ = 7.26 ppm (for ^{1}H-NMR) or 77.16 ppm (for ^{13}C-NMR)). Mass spectral analyses were conducted using a JEOL spiralTOF JMS-S3000 spectrometer (for Matrix-assisted later desorption ionization mass spectral analysis (MALDI-MS)) or a JEOL JMS-700 MStation (for electron-spray ionization mass spectra (EI-MS). X-ray crystallographic data were collected on a Rigaku AXIS-RAPID Imaging Plate diffractometer. Fourier-Transform Infrared (FT-IR) spectra were recorded on a JASCO FT-IR-6100TRV spectrophotometer.

Stability test for Ru complexes. In a glove box filled with N_2, a Ru complex (2.0–7.5 mM) was dissolved in 600 μL of $CDCl_3$ (degassed by a freeze-and-pump-thaw cycle) that contained hexamethyldisiloxane (HMDSO, 2 mM) as an internal standard. The solution was transferred into an NMR tube with a J-young cap. The solution was incubated at 25 °C, and ^{1}H NMR spectra were measured several times over 24 h. The peak intensities were referenced to that of HMDSO (δ 0.066 ppm).

Observation of ligand exchange reaction. In a glove box filled with N_2, HG-II (**1**) and a ligand (0.025 mmol) were dissolved in 600 μL of $CDCl_3$ (degassed by a freeze-and-pump-thaw cycle) that contained hexamethyldisiloxane (HMDSO, 4 mM) as an internal standard, and the solution (*i.e.*, [HG-II (**1**)] = [ligand] = 42 mM) was transferred into an NMR tube with a J-young cap. The solution was incubated at 25 °C, and the reaction was monitored by ^{1}H NMR spectroscopic measurements several times over 24 h . The ligand exchange reactions were evaluated as the ratio of two complexes (HG-II (**1**) and a complex produced by a ligand exchange reaction), where the intensities of characteristic peaks to each complex (see below) were calculated with respect to the peak intensity of HMDSO (δ 0.066 ppm).

To determine the ratio of complexes in the reactions of HG-II (**1**) with **5-amide**, **6-amide**, **8-amide**, or **11-ester**, the peak intensity ratios of the benzylidene protons of HG-II (**1**) (16.560 ppm) to that of a Ru complex with each ligand was calculated. (**[*Ru*]$_{5\text{-amide}}$**: 16.640 ppm, **[*Ru*]$_{6\text{-amide}}$**: 16.592 ppm, **[*Ru*]$_{8\text{-amide}}$**: 16.512 and **[*Ru*]$_{11\text{-ester}}$**:16.548 ppm). To confirm the reliability of the complex ratio values from benzylidene protons, the complex ratios were also calculated from the peak intensities of ^{i}Pr- methyl protons (1.268 ppm) in HG-II (**1**) and the terminal methyl protons of a Ru complex with each ligand (**[*Ru*]$_{5\text{-amide}}$**: 1.882 ppm, **[*Ru*]$_{6\text{-amide}}$**: 1.817 ppm, **[*Ru*]$_{8\text{-amide}}$**: 2.867 ppm (*cis*-form) + 2.897 ppm (*trans*-form) and **[*Ru*]$_{11\text{-ester}}$**: 2.078 ppm). The complex ratios determined by the two methods were identical within ± 2% value. For **[*Ru*]$_{6\text{-amide}}$**, the peak at 1.817 ppm was treated as five protons because the peak of the methyl protons overlaps with that of methylene linker protons.

For determination of the complex ratios in the reactions of HG-II (**1**) and **7-amide**, **9-ester**, **10-ester**, or **11-ester**, the calculation from the peak ratio of benzylidene protons was impossible because the benzylidene protons of these complexes have identical chemical shifts. Accordingly, the complex ratios were calculated from the peak intensities of ^{i}Pr-methyl protons (1.268 ppm) in HG-II (**1**) and the terminal methyl or ^{t}Bu protons of a Ru complex with each ligand (**[*Ru*]$_{7\text{-amide}}$**: 1.113 ppm, **[*Ru*]$_{9\text{-ester}}$**: 2.011 ppm, and **[*Ru*]$_{10\text{-ester}}$**: 2.047 ppm).

For the observation of the reverse reaction in a mixture of HG-II (**1**) and **5-amide** (i.e. conversion of **[*Ru*]$_{5\text{-amide}}$** into HG-II (**1**)), excess **^{i}Pr-L** (20 eq. 840 mM) was added to the reaction mixture at 24 h since a ligand exchange started, and the solution was incubated at 25 ˚C for further 24 h. In final, ^{1}H-NMR measurement was conducted.

Monitoring of H/D exchange reaction. In a glove box filled with N_2, **5-amide** or **[*Ru*]$_{5\text{-amide}}$** (0.012 mmol) was dissolved in 600 μL of $CDCl_3$ (degassed by a freeze-and-pump-thaw cycle), and the solution was transferred into an NMR tube equipped with a J-young cap. Immediately before the measurement started, degassed D_2O (6 μL, 0.332 mmol) was added to the solution, and the mixture was vigorously shaken. The solution was incubated at 25 °C in dark, followed by monitoring with ^{1}H NMR spectroscopic measurements at defined times. The relative intensities of the N–H proton signals were referenced to the peak intensities of an unexchangeable proton (**5-amide**: 5.258 ppm, **[*Ru*]$_{5\text{-amide}}$**: 16.640 ppm).

IR measurements. In an assembly cell (USP-CL-T2, UNISOKU Co. Ltd) equipped with a Teflon spacer (L = 0.5 mm) and CaF_2 windows, a solution of **5-amide**, **[*Ru*]$_{5\text{-amide}}$** or

HG-II(**1**) (83 mM) in $CHCl_3$ was placed. Each spectrum was collected at a resolution of 0.5 cm^{-1} and 25 °C (accumulation number of 256). The background spectrum of chloroform was subtracted from each collected spectrum, to obtain the net spectrum of the ligand or complex.

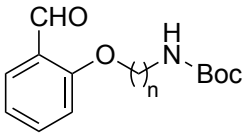
X-ray crystallographic analyses. Single crystals of Ru complexes were prepared by vapor diffusion of hexane into a $CHCl_3$ solution at 5 ˚C. X-ray diffraction was collected at 125 ± 0.1 K using multi-layer mirror monochromated Mo-Kα radiation.

Evaluation of ring-closing metathesis (RCM) activities. For reactions of compound **25**, the substrate (42 mmol) and a Ru complex (2.1 mmol, 5 mol%) were dissolved in $CDCl_3$ (degassed by a freeze-and-pump-thaw cycle) that contained HMDSO (4 mM) as an internal standard, and the solution was transferred into an NMR tube with a J-young cap. The solution was incubated at 25 °C in dark, followed by monitoring with ^{1}H NMR spectroscopic measurements at defined times. The RCM product yields were calculated from the peak intensities at 6.435 ppm with reference to the intensity of HMDSO.

The reactions of compound **27** at 25 ˚C were conducted as described above except for the employment of toluene (42 mM) as an internal standard. The reactions of compound **27** at 45 ˚C were conducted with a 50-mL two-neck flask equipped with a condenser under a N_2 atmosphere. The RCM product yields (compound **28**) were calculated from the peak intensities at 4.115 ppm with respect to methyl protons in toluene (2.356 ppm).

Evaluation of cross metathesis (CM) activities. In a 20-mL Schlenk tube, compounds **29** (42 mmol), **30** (84 mmol) and HMDSO (4 mM) were anaerobically dissolved in $CDCl_3$ (2.5 mL, degassed by a freeze-and-pump-thaw cycle). A Ru complex (0.42 mmol, 1 mol% with respect to compound **29**) in $CDCl_3$ (0.5 mL) was added to the substrate solution to start a reaction at 25 °C in dark under a N_2 atmosphere. At defined times, a part of the reaction solution (ca. 0.6 mL) was sampled and subjected to ^{1}H-NMR measurements. The CM product yields were calculated from the peak intensities of allylic protons in **31** (4.443 ppm) and **32** (4.332 ppm) in the same manner as a previous report,[5] The assignment of products on ^{1}H-NMR spectra was based on previously reported spectral data.[6, 7]

2. Syntheses of amide-type ligands



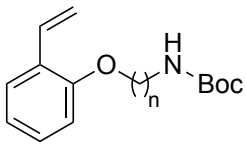
14a (n = 2)
14b (n = 3)

Compounds 14a and 14b. Representatively, the synthesis of **14a** is described. In a 200 mL-round bottom flask, **12a** (4.097 g, 20 mmol) and triethylamine (3 mL, 22 mmol) were dissolved in CH_2Cl_2 (50 mL). After the mixture was stirred at room temperature for 10 min, di-*tert*-butyl dicarbonate (4.81 g, 22 mmol) was added dropwise to the mixture. The reaction mixture was stirred overnight at room temperature. The reaction mixture was washed with water (3 x 50 mL), dried over Na_2SO_4, concentrated under reduced pressure to afford a crude product compound **13a**.

The crude **13a** was dissolved in DMF (50 mL), and K_2CO_3 (4.14 g, 30 mmol) was added to the solution. After the mixture was stirred for 5 min at room temperature, salicylaldehyde (2.1 mL, 2.268 g (d = 1.08 g/mL), 20 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature. The mixture was poured into water (100 mL) and stirred for 30 min before organic materials were extracted with hexane/ethyl acetate = 3/1 (3 x 100 mL). The organic phase was washed with water (2 x 100 mL), brine (1 x 100 mL), and dried over Na_2SO_4. After the solvent was evaporated, the residue was subjected to flash silica gel chromatography (eluent: hexane/ethyl acetate = 3/1 (R_f = 0.23) to 1/1) to yield compounds **14a** as white solids (2.18 g, yield: 41%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.487 (s, 1H, -CHO), 7.840 (dd, J = 7.7 Hz, 1.8 Hz, 1H, arom), 7.550 (ddd, J = 8.4 Hz, 7.7 Hz, 1.8 Hz, 1H, arom), 7.059 (dd, J = 7.7 Hz, 7.7 Hz, 1H, arom), 6.978 (d, J = 8.4 Hz, 1H, arom), 5.004 (br, 1H, NH), 4.154 (t, J = 5.0 Hz, 2H, -OC$\underline{H}_2$CH$_2$NH-), 3.618 (dt, J = 5.0 Hz, 5.5 Hz, 2H, -OCH$_2$C$\underline{H}_2$NH-), 1.456 (s, 9H, ^{t}Bu); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 189.58, 160.80, 155.89, 136.01, 128.85, 124.86, 121.10, 112.48, 79.80, 67.78, 39.95, 28.37; HR-MS (EI, positive) Calcd. 265.1314 ($C_{14}H_{19}NO_4$ for $[M]^+$), found 265.1322.

Compound **14b** was synthesized by the aforementioned procedure from compound **12b** and purified on silica (eluent: hexane/ethyl acetate = 3/1 (R_f = 0.45) to 1/1) to obtain as white solids (yield: 82%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.46 (s, 1H, -CHO), 7.829 (dd, J = 7.8 Hz, 2.0 Hz, 1H, arom), 7.543 (ddd, J = 8.4 Hz, 7.8 Hz, 2.0 Hz, 1H, arom), 7.041 (dd, J = 7.8 Hz, 7.8 Hz, 1H, arom), 6.983 (d, J = 8.4, 1H, arom), 4.886 (br, 1H, -NH), 4.150 (t, J = 6.0 Hz, 2H, -OC$\underline{H}_2$CH$_2$CH$_2$NH-), 3.363 (dt, J = 6.0, 5.6 Hz, 2H, -OCH$_2$CH$_2$C$\underline{H}_2$NH-), 2.068 (dt, J = 6.0 Hz, 6.0 Hz, 2H, -OCH$_2$C$\underline{H}_2$CH$_2$NH-), 1.440 (s, 9H, ^{t}Bu); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 189.67, 160.92, 156.03, 135.94, 129.06, 124.83, 120.80, 112.34, 79.34, 66.45, 37.95, 29.53, 28.38; HR-MS (EI, positive) Calcd. 279.1471 ($C_{15}H_{21}NO_4$ for $[M]^+$), found 279.1472.

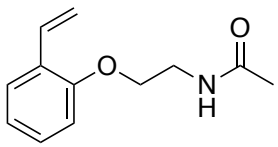
Compounds 15a and 15b. Representatively, the synthesis of **15a** is described. In a 200-mL three neck flask equipped with two dropping funnels, CH_3PPh_3Br (4.002 g, 11.2 mmol) was suspended in anhydrous THF (40 mL) under an N_2 atmosphere and stirred at 0 ˚C for 30 min. ^{n}BuLi solution in hexane (1.6 M, 6.5 mL, 8.5 mmol) was slowly added from a dropping funnel to the suspension, and then the suspension was stirred for 1 h at 0 ˚C (The mixture was orange in color). While the mixture was stirred, compound **14a** (1.99 g, 7.4 mmol) in anhydrous THF (10 mL) in a separate flask was transferred into another dropping funnel using a syringe. The solution of **14a** was dropwise added to the main reaction mixture, and the reaction mixture was stirred at room temperature overnight under an N_2 atmosphere. Afterward, the reaction was quenched by water (30 mL), and the solution was stirred for 30 min. The organic materials were extracted with diethyl ether (4 x 50 mL). After the organic phases was sequentially washed with water (3 x 50 mL), sat $NaHCO_3$ solution (1 x 50 mL), and brine (1 x 50 mL), the ether solutions was dried over Na_2SO_4. The solvent was evaporated and the residue was subjected to flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 3/1, R_f = 0.5) to obtain yellow oil **15a** (1.17 g, yield: 60%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.492 (dd, J = 7.6 Hz, 1.7 Hz, 1H, arom), 7.225 (ddd, J = 8.2 Hz, 7.6 Hz, 1.7 Hz, 1H, arom), 7.043 (dd, J = 17.9, 11.0 Hz, 1H, -C$\underline{H}$=CH_2), 6.957 (dd, J = 7.6 Hz, 7.6 Hz, 1H, arom), 6.849 (d, J = 8.2 Hz, 1H, arom), 5.745 (dd, J = 17.9, 1.2 Hz, 1H, -CH=C$\underline{H}_{2a}$), 5.274 (dd, J = 11.0, 1.2 Hz, 1H, -CH=C$\underline{H}_{2b}$), 4.965 (br, 1H. -NH), 4.050 (t, J = 5.2 Hz, 2H, -OC$\underline{H}_2$$CH_2$NH-), 3.578 (td, J = 5.6, 5.2 Hz, 2H, -OCH_2C$\underline{H}_2$NH-), 1.456 (s, 9H, ^{t}Bu); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.89, 155.60, 131.40, 128.93, 126.75, 126.49, 121.08, 114.53, 111.96, 79.56, 67.65, 40.19, 28.38; HR-MS (EI, positive) Calcd. 263.1521 ($C_{15}H_{21}NO_3$ for $[M]^+$), found 263.1523.



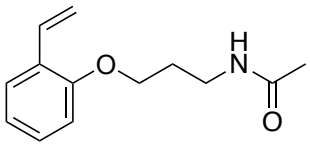
15a (n = 2)
15b (n = 3)

Compound **15b** was synthesized in the same manner as the aforementioned procedure from compound **14b** and purified on silica (eluent: hexane/ethyl acetate = 3/1, R_f = 0.45 to 1/1) to obtain as yellow oil (yield: 79%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.479 (dd, J = 7.5, 1.6 Hz, 1H, arom), 7.224 (ddd, J = 8.4 Hz, 7.5 Hz, 1.6 Hz, 1H, arom), 7.044 (dd, J = 17.8, 10.8 Hz, 1H, -C$\underline{H}$=CH_2), 6.942 (dd, J = 7.5 Hz, 7.5 Hz, 1H, arom), 6.859 (d, J = 8.4 Hz, 1H, arom), 5.731(dd, J = 17.6, 1.6 Hz, 1H, -CH=C$\underline{H}_{2a}$), 5.265 (dd, J = 10.8, 1.6 Hz, 1H, -CH=C$\underline{H}_{2b}$), 4.833 (br, 1H, -NH), 4.058 (t, J = 6.0 Hz, 2H, -OC$\underline{H}_2$$CH_2CH_2$NH-), 3.559 (dt, J = 6.8, 6.0 Hz, 2H, -OCH_2CH_2C$\underline{H}_2$NH-), 2.024 (td, J = 6.8, 6.0 Hz, 2H, -OCH_2C$\underline{H}_2$$CH_2$NH-), 1.444 (s, 9H, ^{t}Bu); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.99, 155.78, 131.52, 128.85, 126.83, 126.51, 120.80, 114.63, 111.67, 79.17, 66.32, 38.31, 29.50, 28.40; HR-MS (EI, positive) Calcd. 277.1678 ($C_{16}H_{23}NO_3$ for $[M]^+$), found 277.1675.

Compound 5-amide. In a 100-mL round-bottom flask, compound **15a** (1.036 g, 3.77 mmol) was dissolved in 40 mL of HCOOH and stirred for 2 h. The reaction mixture was concentrated under reduced pressures and neutralized by pouring sat. $NaHCO_3$. Afterwards, organic materials were extracted with CH_2Cl_2 (3 x 30 mL). The organic phase was dried over Na_2SO_4, and the solvent was evaporated to yield a crude product **16a**. In a 100-mL two-neck flask, crude **16a** was dissolved in 10 mL of CH_2Cl_2 and stirred for 10 minutes. To the solution was added triethylamine (1.1 mL, 7.92 mmol) and acetic anhydride (0.4 mL, 3.96 mmol). The mixture was stirred for 18 h at room temperature. Afterwards, 5% $NaHCO_3$ (20 mL) was added to the reaction solution and stirred for 30 min. The organic phase was separated, washed with water (2 x 30 mL), and dried over Na_2SO_4. The solvent was evaporated, and the residue was subjected to column chromatography on silica gel (eluent: ethyl acetate 100%, R_f = 0.27 to obtain **5-amide** as white solids (0.302 g, yield: 39%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.493 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H, arom), 7.213 (ddd, *J* = 8.2 Hz, 7.6 Hz, 1.6 Hz, 1H, arom), 7.019 (dd, *J* = 18.0, 11.2 Hz, 1H, -C*H*=CH$_2$), 6.969 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, arom), 6.852 (d, *J* = 8.2 Hz, 1H, arom), 5.919 (br, 1H, -NH), 5.753 (dd, *J* = 18.0, 1.4 Hz, 1H, -CH=C*H*$_{2a}$), 5.289 (dd, *J* = 11.2, 1.4 Hz, 1H, -CH=C*H*$_{2b}$), 4.080 (t, *J* = 5.5 Hz, 2H, -OC*H*$_2$CH$_2$NH-), 3.700 (dt, *J* = 5.5 Hz, 5.5 Hz, 2H, -OCH$_2$C*H*$_2$NH-), 2.014 (s, 3H, Me); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.42, 155.52, 131.55, 129.01, 126.73, 126.58, 121.24, 114.64, 112.11, 67.40, 39.12, 23.27; HR-MS (EI, positive): Calcd. 205.1103 ($C_{12}H_{15}NO_2$ for $[M]^+$), found 205.1110.



Compound 6-amide. Ligand **6-amide** was prepared from compound **15b** in the same manner as the synthesis of **5-amide** and obtained as white solids (yield: 40%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.478 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H, arom), 7.234 (ddd, 8.1 Hz, 7.7 Hz, 1.5 Hz, 1H, arom), 7.033 (dd, *J* = 18.0 Hz, 11.0 Hz, 1H, -C*H*=CH$_2$), 6.953 (dd, *J* = 7.7 Hz, 7.7 Hz, 1H, arom), 6.867 (d, *J* = 8.1 Hz, 1H, arom), 6.059 (br, 1H, -NH), 5.747 (dd, *J* = 18.0, 1.5 Hz, 1H, -CH=C*H*$_{2a}$), 5.276 (dd, *J* = 11.0, 1.5 Hz, 1H, -CH=C*H*$_{2b}$), 4.072 (t, *J* = 6.0 Hz, 2H, -OC*H*$_2$CH$_2$CH$_2$NH-), 3.470 (dt, *J* = 6.4 Hz, 6.0 Hz, 2H, -OCH$_2$CH$_2$C*H*$_2$NH-), 2.040 (td, *J* = 6.4 Hz, 6.0 Hz, 2H, -OCH$_2$C*H*$_2$CH$_2$NH-), 1.965 (s, 3H, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.17, 155.56, 131.48, 128.90, 126.59(2C), 120.86, 114.78, 111.56, 66.64, 37.61, 28.81, 23.21; HR-MS (EI, positive): Calcd. 219.1259 ($C_{13}H_{17}NO_2$ for $[M]^+$), found 219.1260.



Compound 7-amide. In a 100-mL two-neck flask, crude **15a** (0.215 g, 1.316 mmol) was dissolved in CH_2Cl_2 (8 mL) and cooled with an ice-bath. To the solution was added pivaloyl chloride (162 μL, 0.159 g (d = 0.980 g/mL), 1.316 mmol) and diisopropylethylamine (229 μL, 0.170 g (d = 0.742 g/mL), 1.316 mmol). The solution was stirred at room temperature overnight and washed with water. The organic phase was dried over Na_2SO_4, and the solvent was evaporated. The resultant residue was subjected to flash silica chromatography (eluent: hexane/ethyl acetate = 3/1, R_f = 0.2) to yield **7-amide** as white solids (0.258 g, yield: 79%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.479 (dd, J = 7.3, 1.2 Hz, 1H, arom), 7.233 (ddd, J = 8.2 Hz, 7.3 Hz, 1.2 Hz, 1H, arom), 7.023 (dd, J = 17.9 Hz, 11.0 Hz, 1H, -C$\underline{H}$=CH_2), 6.967 (dd, J = 7.3 Hz, 7.3 Hz, 2H, arom), 6.868 (d, J = 8.2 Hz, 1H, arom), 6.122 (br, 1H, -NH), 5.753 (dd, J =17.9, 1.4 Hz, 1H, -CH=C$\underline{H}_{2a}$), 5.285 (dd, J = 11.0 Hz, 1.4 Hz, 1H, -CH=C$\underline{H}_{2b}$), 4.089 (t, J = 5.0 Hz, 2H, -OC$\underline{H}_2$$CH_2$NH-), 3.683 (dd, J = 5.0 Hz, 5.0 Hz, 2H, -OCH_2C$\underline{H}_2$NH-), 1.192 (s, 9H, ^{t}Bu); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.62, 155.62, 131.46, 128.99, 126.92, 126.76, 121.29, 114.86, 112.41, 67.36, 39.06, 38.70, 27.52 (2C).; HR-MS（EI, positive）Calcd. 247.1572 ($C_{15}H_{21}NO_2$ for $[M]^+$), found 247.1579.

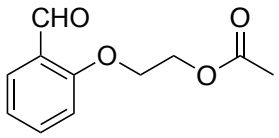
Compound 8-amide. In a 100-mL three-neck flask, compound **15a** (0.314 g, 1.2 mmol) was dissolved in dry DMF (7 mL) under an N_2 atmosphere and cooled with an ice-bath. To the solution was added NaH (60% oil dispersion, 62 mg, 1.6 mmol) dropwise. After the mixture was stirred for 1 h at 0 ˚C, CH_3I (0.11 mL, 0.254 g (d = 2.279 g/mL), 1.8 mmol) was added. The solution was stirred at room temperature for 3 h. The reaction was quenched by NH_4Claq. The solution was stirred for 30 min and diluted with water (30 mL). Organic materials were extracted with ethyl acetate and washed with water and brine. The organic phase was dried over Na_2SO_4, and the solvent was evaporated to yield crude compound **17** as oily residue. Sequentially, the oil was dissolved in 98% formic acid (16 mL) and stirred for 2 h at room temperature. After the solution was concentrated under reduced pressure, the resultant residue was suspended in sat. $NaHCO_3$. Organic materials were extracted with CH_2Cl_2. Organic phases were combined and dried over Na_2SO_4. After the solvent was evaporated, the resultant residue was dissolved in CH_2Cl_2 (7 mL). The solution was cooled with an ice-bath, and acetic anhydride (124 μL, 0.314 g (d = 1.08 g/mL), 1.3 mmol) and triethylamine (365 μL, 0.265 g (d = 0.726 g/mL), 2.6 mmol) were dropwise added to the solution. The mixture was stirred at room temperature overnight before quenched with 5% $NaHCO_3$. The solution was diluted with

CH_2Cl_2, and the organic phase was separated. After the solution was dried over Na_2SO_4, the solvent was evaporated. The resultant residue was subjected to silica gel chromatography (eluent: hexane/ethyl acetate = 4/1, R_f = 0.35 to yield **8-amide** as white solids (0.210 g, yield: 80%). Compound **8-amide** was obtained as a *cis/trans* mixture. HR-MS (CI, positive): Calcd. 220.1338 ($C_{13}H_{18}NO_2$ for $[M + H]^+$), found 220.1331.

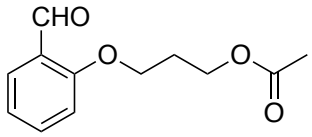
Major configuration: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.489 (dd, *J* = 7.6 Hz, 1.4 Hz), 7.222 (ddd, *J* = 8.2 Hz, 7.6 Hz, 1.4 Hz, 1H, arom), 7.042 (dd, *J* = 17.9 Hz, 11.0 Hz, 1H, -C*H*=CH_2), 7.021-6.922 (m, 2H, arom), 6.839 (d, *J* = 8.2 Hz, arom), 5.719 (dd, *J* = 17.9 Hz, 1.4 Hz, 1H, -CH=C*H*$_{2a}$), 5.253 (dd, *J* =11.7, 1.4 Hz, -CH=C*H*$_{2b}$), 4.159 (t, *J* = 5.2 Hz, 1H, -OC*H*$_2$$CH_2$NH-), 3.793 (dd, *J* = 4.8 Hz, 4.8 Hz, 1H, -OCH_2C*H*$_2$NH-), 3.179 (s, 3H, -NMe), 2.101 (s, 3H, -N(Me)COC*H*$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.97, 155.61, 131.41, 129.00, 127.18, 126.31, 120.88, 114.38, 111.51, 66.93, 47.83, 38.42, 21.91.

Minor configuration: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.489 (dd, *J* = 7.6 Hz, 1.4 Hz, arom), 7.222 (ddd, *J* = 8.2 Hz, 7.6 Hz, 1.4 Hz, 1H, arom), 7.042 (dd, *J* = 17.9 Hz, 11.0 Hz, 1H, -C*H*=CH_2), 7.021-6.922 (m, 2H, arom), 6.839 (d, *J* = 8.2 Hz, arom), 5.693 (dd, *J* = 17.9 Hz, 1.4 Hz, 1H, -CH=C*H*$_{2a}$), 5.262 (dd, *J* =11.7, 1.4 Hz, -CH=C*H*$_{2b}$), 4.117 (t, *J* = 5.2 Hz, 1H, -OC*H*$_2$$CH_2$NH-), 3.751 (dd, *J* = 4.8 Hz, 4.8 Hz, 1H, -OCH_2C*H*$_2$NH-), 3.028 (s, 3H, -NMe), 2.202 (s, 3H, -N(Me)COC*H*$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.91, 155.22, 131.12, 128.88, 128.25, 126.59, 121.46, 114.89, 111.69, 65.59, 50.04, 33.76, 21.54.

3. Syntheses of ester-type ligands



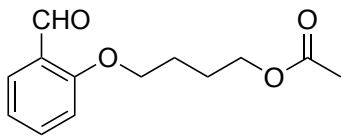
Compound 23a. In a 200-mL two neck-flask, 2-bromoethanol (**18**) (6.25 g, 50 mmol) and DMAP (0.61 g, 5 mmol) were dissolved in CH_2Cl_2 (63 mL). After the mixture was stirred at 0 ˚C for 15 min, triethylamine (8.4 mL, 6.071 g (d = 0.726 g/mL), 60 mmol) and acetic anhydride (1.7 mL, 1.836 g (d = 1.08 g/mL), 18 mmol) were dropwise added to the mixture. The reaction mixture was stirred at room temperature overnight. To quench the reaction, 5% $NaHCO_3$ solution (20 mL) was added to the reaction mixture, and the solution was stirred for 30 min. The organic phase was separated, and washed with water (2 x 25 mL) and brine (1 x 25 mL). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure to afford crude compound **19**. Sequentially, the crude **19** was dissolved in DMF (107 mL), and K_2CO_3 (8.942 g, 64.7 mmol) and salicylaldehyde (4.5 mL, 5.263 g (d = 1.167 g/mL), 4.5 mmol) were added to the solution. The reaction mixture was stirred at room temperature overnight and diluted with water. Organic materials were extrated with hexane/ethyl acetate = 3/1, and the organic phase was dried over Na_2SO_4. After the solvent was evaporated, the resultant residue was subjected to flash silica gel chromatography (elution: hexane/ethyl acetate =3/1, R_f = 0.6) to yield compound **23a** as oil (5.44 g, yield: 61%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.498 (s, 1H, -CHO), 7.846 (dd, J = 7.7 Hz, 1.8 Hz, 1H, arom), 7.556 (ddd, J = 8.4 Hz, 7.7 Hz, 1.8 Hz, 1H, arom), 7.060 (dd, J = 7.7 Hz, 7.7 Hz 1H, arom), 6.987 (d, J = 8.4 Hz, 1H, arom), 4.495 (t, J = 5.1, 2H, -Phe-OC$\underline{H_2}$CH$_2$OC(=O)-), 4.305 (t, J = 5.1 Hz, 2H, -Phe-OCH$_2$C$\underline{H_2}$OC(=O)-), 2.091 (s, 3H, Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 189.62, 170.89, 160.79, 135.94, 128.34, 125.08, 121.28, 112.59, 66.53, 62.34, 20.83; HR-MS (EI, positive): Calcd. 208.0736 ($C_{11}H_{12}O_4$ for $[M]^+$), found 208.0742.



Compound 23b. In a 200-mL two-neck flask, 2-chloropropanol **20** (3.782 g, 40 mmol) was dissolved in 30 mL of CH_2Cl_2 before addition of DMAP (0.488 g, 4 mmol). The solution was cooled with an ice-bath, and acetic anhydride (4.5 mL, 4.90 g (d = 1.08 g/mL), 48 mmol) and triethylamine (6.5 mL, 4.85 g (d = 0.742 g/mL), 48 mmol) were dropwise added. The reaction mixture was stirred at room temperature overnight and washed with water. The organic phase was dried over Na_2SO_4. After the solvent was evaporated, the resultant residue was dissolved in acetone (50 mL). To the solution was added NaI (10.40 g, 69.9 mmol). The mixture was stirred at 50 ˚C for 24 h. After the solvent was evaporated, the resultant residue was dissolved in ether and filtered. The mother liquor was washed with water and dried over Na_2SO_4. The

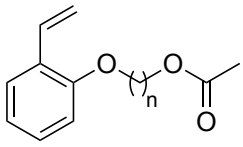
evaporation of solvent gave crude compound **21**, which was used for next reaction without further purification. Sequentially, the crude **21** was dissolved in DMF (107 mL), and K_2CO_3 (5.50 g, 39.8 mmol) and salicylaldehyde (2.1 mL, 2.430 g (d = 1.167 g/mL), 19.9 mmol) were added to the solution. The reaction mixture was stirred at room temperature overnight and diluted with water. Organic materials were extrated with hexane/ethyl acetate = 3/1, and the organic phase was dried over Na_2SO_4. After the solvent was evaporated, the resultant residue was subjected to flash silica gel chromatography (elution: hexane/ethyl acetate =3/1, R_f = 0.37 to yield compound **23b** as oil (2.64 g, yield: 59%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.503 (s, 1H, -CHO), 7.837(dd, J = 7.7, 1.8 Hz, 1H, arom), 7.550 (ddd, J = 8.4 Hz, 7.7 Hz, 1.8 Hz, 1H, arom), 7.037 (dd, J = 7.7 Hz, 7.7 Hz, 1H, arom), 6.992 (d, J = 8.4 Hz, 1H, arom), 4.297 (t, J = 6.6 Hz, 2H, -Phe-OC$\underline{H}_2$CH$_2$CH$_2$OC(=O)-), 4.180 (t, J = 6.2 Hz, 2H, -Phe-OCH$_2$CH$_2$C$\underline{H}_2$OC(=O)-), 2.207 (dt, J = 6.6 Hz, 6.2 Hz, 2H, -Phe-OCH$_2$C$\underline{H}_2$CH$_2$OC(=O)-), 2.070 (s, 3H, Me); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 189.56, 170.99, 161.04, 135.95, 128.38, 124.85, 120.86, 112.35, 64.99, 61.06, 28.50, 20.94. HR-MS (EI, positive): Calcd. 222.0892 ($C_{12}H_{14}O_4$ for $[M]^+$), found 222.0900.

Compound 23c. In a 100-mL flask equipped with a $CaCl_2$-tube, tetrahydrofuran (1.6 mL, 1.799 g (d = 0.8892 g/mL), 20 mmol) and KBr (2.82 g, 23.76 mmol) were suspended in acetonitrile (20 mL). After the mixture was cooled with an ice-bath, acetyl chloride (15 mL, 1.641 g (d = 1.105 g/mL), 20.9 mmol) was dropwise added. The reaction mixture was stirred at room temperature overnight and filtered. The mother liquor was concentrated, and the resultant residue was dissolved in ethyl acetate. The solution was washed with water and dried over Na_2SO_4 before evaporation of solvent. Sequentially, the obtained crude **22** was dissolved in DMF (40 mL), and K_2CO_3 (3.18 g, 23.0 mmol) and salicylaldehyde (1.6 mL, 1.868 g (d = 1.167 g/mL), 15.3 mmol) were added to the solution. The reaction mixture was stirred at room temperature overnight and diluted with water. Organic materials were extrated with hexane/ethyl acetate = 3/1, and the organic phase was dried over Na_2SO_4. After the solvent was evaporated, the resultant residue was subjected to flash silica gel chromatography (elution: hexane/ethyl acetate =3/1, R_f = 0.33) to yield compound **23b** as oil (3.28 g, yield: 69%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.535 (s, 1H- CHO), 7.835 (dd, J = 7.7, 1.8 Hz, 1H, arom), 7.541 (ddd, J = 8.4 Hz, 7.7 Hz, 1.8 Hz, 1H, arom), 7.025 (dd, J = 7.7 Hz, 7.7 Hz, 1H, arom), 6.976 (d, J = 8.4 Hz, 1H, arom), 4.156 (t, J = 6.6 Hz, 2H, -Phe-OC$\underline{H}_2$CH$_2$CH$_2$CH$_2$OC(=O)-), 4.120 (t, J = 6.2 Hz, 2H, -Phe-



$OCH_2CH_2CH_2C\underline{H}_2OC(=O)$-), 2.062 (s, 3H, Me), 1.941 (m, 2H, -Phe-$OCH_2C\underline{H}_2CH_2CH_2OC(=O)$-), 1.866 (m, 2H, -Phe-$OCH_2CH_2C\underline{H}_2CH_2OC(=O)$-); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 189.76, 171.19, 161.30, 136.02, 128.40, 124.89, 120.75, 112.43, 67.81, 63.94, 25.81, 25.37, 21,02; Calcd. 236.1049 ($C_{13}H_{16}O_4$ for $[M]^+$), found 236.1054.

Ester ligands (9-ester, 10-ester, and 11-ester). Ester ligands (**9-ester, 10-ester, and 11-ester**) were prepared from the corresponding aldehydes (compounds **23a**, **23b** or **23c**) through Wittig reaction in common method. Representatively, the synthesis of **9-ester** is described. In a 200-mL three-neck flask, equipped with two dropping funnels CH_3PPh_3Br (3.28 g, 9.2 mmol) was suspended in anhydrous THF (28 mL) under an N_2 atmosphere. The suspension was stirred at 0 ˚C for 30 min, and ^{n}BuLi solution (1.6 M, 5.3 mL, 8.5 mmol) was slowly added from a dropping funnel to the suspension and then stirred for 1 h at 0 ˚C. (The mixture was orange in color). During this procedure, compound **23a** (1.27 g, 6.13 mmol) solution in anhydrous THF (10 mL) in a separate flask was anaerobically transferred into another dropping funnel. After the solution of **23a** was dropwise to the main reaction mixture, the final mixture was stirred at room temperature overnight under N_2 atmosphere. Afterward, the reaction was quenched with water (30 mL), and the solution was further stirred for 30 min. Organic materials were extracted with diethyl ether (4 x 30 mL), and the organic phase was washed with water (3 x30 mL), sat $NaHCO_3$ solution (1 x 30 mL), and brine (1 x 30 mL) followed by being dried over Na_2SO_4. The solvent was concentrated under reduced pressure to afford a crude product. The crude was subjected to column chromatography on silica gel (eluent: hexane/ethyl acetate = 6/1, R_f = 0.43) to obtain **9-ester** as colorless oil (0.328 g, yield: 26%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.491 (dd, J = 7.5 Hz, 1.5 Hz, 1H, arom), 7.226 (ddd, J = 8.2 Hz, 7.5 Hz, 1.5 Hz, 1H, arom), 7.050 (dd, J = 17.8, 11.3 Hz, 1H,-$C\underline{H}$=CH_2), 6.965 (ddd, J = 7.5 Hz, 7.5 Hz, 1.0 Hz, 1H, arom), 6.857 (dd, J = 8.2, 1.0 Hz, 1H, arom), 5.762 (dd, J = 17.6 Hz, 1.5 Hz, 1H, -CH=C$\underline{H}_{2a}$), 5.272 (dd, J = 11.3 Hz, 1.5 Hz, 1H, -CH=C$\underline{H}_{2b}$), 4.458 (t, J = 4.8, 2H, -OC$\underline{H}_2CH_2OC(=O)$-), 4.198 (t, J = 4.8, 4.4 Hz, 2H, -$OCH_2C\underline{H}_2OC(=O)$-), 2.103 (s, 3H, Me); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.05, 155.61, 131.43, 128.81, 127.11, 126.64, 121.29, 114.63, 112.28, 66.44, 62.78, 20.92; HR-MS (EI, positive) Calcd. 206.0943 ($C_{12}H_{14}O_3$ for $[M]^+$), found 206.0945.



9-ester (n = 2)
10-ester (n = 3)
11-ester (n = 4)

Compound **10-ester** was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 3/1, R_f = 0.56) to obtain as colorless oil (yield: 35%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.484 (dd, J = 7.3 Hz, 1.8 Hz, 1H, arom), 7.222 (ddd, J = 8.2 Hz,

7.3 Hz, 1.8 Hz, 1H, arom), 7.046 (dd, J = 17.8 Hz, 11.0 Hz, 1H, -C$\underline{H}$=CH_2), 6.939 (ddd, J = 7.3 Hz, 7.3 Hz, 1.0 Hz, 1H, arom), 6.861 (dd, J = 8.2 Hz, 1.0 Hz, 1H, arom), 5.738 (dd, J = 17.6, 1.6 Hz, 1H, -CH=C$\underline{H}_{2a}$), 5.254 (dd, J = 11.2 Hz, 1.6 Hz, 1H, -CH=C$\underline{H}_{2b}$), 4.291 (t, J = 6.4 Hz, 2H, , -OC$\underline{H}_2CH_2CH_2OC$(=O)-), 4.078 (t, J = 6.0 Hz, 2H, -$OCH_2CH_2C\underline{H}_2OC$(=O)-), 2.159 (dt, J = 6.4 Hz, 6.0 Hz, 2H, -$OCH_2C\underline{H}_2CH_2OC$(=O)-), 2.061 (s, 3H, Me); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.09, 155.80, 131.47, 128.81, 126.80, 126.48, 120.79, 114.41, 111.76, 64.63, 61.41, 28.67, 20.98; HR-MS (EI, positive): Calcd. 220.1099 ($C_{13}H_{16}O_3$ for $[M]^+$), found 220.1103.

Compound **11-ester** was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 3/1, R_f = 0.68 to obtain as colorless oil (yield: 35%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.480 (dd, J = 7.8 Hz, 1.8 Hz, 1H, arom), 7.215 (ddd, J = 8.2 Hz, 7.8 Hz, 1.8 Hz, 1H, arom), 7.057 (dd, J = 17.6, 11.0 Hz, 1H, -C$\underline{H}$=CH_2), 6.929 (ddd, J = 7.8 Hz, 7.8 Hz, 1.0 Hz, 1H, arom), 6.849 (dd, J = (8.2 Hz, 1.0 Hz, 1H, arom), 5.746 (dd, J = 17.6 Hz, 1.6 Hz, 1H, -CH=C$\underline{H}_{2a}$), 5.256 (dd, J = 11.0, 1.6 Hz, 1H, -CH=C$\underline{H}_{2b}$), 4.150 (t, J = 6.4 Hz, 1H, -OC$\underline{H}_2CH_2CH_2CH_2OC$(=O)-), 4.018 (t, J = 6.4 Hz, 1H, -$OCH_2CH_2CH_2C\underline{H}_2OC$(=O)-), 2.056 (s, 3H, Me), 1.94-1.82 (m, 4H, -$OCH_2C\underline{H}_2C\underline{H}_2CH_2OC$(=O)-); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.16, 155.98, 131.57, 128.80, 126.72, 126.45, 120.62, 114.29, 111.76, 67.51, 64.12, 25.94, 25.46, 20.98; Calcd. 234.1256 ($C_{14}H_{18}O_3$ for $[M]^+$), found 234.1260.

4. Synthesis of Ru complexes

General procedure. In a 50-mL two-neck flask equipped with a condenser, Grubbs second generation complex (**24**, 50 mg, 0.058 mmol) and CuCl (5.8 mg, 0.058 mmol) was dissolved in dry and degassed CH_2Cl_2 (3.5 mL) under an N_2 atmosphere. Separately, a ligand (0.058 mmol) solution in dry and degassed CH_2Cl_2 (1.5 mL) was anaerobically prepared and added to the solution of the Ru complex. The resulting mixture was refluxed for 4 h under an N_2 atmosphere. The reaction mixture was concentrated *in vacuo*. The resultant residue was subjected to column chromatography on silica gel (see the solvent system below), and eluted solutions were fractioned into several test tubes after purple leading band (unreacted Grubbs complex **24**) was removed. Although green band was collected, fractions with impurities (unreacted ligand compound) were discarded.

[*Ru*]$_{\textbf{5-amide}}$: Yield 52% (purified with elution of hexane/ethyl acetate = 1/2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.640 (s, 1H, benzylidene proton), 7.533 (ddd, J = 3.9 Hz, 4.5 Hz, 8.8 Hz, 1H, aromatic proton in **5-amide** ligand), 7.201 (br, 1H, -NH), 7.077 (s, 4H, aromatic protons in mesityl group), 6.95–6.93 (m, 2H, aromatic protons in **5-amide** ligand), 6.843 (d, J = 8.4 Hz, 1H, aromatic proton in ligand), 4.205 (s, 4H, NHC protons), 4.178 (t, J = 4.8 Hz, 2H, -OC$\underline{H_2}$CH$_2$NH-), 3.408 (td, J = 4.8 Hz, 4.8 Hz, 2H, -OCH$_2$C$\underline{H_2}$NH-), 2.455 (s, 12H, *o*-methyl protons in mesityl group), 2.409 (s, 6H, *p*-methyl protons in mesityl group), 1.884 (s, 3H, methyl group in **5-amide** ligand); ^{13}C-NMR (100 MHz, $CDCl_3$): 298.26, 210.00, 170.14, 153.64, 144.85, 139.51, 139.05, 130.52, 129.59, 123.81, 122.71, 112.84, 70.68, 51.67, 36.67, 23.21, 21.26, 19.45; HR-MS (MALDI, positive, matrix: 9-nitroanthracene): Calcd. 669.1462 ($C_{32}H_{38}N_3O_2Ru$ for $[M]^+$), found 669.1463.

[*Ru*]$_{\textbf{6-amide}}$: Yield 49% (purified with elution of hexane/ethyl acetate = 1/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.592 (s, 1H, benzylidene proton), 7.516 (ddd, J = 3.9 Hz, 4.5 Hz, 8.8 Hz, 1H, aromatic proton in **6-amide** ligand), 7.082 (s, 4H, aromatic protons in mesityl group), 6.94-6.89 (m, 3H, aromatic protons in **5-amide** ligand), 6.535 (br, 1H, -NH), 4.227 (t, J = 6.0 Hz, 2H, -OC$\underline{H_2}$CH$_2$CH$_2$NH-), 4.181 (s, 4H, NHC protons), 3.169 (td, J = 6.0 Hz, 6.0 Hz, 2H, -OCH$_2$CH$_2$C$\underline{H_2}$NH-), 2.460 (s, 12H, *o*-methyl protons in mesityl group), 2.415 (s, 6H, *p*-methyl protons in mesityl group), 1.83–1.77 (m, 5H, -OCH$_2$C$\underline{H_2}$CH$_2$NH- + methyl group in **6-amide** ligand); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 297.32, 210.22, 170.83, 153.88, 145.23, 139.23(2C), 130.31, 129.59, 123.68, 122.58, 113.43, 68.99, 51.68, 36.77, 27.45, 23.15, 21.29, 19.42; HR-MS (MALDI, positive,

matrix: 9-nitroanthracene): Calcd. 683.1617 ($C_{33}H_{41}N_3O_2Ru$ for $[M]^+$), found 683.1609.

[*Ru*]$_{\textbf{7-amide}}$: Yield 90% (purified with elution of hexane/ethyl acetate = 2/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.555 (s, 1H, benzylidene proton), 7.505 (ddd, *J* = 3.9 Hz, 4.5 Hz, 8.8 Hz, 1H, aromatic proton in **7-amide** ligand), 7.12-7.05 (m, 5H, aromatic protons in mesityl group + -NH), 6.95-6.90 (m, 2H, aromatic protons in **7-amide** ligand), 6.832 (d, *J* = 8.4 Hz, 1H, aromatic proton in **7-amide** ligand), 4.203 (s, 4H, NHC protons), 4.173 (t, *J* = 4.5 Hz, 2H, -OC$\underline{H_2}$CH$_2$NH-), 3.303 (td, *J* = 4.5 Hz, 4.5 Hz, 2H, -OCH$_2$C$\underline{H_2}$NH-), 2.452 (s, 12H, *o*-methyl protons in mesityl group), 2.396 (s, 6H, *p*-methyl protons in mesityl group), 1.132 (s, 9H, ^{t}Bu); ^{13}C-NMR (400 MHz, $CDCl_3$): 297.54, 210.47, 179.03, 153.91, 145.13, 139.54 (2C), 130.33, 129.54, 123.69, 122.57, 112.88, 70.50, 51.72, 38.78, 36.97, 27.67, 21.23, 19.41; HR-MS (MALDI, positive, matrix: 9-nitroanthracene): Calcd. 711.1932 ($C_{35}H_{45}Cl_2N_3O_2Ru$ for $[M]^+$), found 711.1920.

[*Ru*]$_{\textbf{8-amide}}$: Yield 52% ((urified with elution of hexane/ethyl acetate = 2/1; obtained as a *cis*/*trans* mixture); HR-MS (MALDI, positive, matrix: 9-nitroanthracene): Calcd. 683.1619 ($C_{33}H_{41}Cl_2N_3O_2Ru$ for $[M]^+$), found 683.1622.
Major configuration: ^{1}H-NMR (400 MHz, $CDCl_3$); δ 16.512 (s, 1H, benzylidene proton), 7.58–7,45 (m, 1H, aromatic proton in **8-amide** ligand), 7.072 (s, 4H, aromatic protons in mesityl group), 6.97-6.81 (m, 3H, aromatic protons in **8-amide** ligand), 4.187 (s, 4H, NHC protons), 4.147 (m, 2H, -OC$\underline{H_2}$CH$_2$NH-), 3.60–3.49 (m, 2H, -OCH$_2$C$\underline{H_2}$NH-), 2.885 (s, 3H, -NMe), 2.462 (s, 12H, *o*-methyl protons in mesityl group), 2.385 (s, 6H, *p*-methyl protons in mesityl group), 2.046 (s, 3H, Me in **8-amide** ligand); ^{13}C-NMR (100 MHz, $CDCl_3$); 294.90, 210.53, 171.20, 152.63, 144.32, 139.14, 139.09, 136.06, 129.93, 129.50, 123.87, 122.67, 112.04, 65.32, 51.43, 47.90, 34.12, 21.16, 19.23 (2C).
Minor configuration: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.492 (s, 1H, benzylidene proton), 7.58–7,45 (m, 1H, aromatic proton in **8-amide** ligand), 7.072 (s, 4H, aromatic protons in mesityl group), 6.97-6.81 (m, 3H, aromatic protons in **8-amide** ligand), 4.333 (m, 2H, -OC$\underline{H_2}$CH$_2$NH-), 4.187 (s, 4H, NHC protons), 3.60–3.49 (m, 2H, -OCH$_2$C$\underline{H_2}$NH-), 2.863 (s, 3H, -NMe), 2.462 (s, 12H, *o*-methyl protons in mesityl group), 2.385 (s, 6H, *p*-methyl protons in mesityl group), 2.032 (s, 3H, Me in **8-amide** ligand); ^{13}C-NMR (100 MHz, $CDCl_3$): 294.06, 210.79, 171.20, 153.41, 144.32, 139.14, 138.82, 136.06, 130.04, 129.50, 123.52, 122.45, 112.79, 67.62, 51.43, 46.96, 37.49, 21.83, 19.23 (2C).

[*Ru*]$_{\textbf{9-ester}}$: Yield 47% (purified with elution of hexane/ethyl acetate = 2/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.553 (s, 1H, benzylidene proton), 7.499 (ddd, *J* = 3.9 Hz, 4.5 Hz, 8.8

Hz, 1H, aromatic proton in **9-ester** ligand), 7.072 (s, 4H, aromatic protons in mesityl group), 6.92-6.82 (m, 3H, aromatic protons in **9-ester** ligand), 4.359 (t, *J* = 5.2 Hz, 2H, -OC*H*$_2$CH$_2$OC(=O)), 4.214 (t, *J* = 5.2 Hz, 2H, -OCH$_2$C*H*$_2$OC(=O)), 4.144 (s, 4H, NHC protons), 2.455 (s, 12H, *o*-methyl protons in mesityl group), 2.414 (s, 6H, *p*-methyl protons in mesityl group), 2.003 (s, 3H, Me in **9-ester** ligand); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 293.86, 210.31, 170.67, 153,16, 144.47, 139.05, 138.87, 135.99, 129.80, 129.61, 123.70, 122.62, 112.57, 67.87, 61.18, 51.74, 21.25, 20.93, 19.41; HR-MS (MALDI, positive, matrix: 9-nitroanthracene): Calcd. 670.1303 ($C_{32}H_{38}Cl_2N_2O_3Ru$ for $[M]^+$), found 670.1302.

[*Ru*]$_{\mathbf{10\text{-}ester}}$: Yield 45% (purified with elution of hexane/ethyl acetate = 2/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.553 (s, 1H, benzylidene proton), 7.511 (ddd, *J* = 4.0 Hz, 4.5 Hz, 8.8 Hz, 1H, aromatic proton in **10-ester** ligand), 7.084 (s, 4H, aromatic protons in mesityl group), 6.96-6.87 (m, 3H, aromatic proton in **10-ester** ligand), 4.226 (t, *J* = 7.6 Hz, 2H, -OC*H*$_2$CH$_2$CH$_2$OC(=O)), 4.180 (s, 4H, NHC protons), 4.020 (t, *J* = 5.6 Hz, 2H, -OCH$_2$CH$_2$C*H*$_2$OC(=O)), 2.464 (s, 12H, *o*-methyl protons in mesityl group), 2.422 (s, 6H, *p*-methyl protons in mesityl group), 2.047 (s, 3H, Me in **10-ester** ligand), 1.928 (td, *J* = 7.6 Hz, 5.6 Hz, 2H, -OCH$_2$C*H*$_2$CH$_2$OC(=O)); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 296.32, 211.04, 171.00, 153.73, 144.94, 139.24, 139.02, 129.84, 129.51, 123.49, 122.52, 112.61, 67.93, 60.95, 51.59, 24.65, 21.26, 21.11, 19.50; HR-MS (MALDI, positive, matrix: 9-nitroanthracene): Calcd. 684.1459 ($C_{33}H_{40}Cl_2N_2O_3Ru$ for $[M]^+$), found 684.1461.

[*Ru*]$_{\mathbf{11\text{-}ester}}$: Yield 45% (purified with elution of hexane/ethyl acetate = 2/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 16.547 (s, 1H, benzylidene proton), 7.497 (ddd, *J* = 4.0 Hz, 4.5 Hz, 8.8 Hz, 1H, aromatic proton in **11-ester** ligand), 7.080 (s, 4H, aromatic protons in mesityl group), 6.93-6.83 (m, 2H, aromatic proton in **11-ester** ligand), 6.856 (d, *J* = 8.3 Hz, 1H, aromatic protons in mesityl group), 4.150 (m, 6H, NHC protons + -OC*H*$_2$CH$_2$CH$_2$CH$_2$OC(=O)), 3.956 (t, *J* = 7.2 Hz, 2H), 2.466 (s, 12H, *o*-methyl protons in mesityl group), 2.418 (s, 6H, *p*-methyl protons in mesityl group), 2.077 (s, 3H, Me in **11-ester** ligand), 1.724 (td, *J* = 7.2 Hz, 7.2 Hz, 2H, -OCH$_2$C*H*$_2$CH$_2$CH$_2$OC(=O)), 1.580 (td, *J* = 7.2 Hz, 7.2 Hz, 2H, -OCH$_2$CH$_2$C*H*$_2$CH$_2$OC(=O)); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 295.60, 210.91, 171.15, 153.78, 144.89, 139.04, 138.93, 129.78, 129.57, 123.34, 122.43, 112.55, 70.01, 64.00, 51.68, 24.69 24.57, 21.22, 21.16, 19.43; HR-MS (MALDI, positive, matrix: 9-nitroanthracene): Calcd. 698.1616 ($C_{34}H_{42}Cl_2N_2O_3Ru$ for $[M]^+$), found 698.1611.

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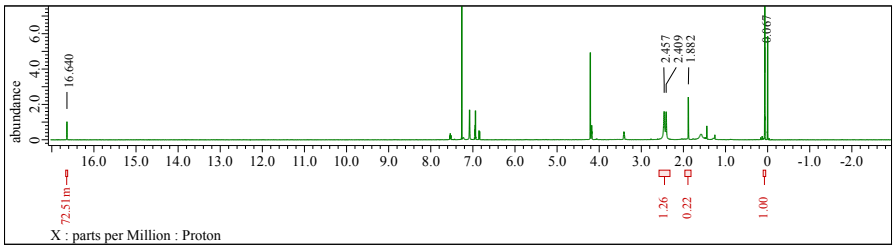
5. Appendix

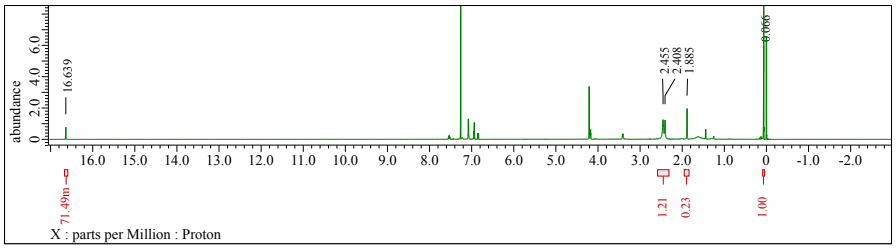
Table S1 Crystal data, diffraction collection details, and structure refinement

Compound	$[Ru]_{5\text{-amide}}$	$[Ru]_{9\text{-ester}}$	$[Ru]_{6\text{-amide}}$	$[Ru]_{10\text{-ester}}$	HG-II
CCDC deposition number	1999870	1999869	1999872	1999868	1999871
Molecular formula	$C_{33}H_{40}Cl_5N_3O_2Ru$	$C_{32}H_{38}Cl_2N_2O_3Ru$	$C_{34}H_{42}Cl_5N_3O_2Ru$	$C_{35}H_{42}Cl_8N_2O_3Ru$	$C_{32}H_{39}Cl_5N_2ORu$
Formula weight / g mol^{-1}	789.03	670.64	803.06	923.42	746.01
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	I-4
Cell metric a / Å	11.5321(2)	10.61291(19)	11.1473(2)	11.8969(2)	25.8626(5)
b / Å	14.4899(3)	15.0273(3)	13.3189(2)	14.0550(3)	--------
c / Å	21.9677(4)	19.3543(4)	24.8255(5)	24.9163(5)	10.8856(2)
b / deg	97.797(7)	92.572(7)	96.698(7)	97.173(7)	--------
Cell volume / Å^3	3636.84(13)	3083.58(10)	3660.69(13)	4133.67(15)	7281.1(2)
Z	4	4	4	4	8
Electrons per cell F_{000}	1616.00	1384.00	1648.00	1880.00	3056.00
Calcd. density / g cm^{-3}	1.441	1.444	1.457	1.484	1.361
m(Mo-$K\alpha$) / cm^{-1}	8.309	7.165	8.268	9.311	8.230
Crystal shape and color	prism, green	prism, green	prism, green	prism, green	prism, green
Crystal size / mm	0.200 x 0.190 x 0.100	0.200 x 0.060 x 0.030	0.100 x 0.080 x 0.070	0.240 X 0.220 X 0.120	0.200 X 0.110 X 0.100
Radiation	MoKα (I = 0.71075 Å)	MoKα (I = 0.71075 Å)	MoKα (I = 0.71075 Å)	MoKα (I = 0.71075 Å)	MoKα (I = 0.71075 Å)
Temperature / K	123	123	123	123	123
w oscillation Range (c = 45.0, f = 0.0)	130.0 - 190.0° (40 sec /degree)	130.0 - 190.0° (100 sec /degree)	130.0 - 190.0° (140 sec /degree)	130.0 - 190.0° (50 sec /degree)	130.0 - 190.0° (45 sec /degree)
w oscillation Range (c = 45.0, f = 0.0)	0.0 - 162.0° (40 sec /degree)	0.0 - 162.0° (40 sec /degree)	0.0 - 162.0° (140 sec /degree)	0.0 - 162.0° (50 sec /degree)	0.0 - 162.0° (45 sec /degree)
w oscillation Range (c = 45.0, f = 90.0)	0.0 - 162.0° (40 sec /degree)	0.0 - 162.0° (40 sec /degree)	0.0 - 162.0° (140 sec /degree)	0.0 - 162.0° (50 sec /degree)	0.0 - 162.0° (45 sec /degree)
No. of Reflections Measured	Total: 61014, Unique: 8332 (R_{int} = 0.0183)	Total: 52057 Unique: 7073 (R_{int} = 0.0196)	Total: 59578 Unique: 8041 (R_{int} = 0.0565)	Total: 68963 Unique: 9475 (R_{int} = 0.0198)	Total: 63479 Unique: 8349 (R_{int} = 0.0183)
Residuals: R_1 ($I > 2\sigma(I)$)	0.0292	0.0266	0.0407	0.0379	0.0180
Residuals: R (All reflections)	0.0307	0.0297	0.0474	0.0395	0.0181
Residuals: wR2 (All reflections)	0.0745	0.0680	0.0964	0.1000	0.0483
Goodness of Fit Indicator	1.090	1.132	1.053	1.107	1.111
Flack parameter	--------	--------	--------	--------	-0.015(3)

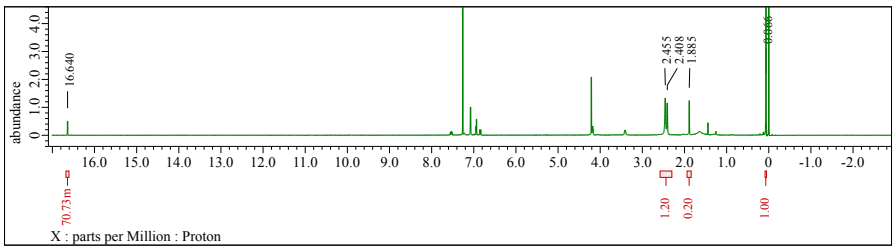
0 h



after 7 h



after 24 h

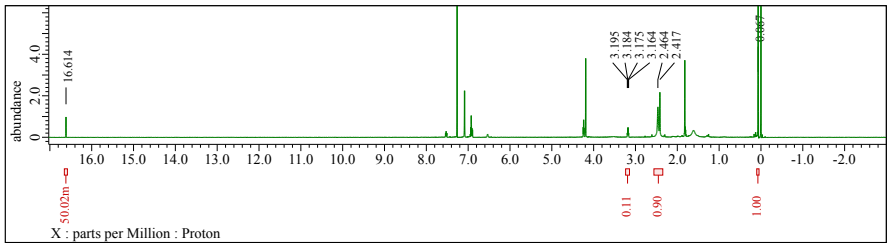


time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	acetamide Me protons (1.89 ppm)	mesityl protons (2.40-2.46 ppm)	benzylidene proton (Ru=CH, 16.64 ppm)
0 h	0.22	1.26	0.0725
after 7 h	0.23	1.21	0.0715
after 24 h	0.21	1.24	0.0707

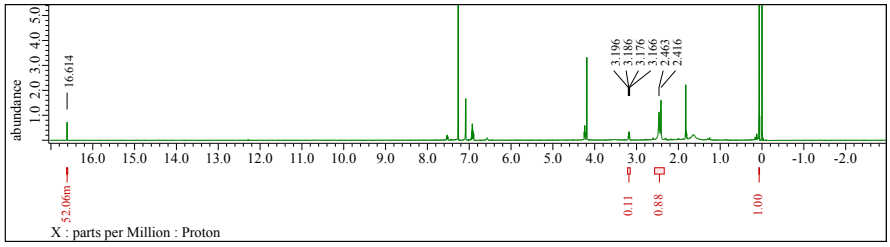
[a] $[\boldsymbol{Ru}]_{\textbf{5-amide}}$ in $CDCl_3$ (2.5 mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 2 mM) was employed as an internal standard.

Fig. S1. ^{1}H-NMR spectra of complex $[\boldsymbol{Ru}]_{\textbf{5-amide}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $[\boldsymbol{Ru}]_{\textbf{5-amide}}$ = 2.5 mM and [HMDSO] = 2 mM (internal standard).

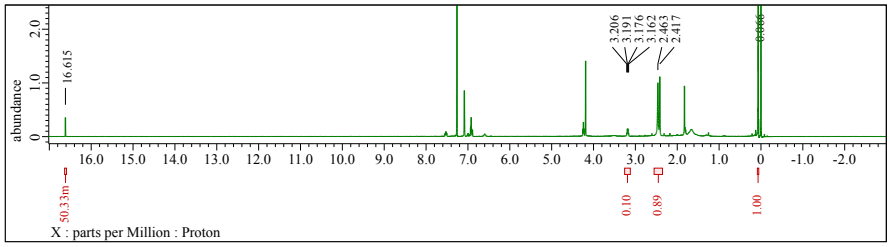
0 h



after 7 h



after 24 h

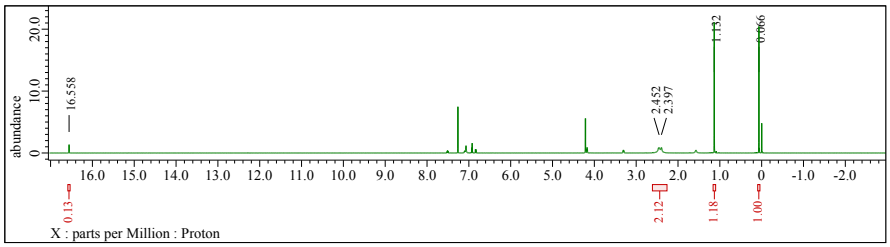


time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	-NHC<u>*H*</u>$_2$CH$_2$CH$_2$O- (1.89 ppm)	mesityl protons (2.41-2.47 ppm)	benzylidene proton (Ru=CH, 16.62 ppm)
0 h	0.11	0.90	0.0502
after 7 h	0.11	0.88	0.0521
after 24 h	0.10	0.89	0.0503

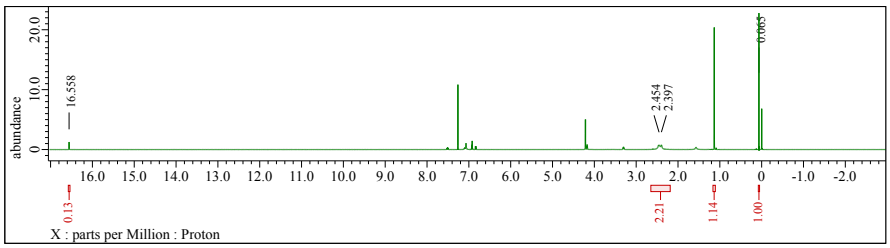
[a]$[\boldsymbol{Ru}]_{\textbf{6-amide}}$ in $CDCl_3$ (2.0 mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 2 mM) was employed as an internal standard.

Fig. S2. ^{1}H-NMR spectra of complex $\boldsymbol{[Ru]_{6\text{-amide}}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $\boldsymbol{[Ru]_{6\text{-amide}}}$ = 2.0 mM and [HMDSO] = 2 mM (internal standard).

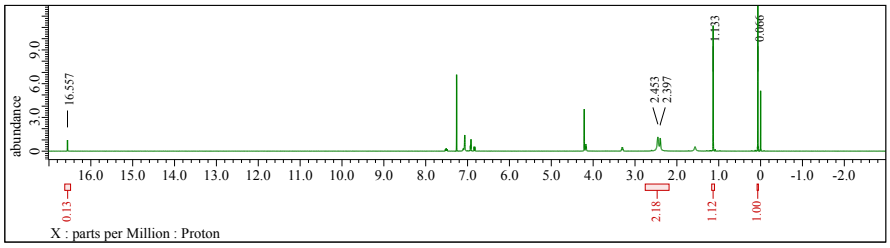
0 h



after 7 h



after 24 h

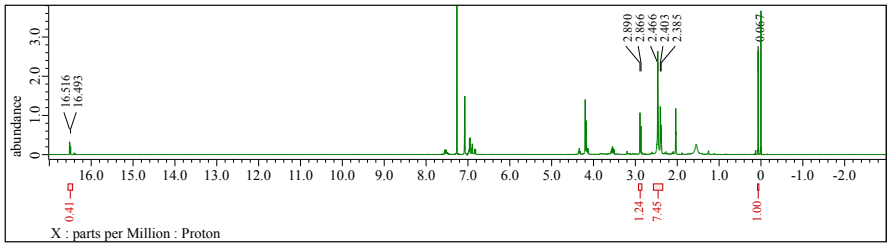


time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	^{t}Bu protons (1.13 ppm)	mesityl protons (2.39-2.46 ppm)	benzylidene proton (Ru= CH, 16.56 ppm)
0 h	1.18	2.12	0.13
after 7 h	1.14	2.21	0.13
after 24 h	1.12	2.18	0.13

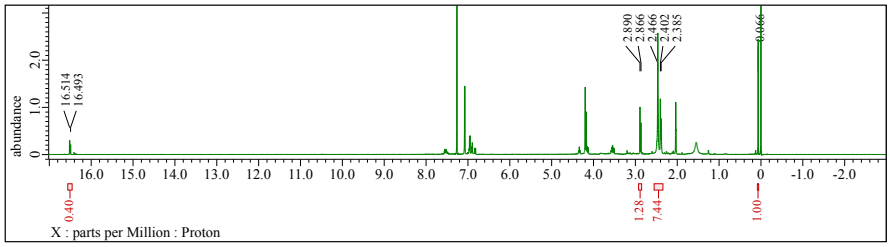
[a]$[\boldsymbol{Ru}]_{\textbf{7-amide}}$ in $CDCl_3$ (4.7mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 2 mM) was employed as an internal standard.

Fig. S3. ^{1}H-NMR spectra of complex $\boldsymbol{[Ru]_{7\text{-amide}}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $\boldsymbol{[Ru]_{7\text{-amide}}}$ = 4.7 mM and [HMDSO] = 2 mM (internal standard).

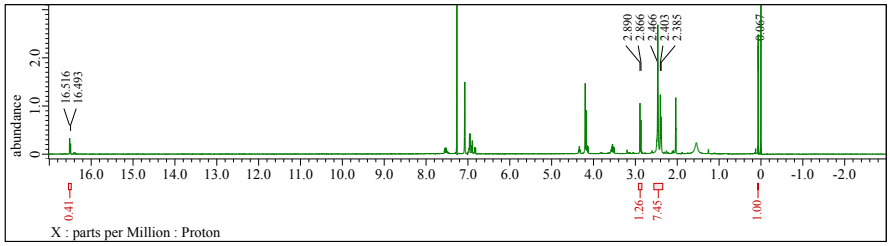
0 h



after 7 h



after 24 h

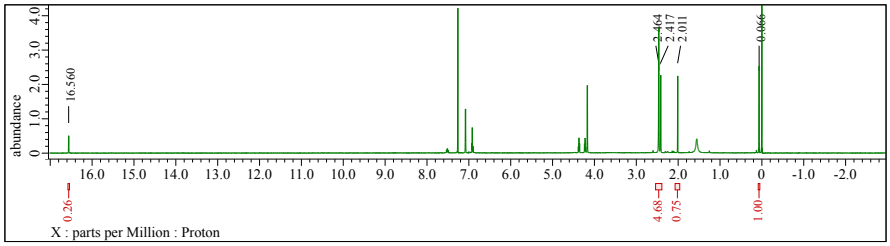


time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	N-Me protons (2.87 ppm and 2.89 ppm)	mesityl protons (2.38-2.47 ppm)	benzylidene protons (Ru=CH, 16.49 ppm and 16.52 ppm)
0 h	1.24	7.45	0.41
after 7 h	1.28	7.44	0.40
after 24 h	1.26	7.45	0.41

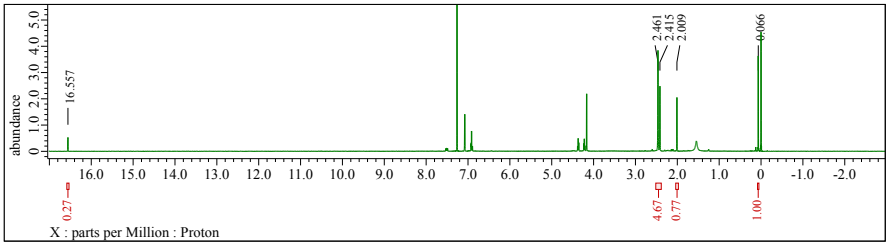
[a] $[\boldsymbol{Ru}]_{\textbf{8-amide}}$ in $CDCl_3$ (7.5 mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 1 mM) was employed as an internal standard.

Fig. S4. ^{1}H-NMR spectra of complex $[\boldsymbol{Ru}]_{\textbf{8-amide}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $[\boldsymbol{Ru}]_{\textbf{8-amide}}$ = 7.5 mM and [HMDSO] = 2 mM (internal standard).

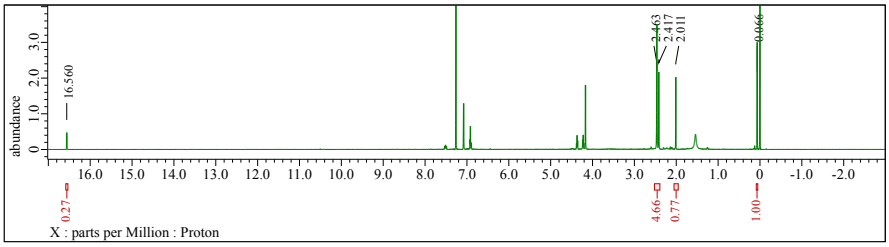
0 h



after 7 h



after 24 h

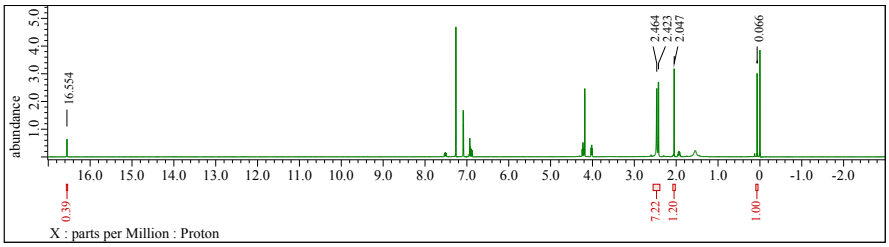


time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	ester Me protons (2.009 ppm)	mesityl protons (2.40-2.47 ppm)	benzylidene proton (Ru= CH, 16.56 ppm)
0 h	0.75	4.68	0.26
after 7 h	0.77	4.67	0.27
after 24 h	0.77	4.66	0.27

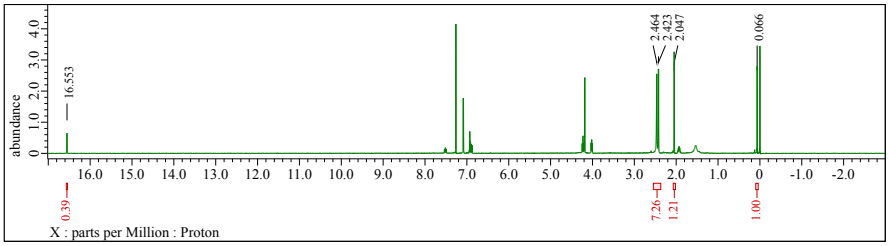
[a]$[\boldsymbol{Ru}]_{\textbf{9-ester}}$ in $CDCl_3$ (3.8 mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 1 mM) was employed as an internal standard.

Fig. S5. ^{1}H-NMR spectra of complex $[\boldsymbol{Ru}]_{\textbf{9-ester}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $[\boldsymbol{Ru}]_{\textbf{9-ester}}$ = 3.8 mM and [HMDSO] = 2 mM (internal standard).

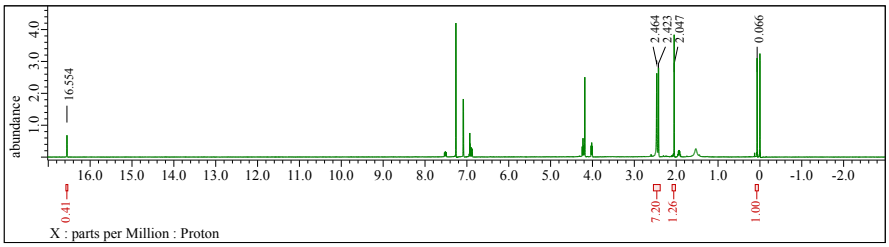
0 h



after 7 h



after 24 h

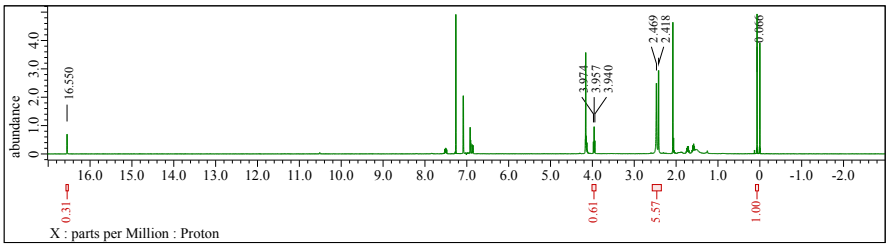


time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	ester Me protons (2.05 ppm)	mesityl protons (2.40-2.47 ppm)	benzylidene proton (Ru=CH, 16.54 ppm)
0 h	1.20	7.22	0.39
after 7 h	1.21	7.26	0.39
after 24 h	1.26	7.20	0.41

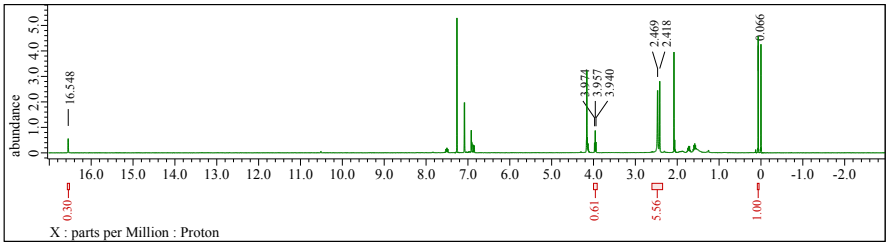
[a]$[\boldsymbol{Ru}]_{\textbf{10-ester}}$ in $CDCl_3$ (6 mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 1 mM) was employed as an internal standard.

Fig. S6. ^{1}H-NMR spectra of complex $\boldsymbol{[Ru]_{10\text{-ester}}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $\boldsymbol{[Ru]_{10\text{-ester}}}$ = 6 mM and [HMDSO] = 2 mM (internal standard).

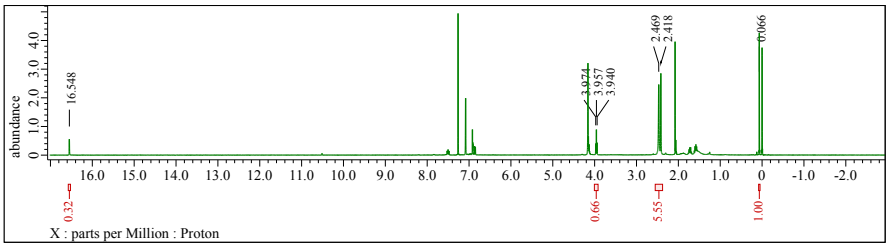
0 h



after 7 h



after 24 h



time[a]	Relative intensity toward internal standard (0.06 ppm)[b]		
	-OC<u>*H*</u>$_2$-$(CH_2)_3$-OPh (3.96 ppm)	mesityl protons (2.41-2.47 ppm)	benzylidene proton (Ru=CH, 16.55 ppm)
0 h	0.61	5.57	0.31
after 7 h	0.61	5.56	0.30
after 24 h	0.66	5.55	0.32

[a]$[\boldsymbol{Ru}]_{\textbf{11-ester}}$ in $CDCl_3$ (5.6 mM) was incubated at 25 ˚C under a N_2 atmosphere. [b]Hexamethyldisiloxane (HMDSO, 1 mM) was employed as an internal standard.

Fig. S7. ^{1}H-NMR spectra of complex $\boldsymbol{[Ru]}_{\textbf{11-ester}}$ in $CDCl_3$ at 25 ˚C over 24 h for the evaluation of complex stability; $\boldsymbol{[Ru]}_{\textbf{11-ester}}$ = 5.6 mM and [HMDSO] = 2 mM (internal standard).

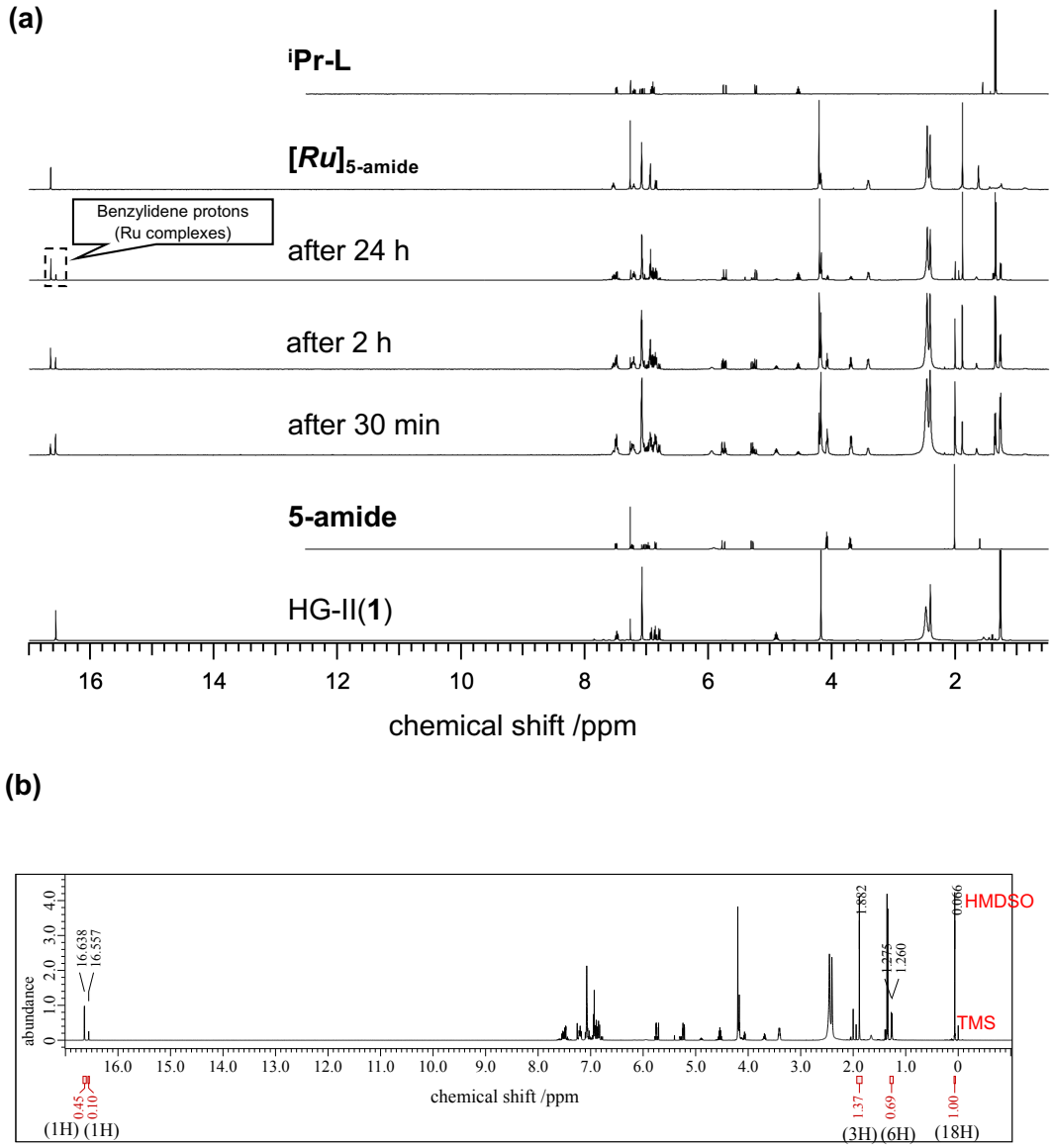


Fig. S8. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **5-amide** (in $CDCl_3$, 25 ˚C under N_2); (a) whole magnetic field region; (b) ^{1}H-NMR spectrum at 24 h (with integration values (vs. HMDSO (4 mM)).

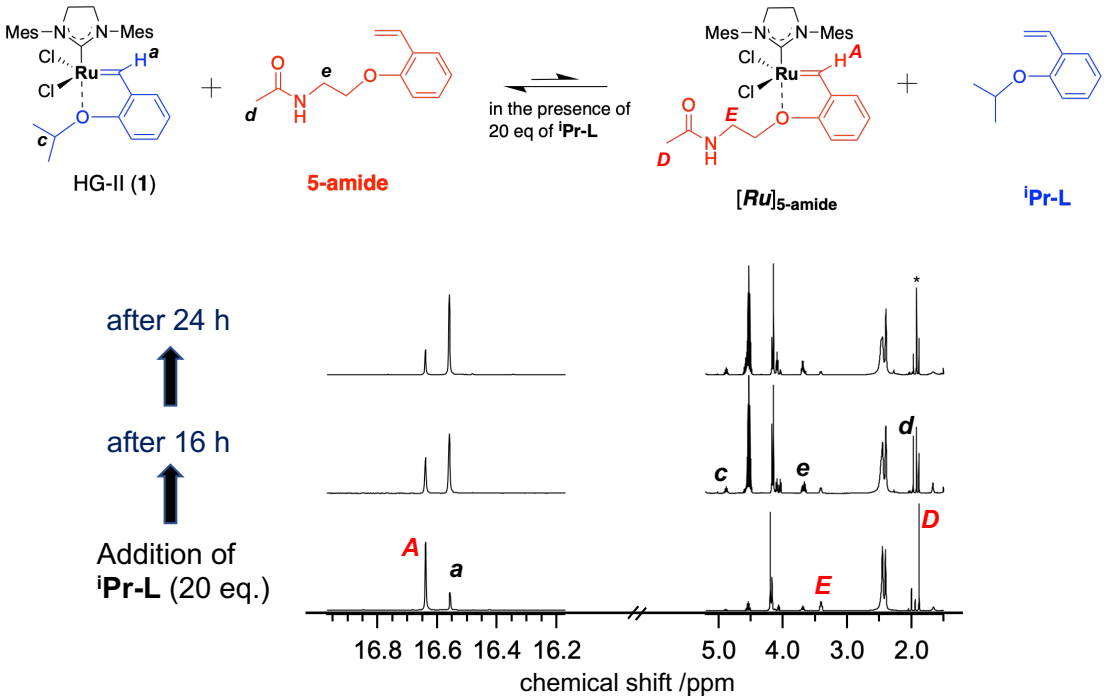
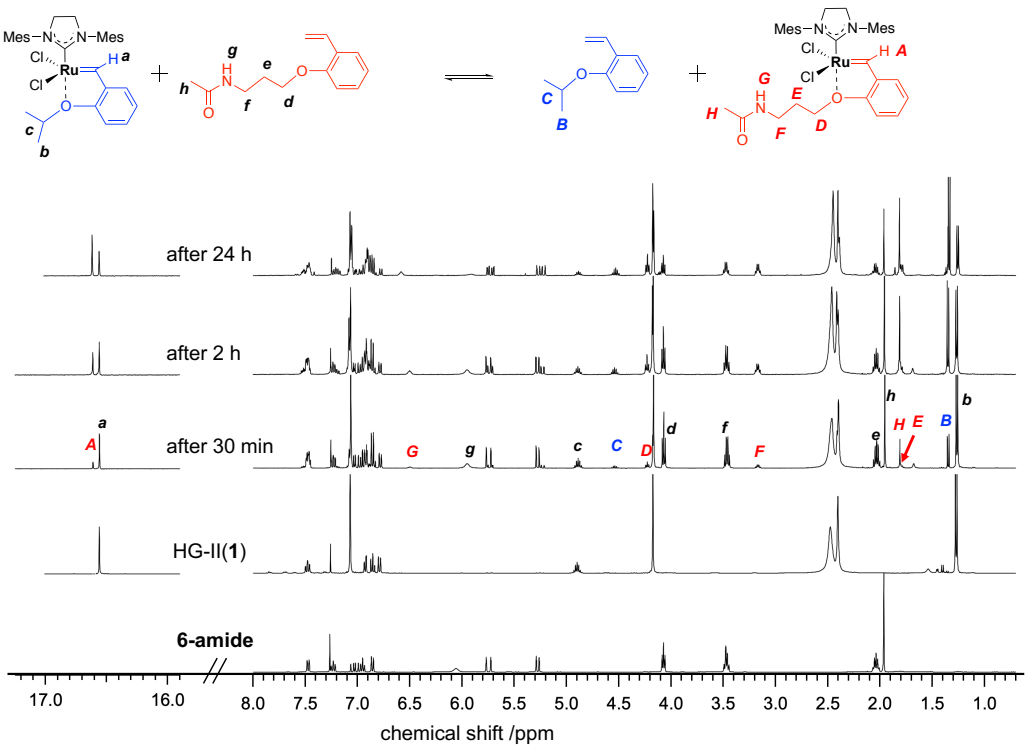


Fig. S9. ^{1}H-NMR spectral changes after addition of excess ^{i}**Pr-L** (840 mM) to a mixture of HG-II(**1**) and **[*Ru*]$_{5\text{-amide}}$** produced by ligand exchange reaction with ligand **5-amide** (initial concentration: [HG-II(**1**)] = [**5-amide**] = 42 mM) in $CDCl_3$, 25 ˚C under N_2). The reversal in the intensities of peak *A* and peak *a* is indicative of the occurrence of reverse reaction (from **[*Ru*]$_{5\text{-amide}}$** to HG-II(**1**)). The increase in the intensities of peaks *c*, *d*, and *e* supports this idea. The peak with an asterisk suggests a cross-metathesis reaction because of the existence of huge excess ^{i}**Pr-L**.

(a)



(b)

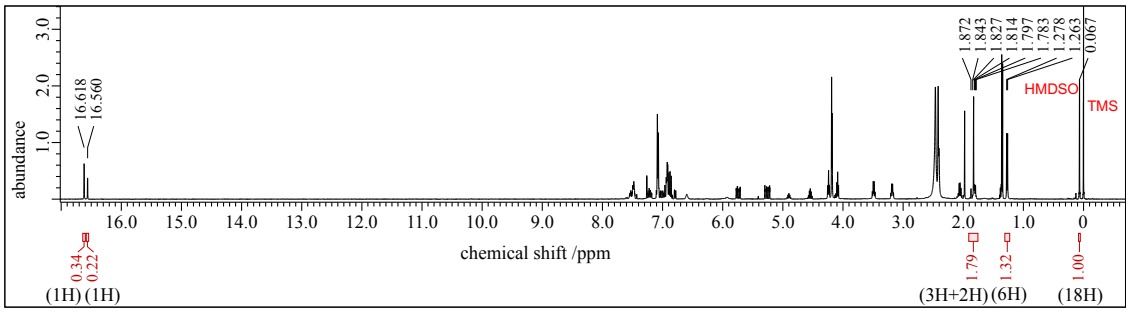


Fig. S10. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **6-amide** (in $CDCl_3$, 25 ˚C under N_2; (a) spectral change over 24 h; (b) ^{1}H-NMR spectrum at 24 h. The spectra of HG-II(**1**) and **6-amide** were separately collected as authentic spectra.

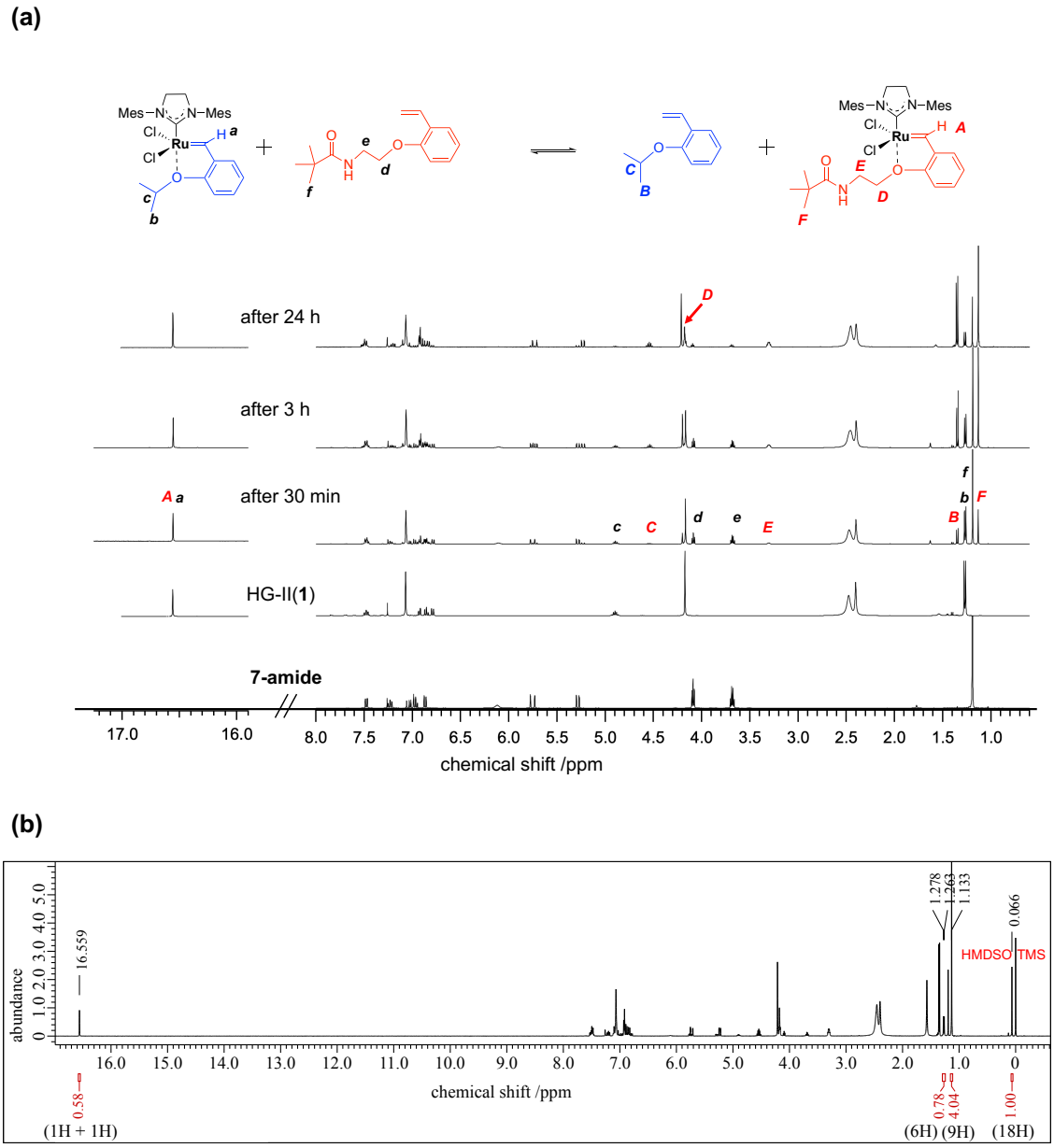
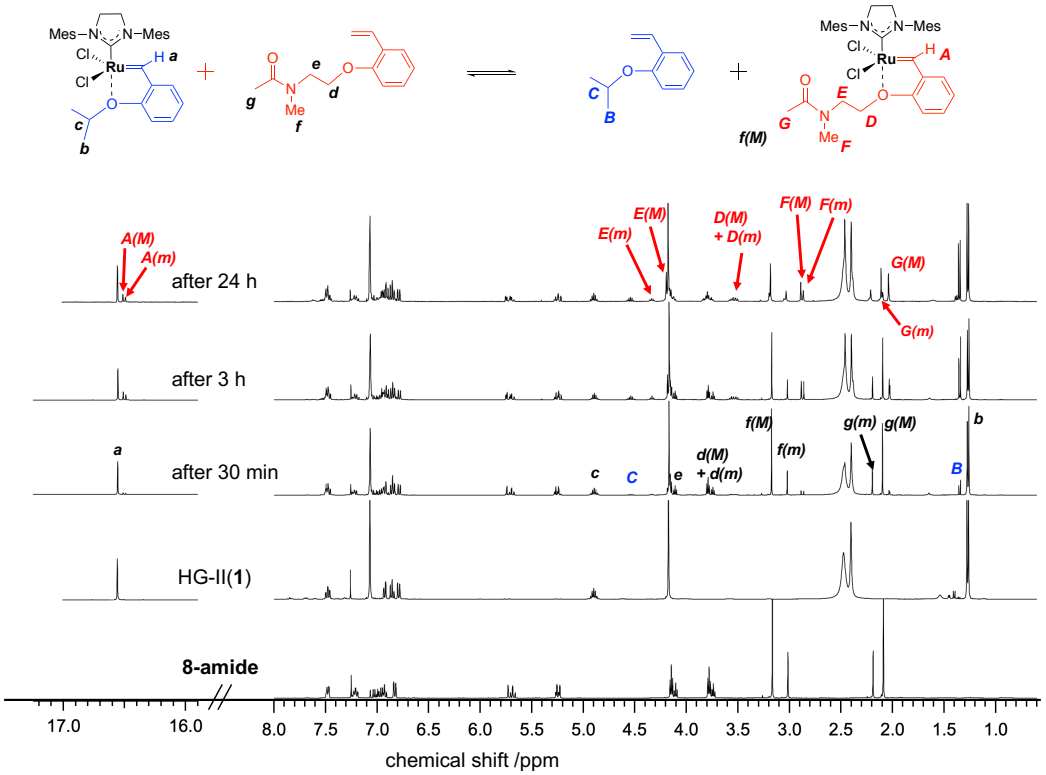


Fig. S11. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **7-amide** (in $CDCl_3$, 25 ˚C under N_2; (a) spectral change over 24 h; (b) ^{1}H-NMR spectrum at 24 h. The spectra of HG-II(**1**) and **7-amide** were separately collected as authentic spectra.

(a)



(b)

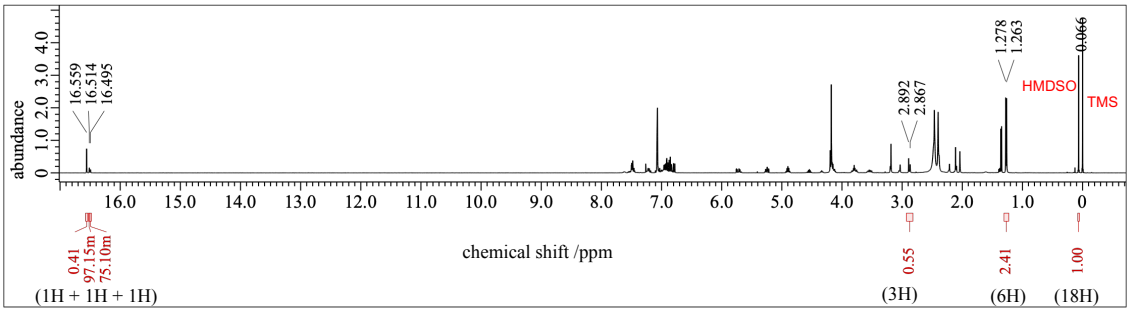


Fig. S12. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **8-amide** (in $CDCl_3$, 25 ˚C under N_2; (a) spectral change over 24 h; (b) ^{1}H-NMR spectrum at 24 h. The spectra of HG-II(**1**) and **8-amide** were separately collected as authentic spectra. In the spectrum collected after 24 h since the reaction start, "(*M*)" and "(*m*)" stand for peaks derived from major and minor configuration complex, respectively.

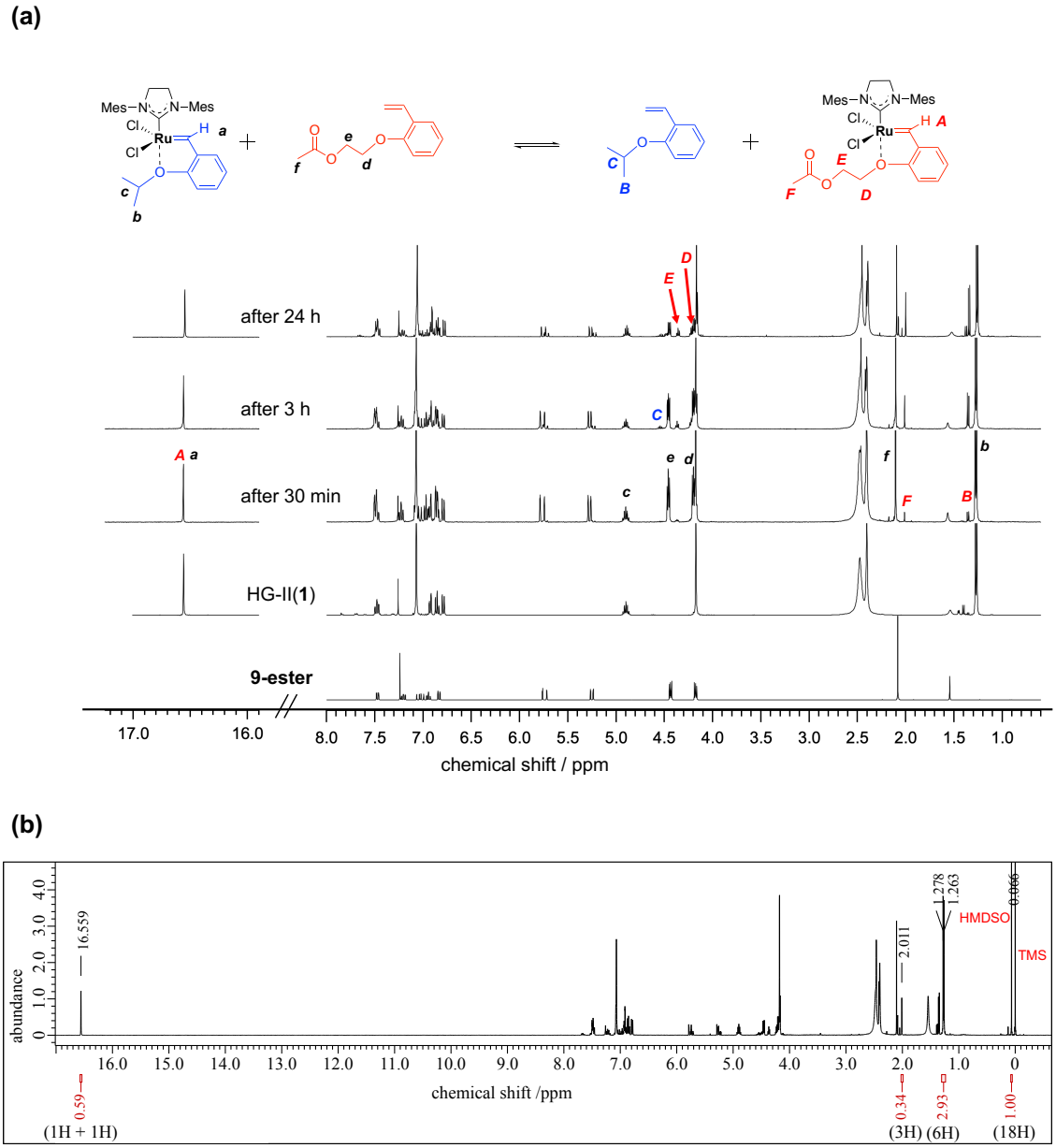


Fig. S13. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **9-ester** (in $CDCl_3$, 25 ˚C under N_2; (a) spectral change over 24 h; (b) ^{1}H-NMR spectrum at 24 h. The spectra of HG-II(**1**) and **9-ester** were separately collected as authentic spectra.

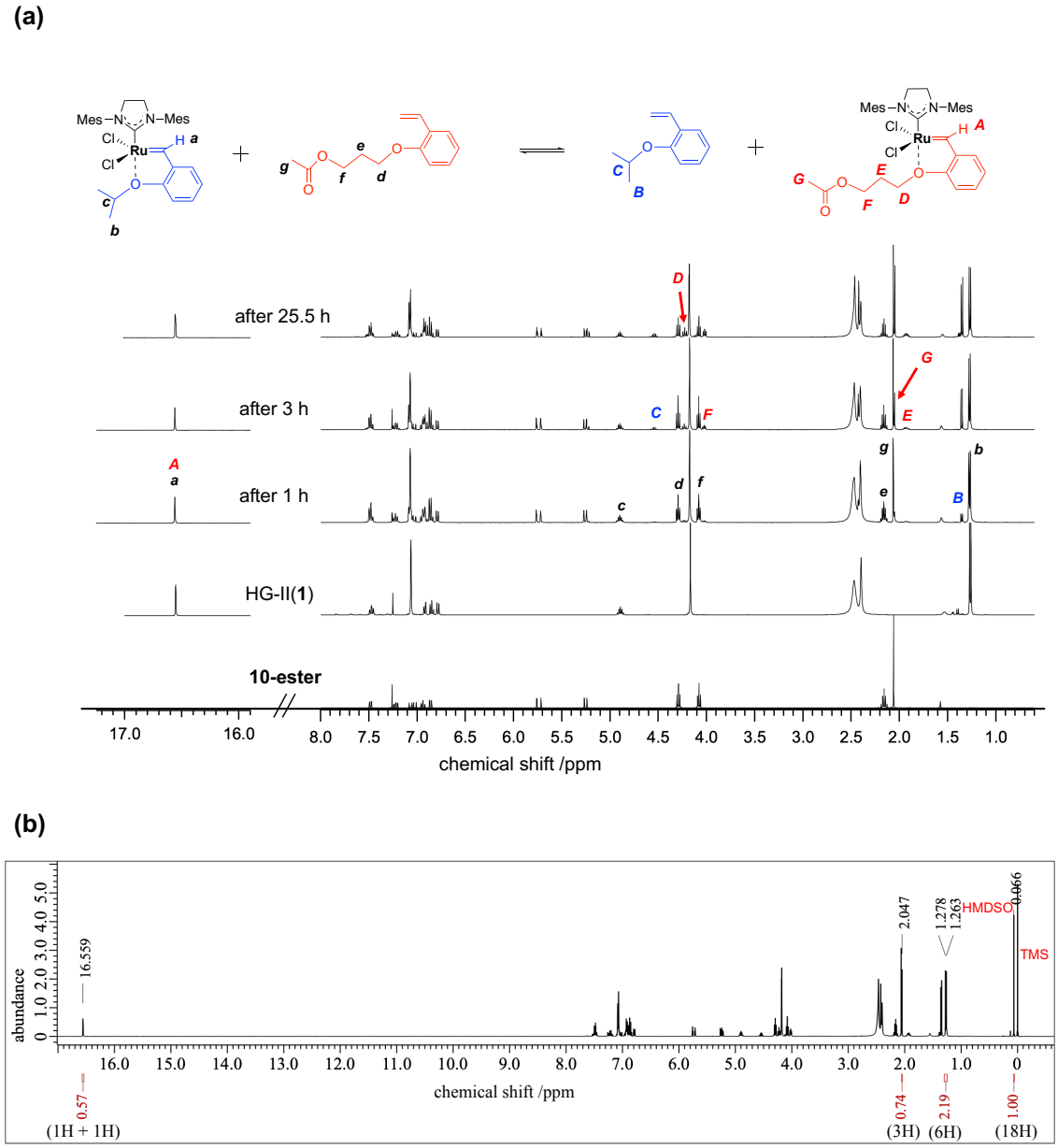


Fig. S14. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **10-ester** (in $CDCl_3$, 25 ˚C under N_2; (a) spectral change over 24 h; (b) ^{1}H-NMR spectrum at 24 h. The spectra of HG-II(**1**) and **10-ester** were separately collected as authentic spectra.

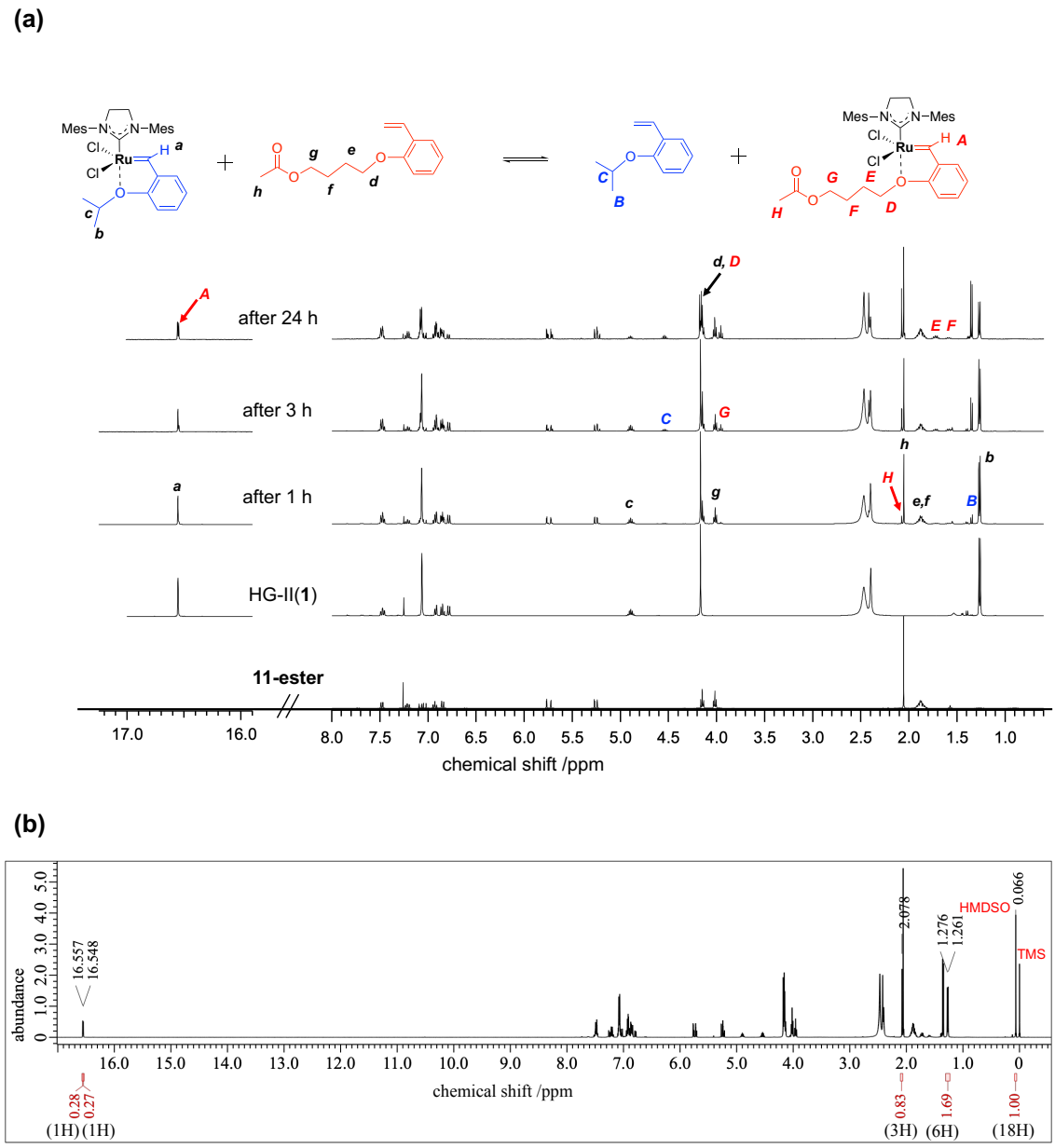


Fig. S15. ^{1}H-NMR spectral change during the ligand exchange between HG-II(**1**) and ligand **11-ester** (in $CDCl_3$, 25 ˚C under N_2; (a) spectral change over 24 h; (b) ^{1}H-NMR spectrum at 24 h. The spectra of HG-II(**1**) and **11-ester** were separately collected as authentic spectra.

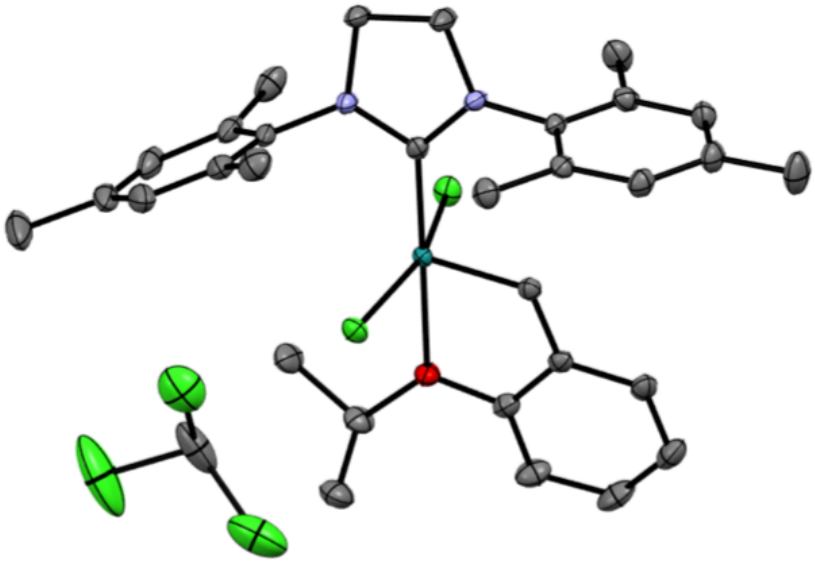


Fig. S16. Single crystal structure of HG-II(**1**). Thermal ellipsoids are drawn at 50% probability level. The crystal was obtained by vapor diffusion of hexane into a $CHCl_3$ solution at 5 ˚C. X-ray diffraction was collected at 125 ± 0.1 K.

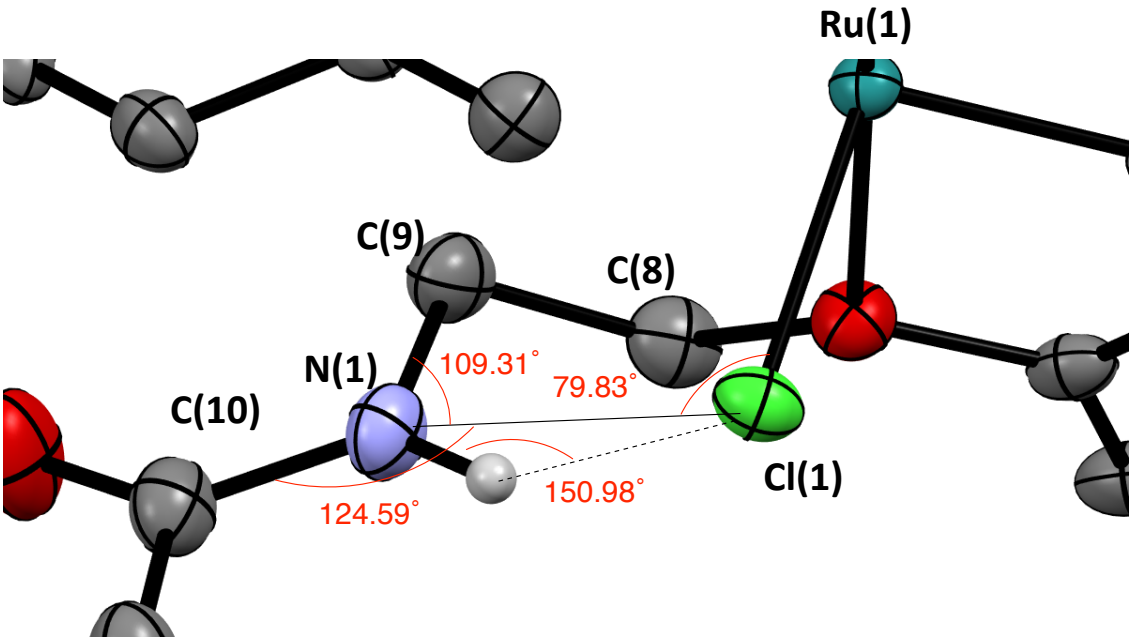


Fig. S17. List of dihedral angles around the amide moiety in **[*Ru*]$_{5\text{-amide}}$**.

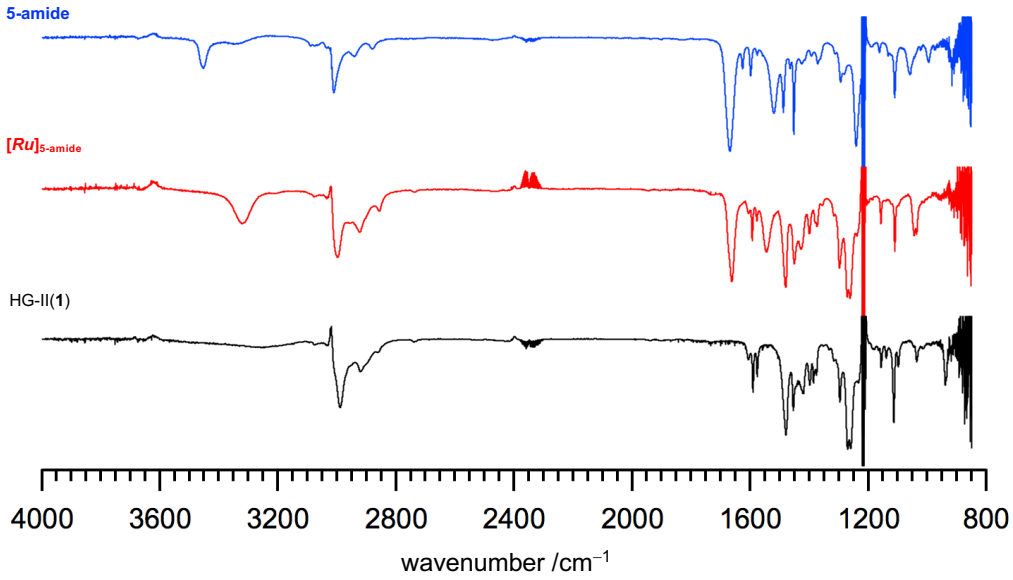


Fig. S18. FT-IR spectra of **5-amide**, $[\boldsymbol{Ru}]_{\textbf{5-amide}}$, and HG-II(**1**) in $CHCl_3$ (whole range, resolution at 0.5 cm^{-1}, L = 0.5 mm, CaF_2 windows, accumulation number: 256). The shown spectra were obtained by subtracting the background spectrum of chloroform from each collected spectrum of ligand or complex spectra.

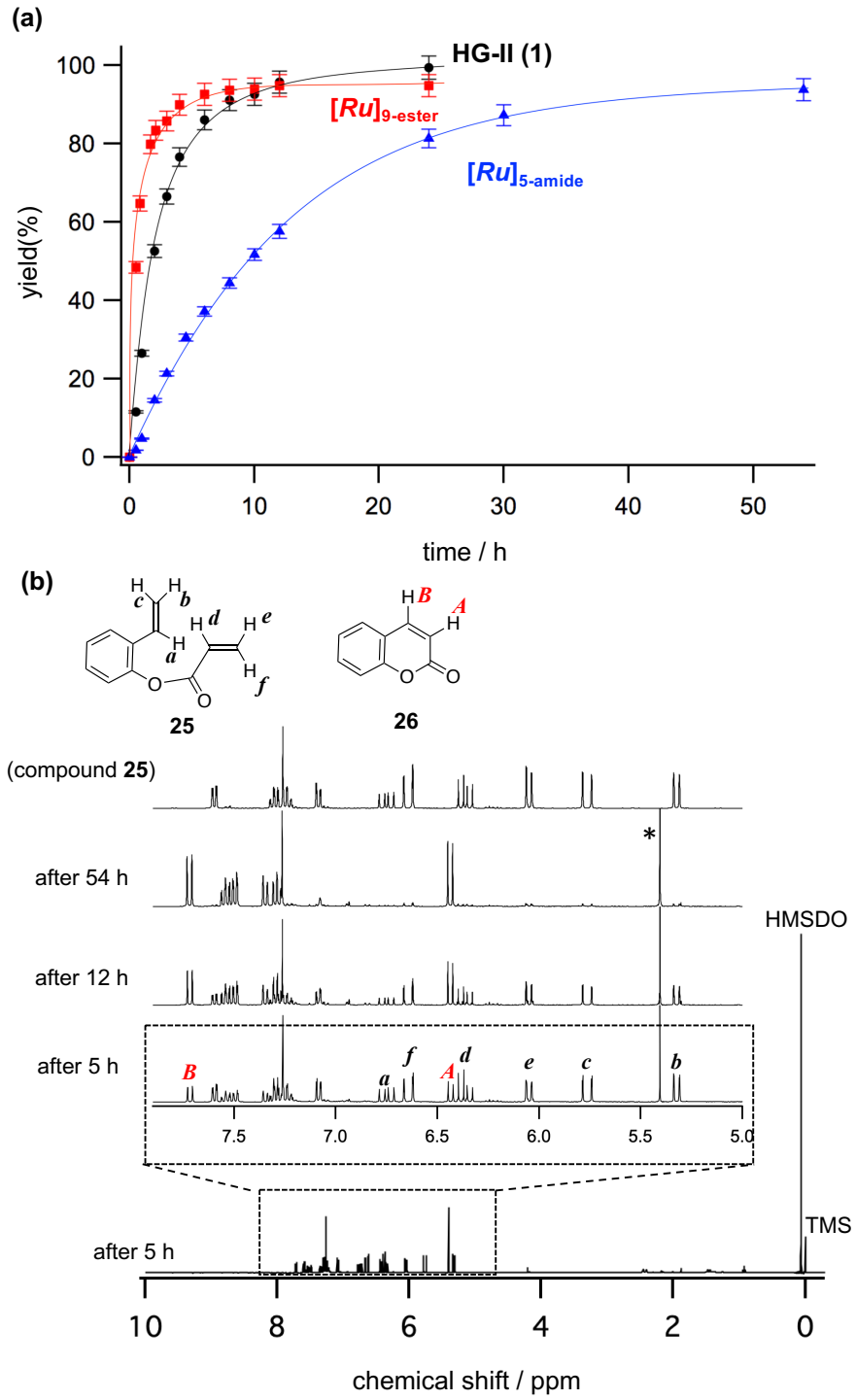


Fig. S19. Time-courses and ^{1}H-NMR spectral change in the **[*Ru*]$_{5\text{-amide}}$**-catalyzed RCM reaction of compound **25**; (a) time-courses; (b) ^{1}H-NMR spectral change. Reaction conditions: [compound **25**] = 42 mM, 5 mol% catalyst load, in $CDCl_3$, at 25 ˚C in the dark. The peak with an asterisk is assigned as ethylene protons.

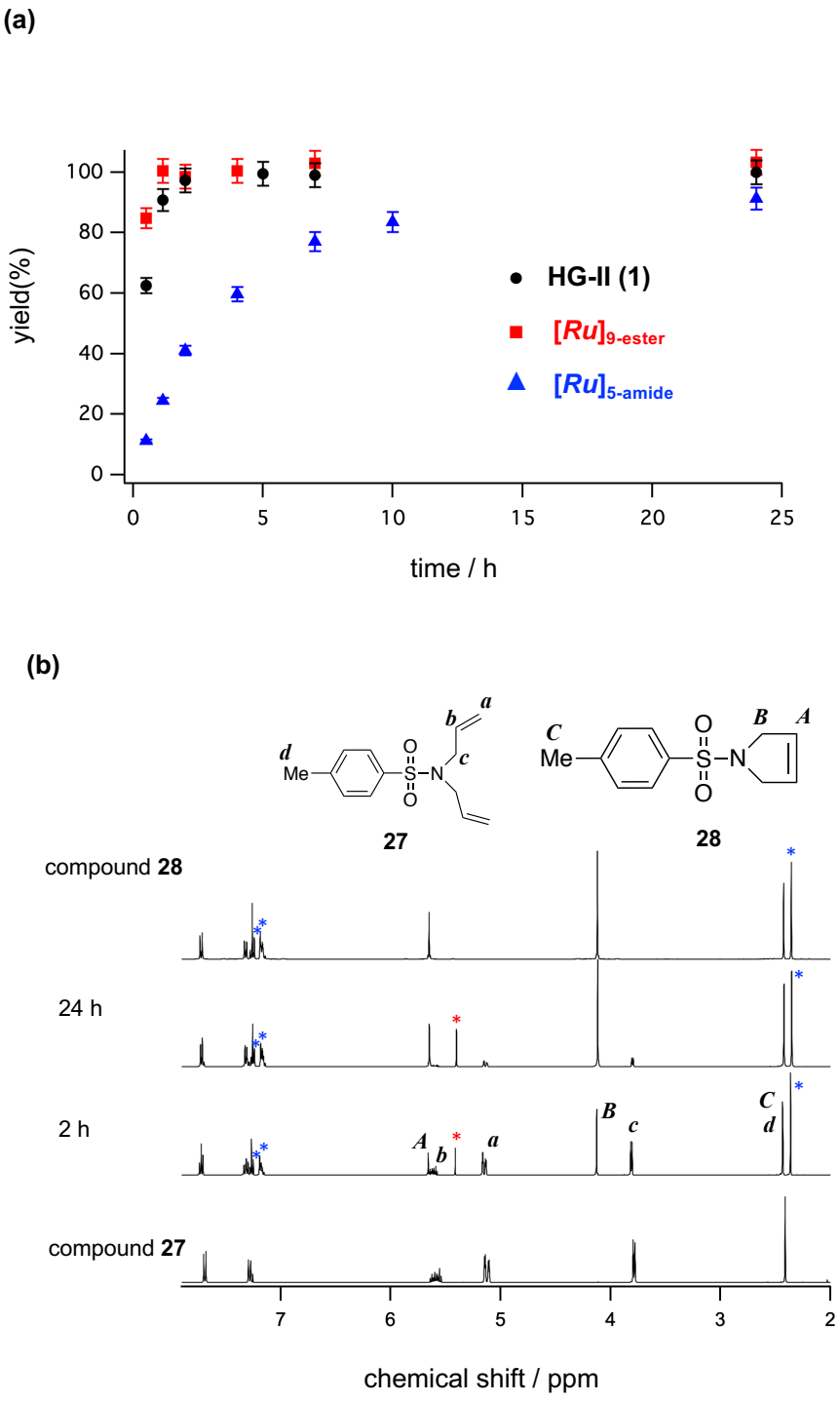


Fig. S20. Time-courses of and ^{1}H-NMR spectral change in the $[Ru]_{5\text{-amide}}$-catalyzed RCM reaction of compound **27**; (a) time-courses; (b) ^{1}H-NMR spectral change. Reaction conditions: [compound **27**] = 42 mM, 0.1 mol% catalyst load, in $CDCl_3$, at 25 ˚C in the dark. The peak with an asterisk is assigned as ethylene protons.

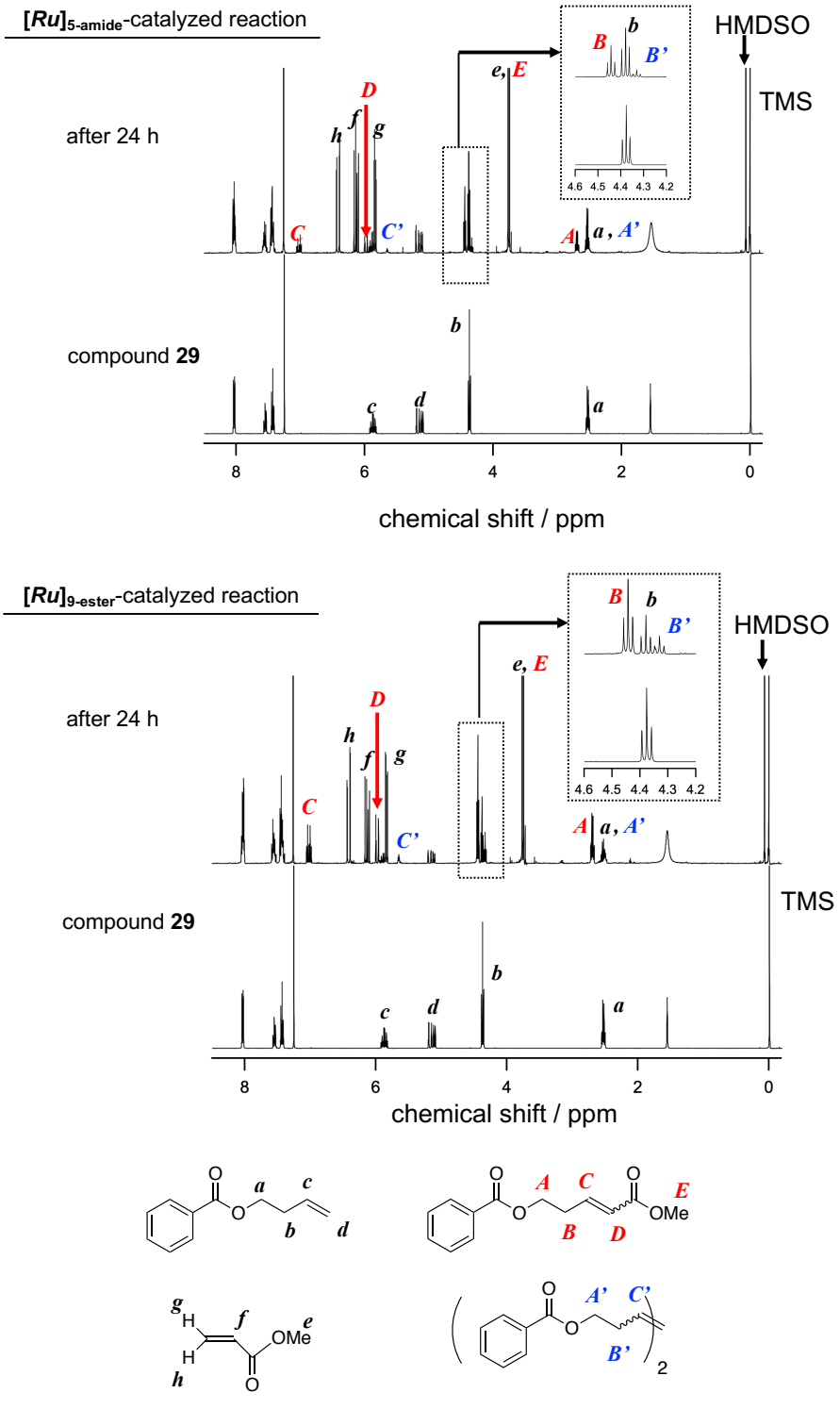


Fig. S21. ^{1}H-NMR spectrum collected at 24 h in the CM reactions of compounds **29** with **30**. Reaction conditions: [compound **29**] = 42 mM, [compound **30**] = 84 mM, 1 mol% catalyst load, in $CDCl_3$, at 25 ˚C in the dark.

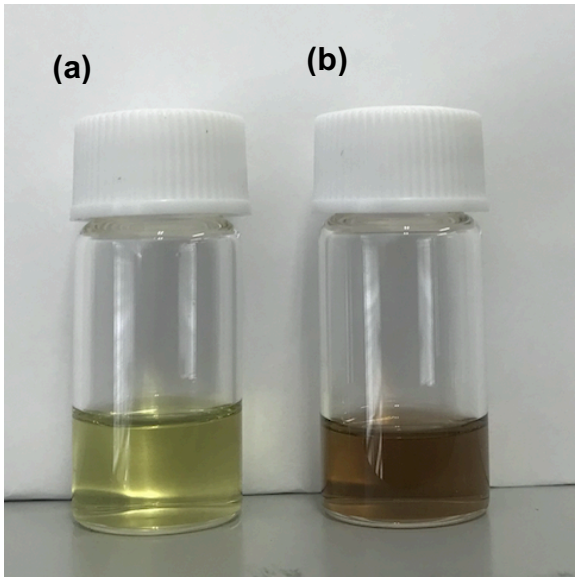
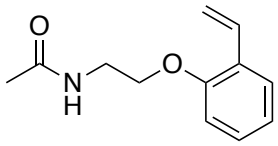
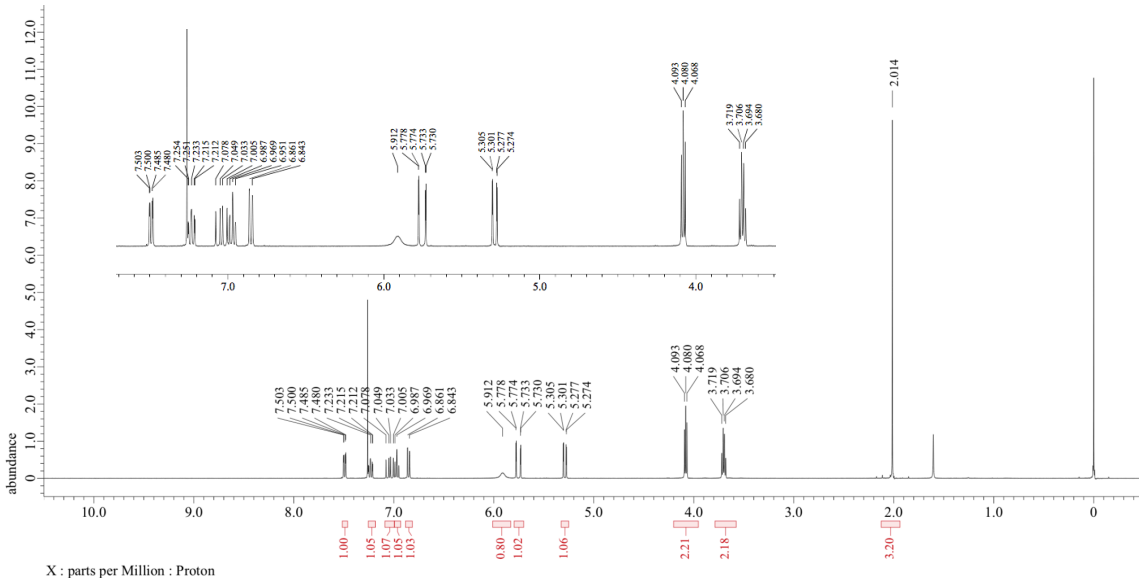


Fig. S22. Photographs of reaction solutions obtained after RCM reactions of compound **27** (at 45 ˚C); (a) solution of **[*Ru*]$_{5\text{-amide}}$**-catalyzed reaction; (b) solution of **[*Ru*]$_{9\text{-ester}}$**-catalyzed reaction. Both solutions were obtained at 30 min after the reactions started (The catalytic reactions had been completed).

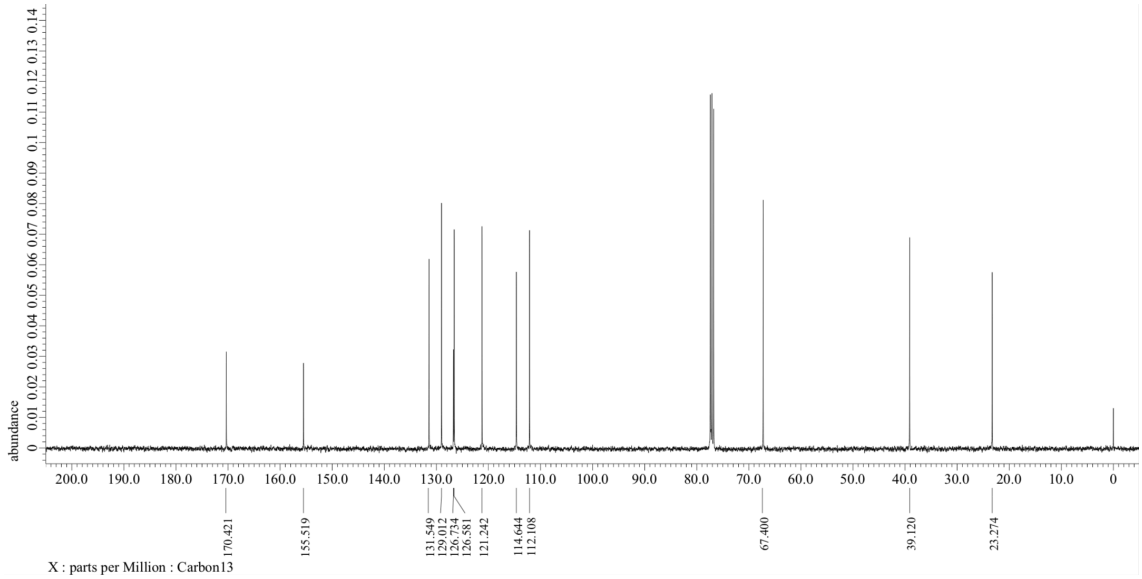
6. NMR Spectra of ligands and complexes

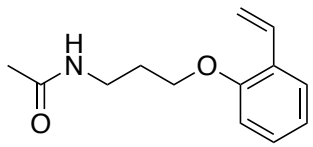


^{1}H-NMR (400 MHz, $CDCl_3$)

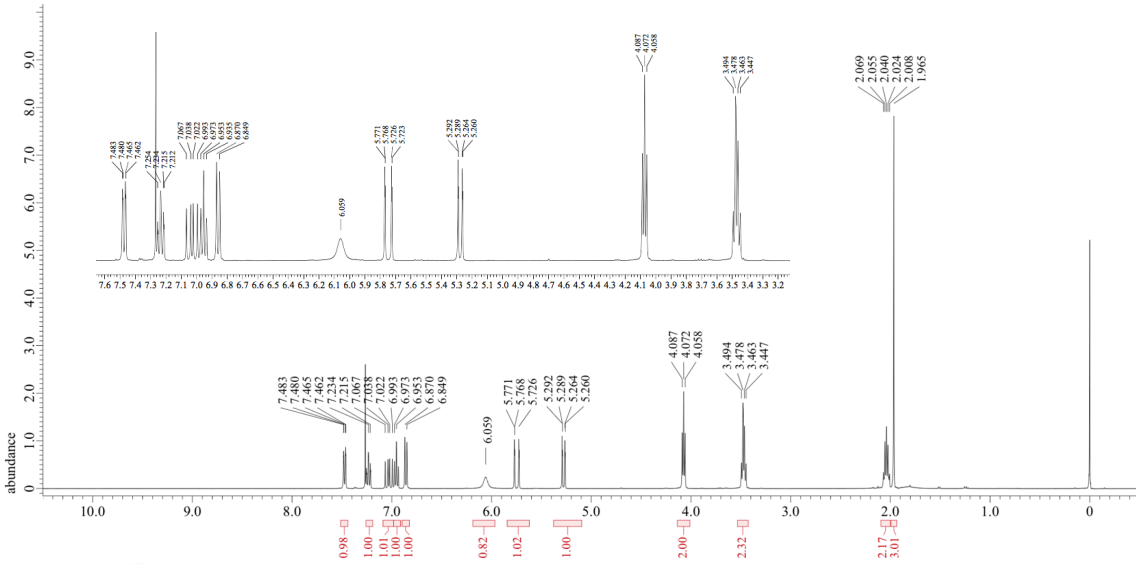


^{13}C-NMR (100 MHz, $CDCl_3$)

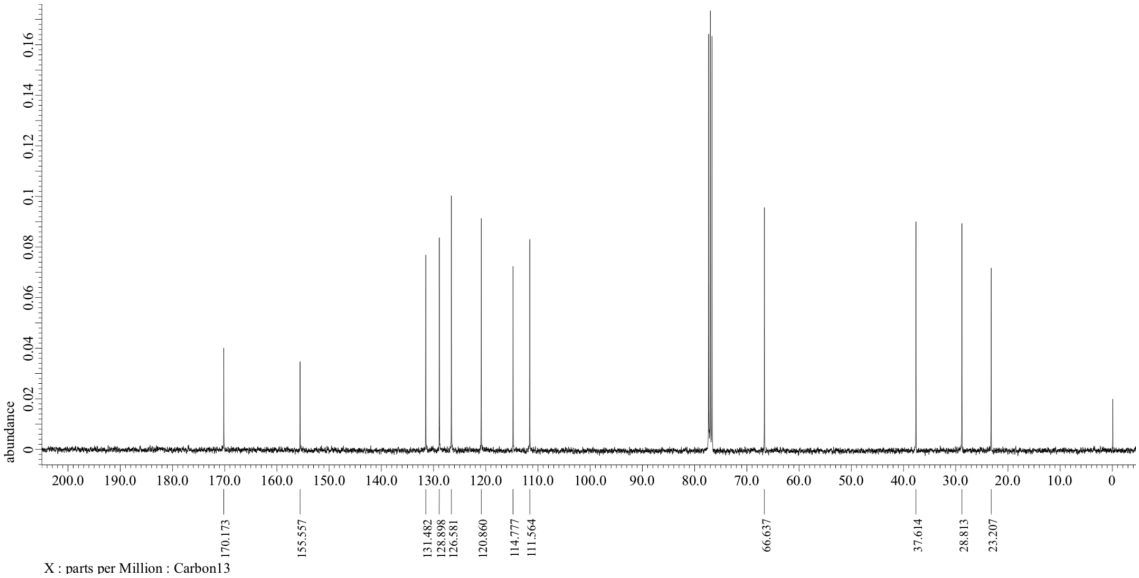


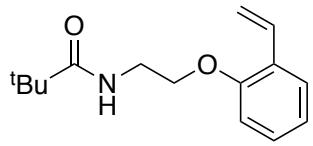


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)





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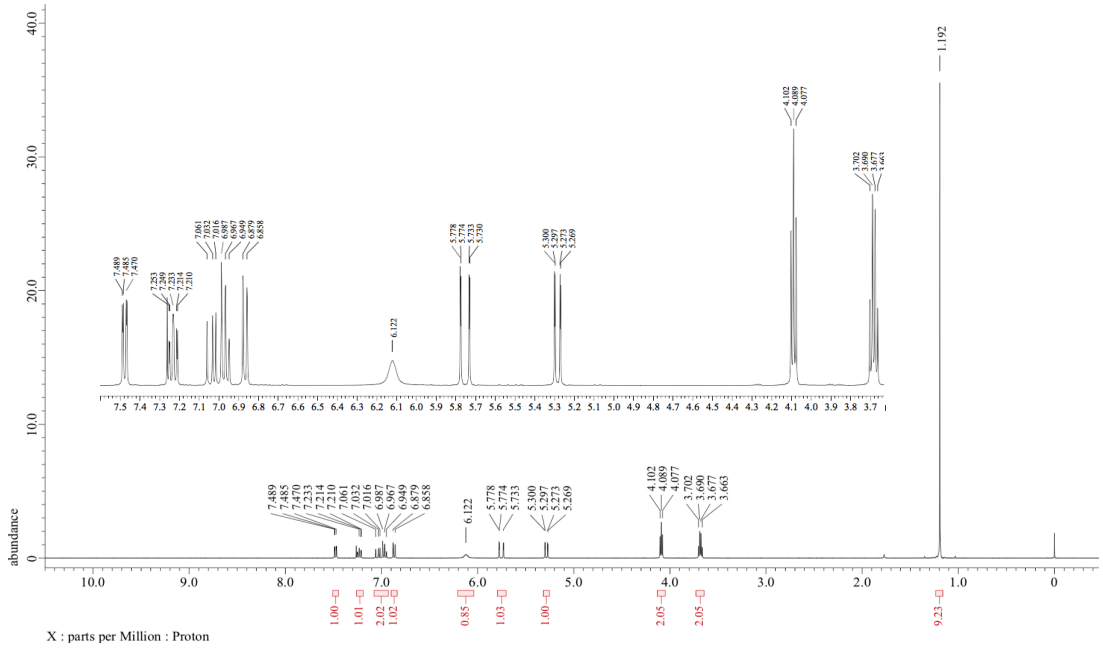
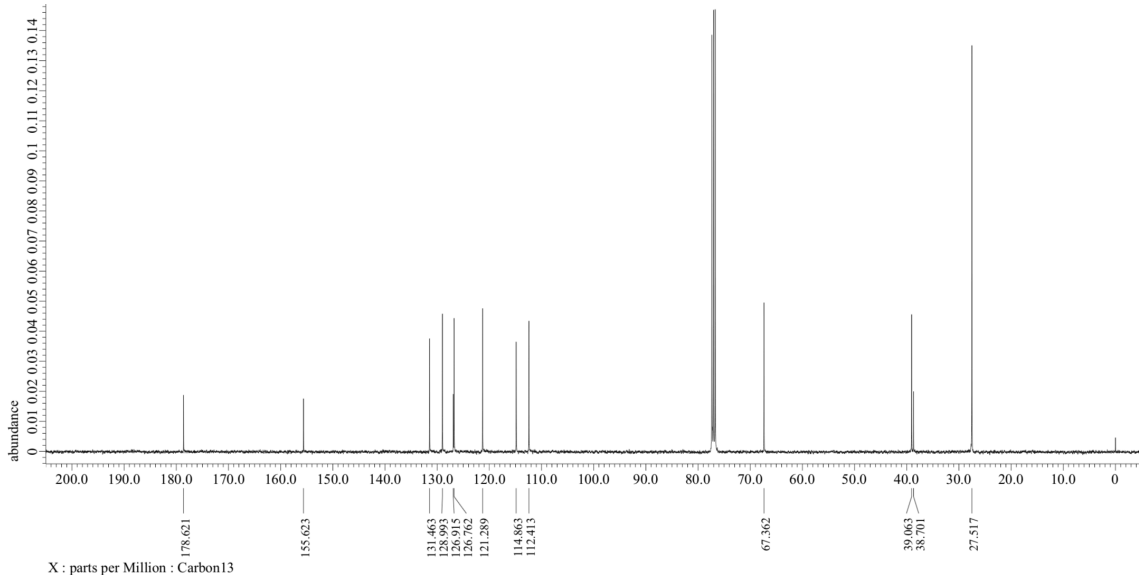
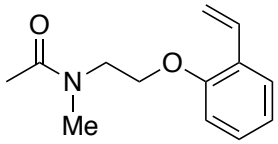
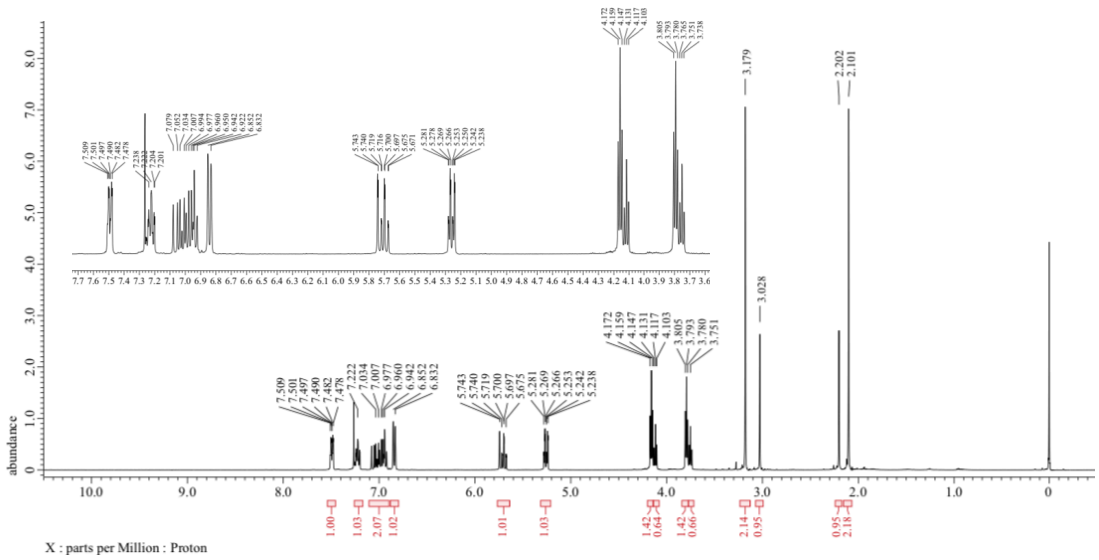


^{13}C-NMR (100 MHz, $CDCl_3$)

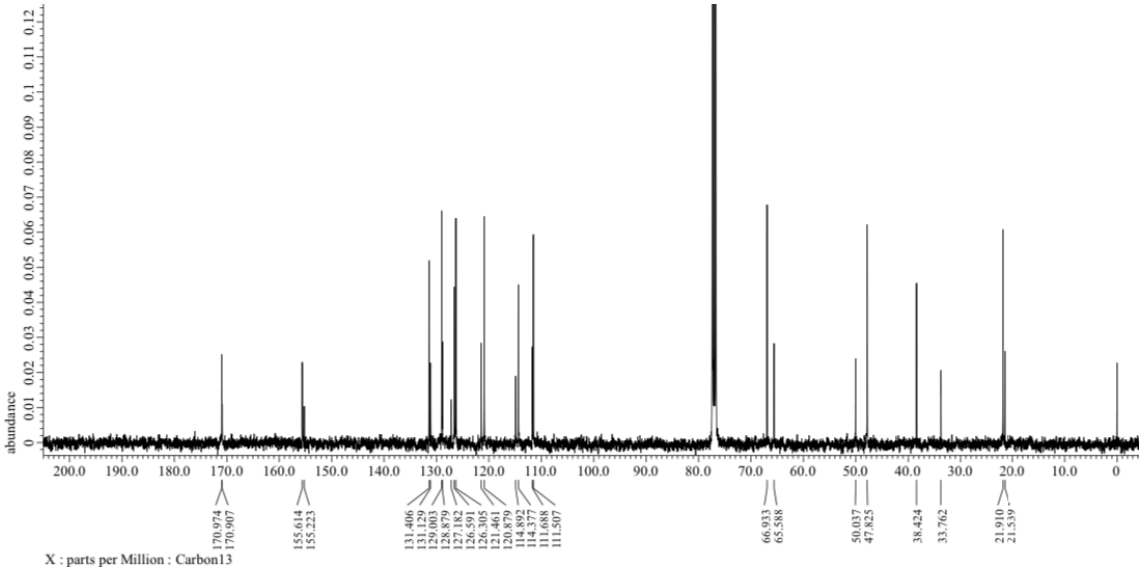


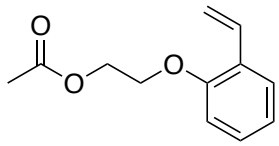


^{1}H-NMR (400 MHz, $CDCl_3$)

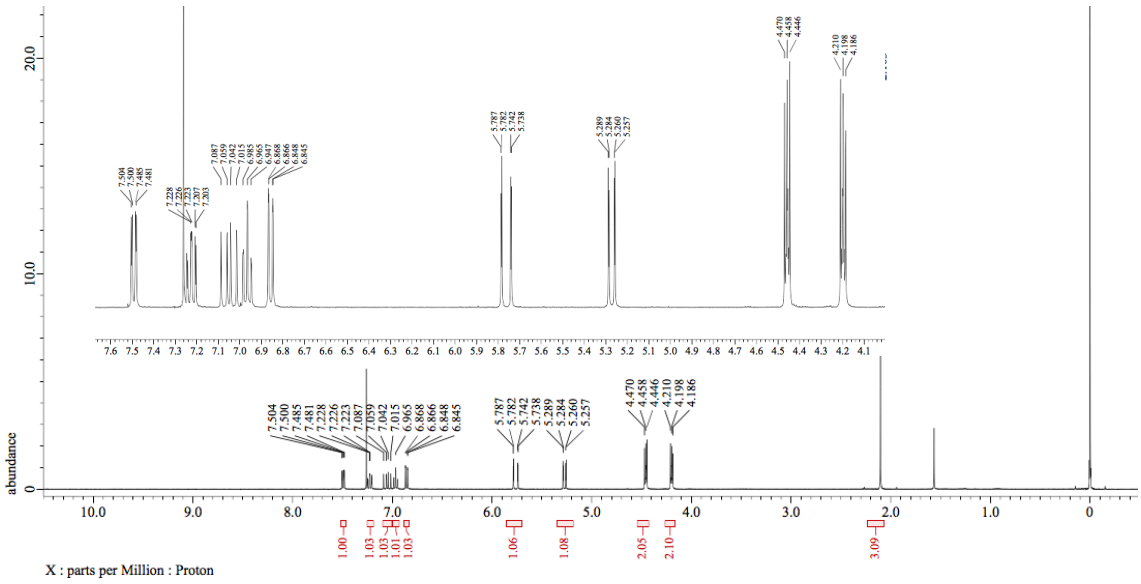


^{13}C-NMR (100 MHz, $CDCl_3$)

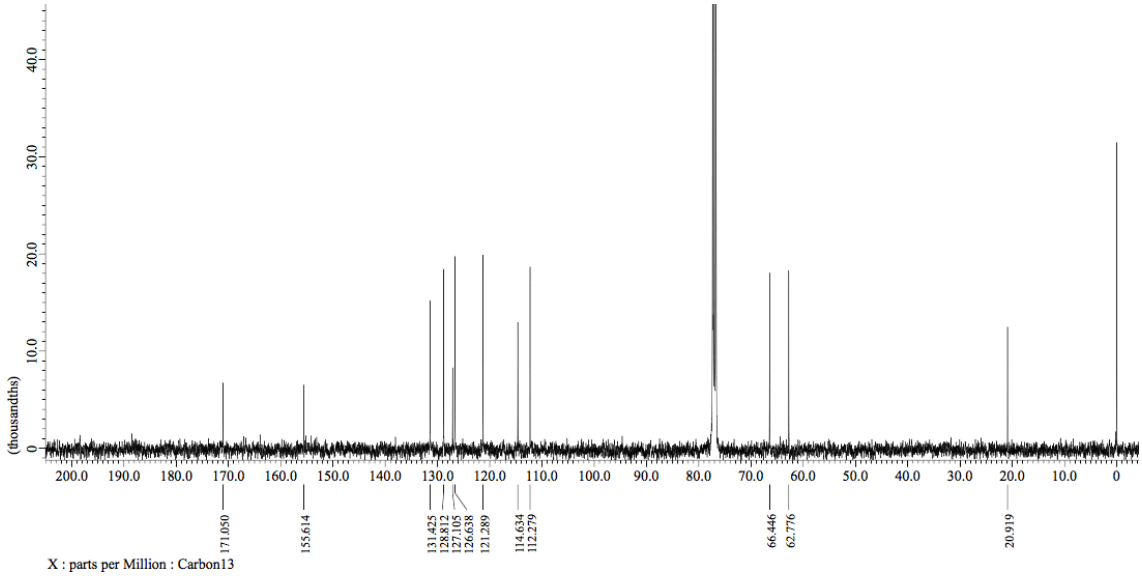


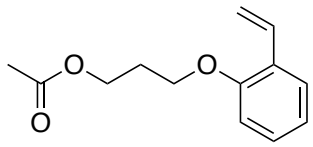


^{1}H-NMR (400 MHz, $CDCl_3$)

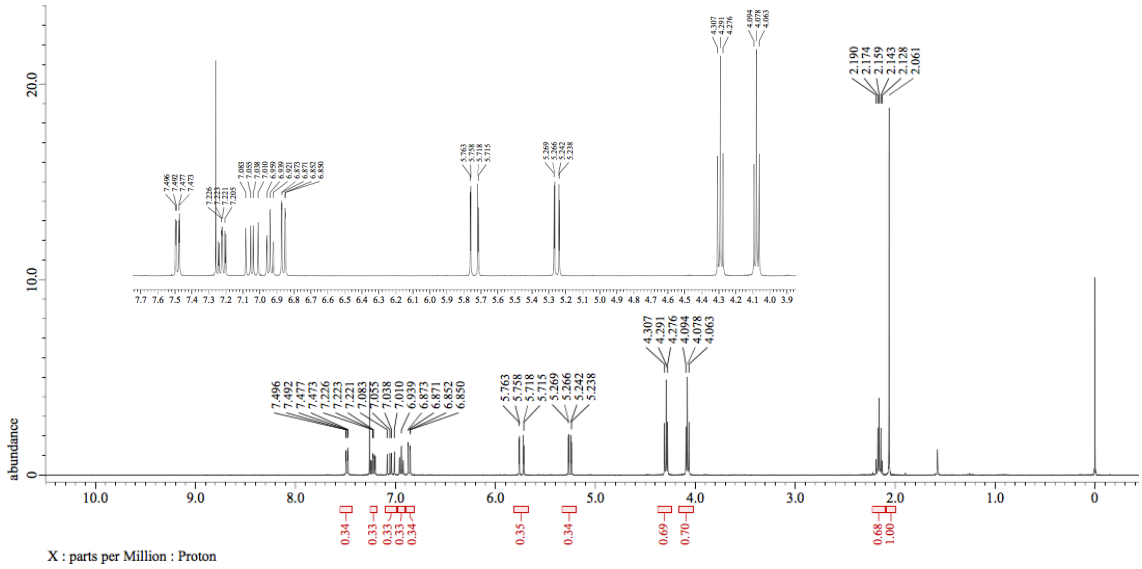


^{13}C-NMR (100 MHz, $CDCl_3$)

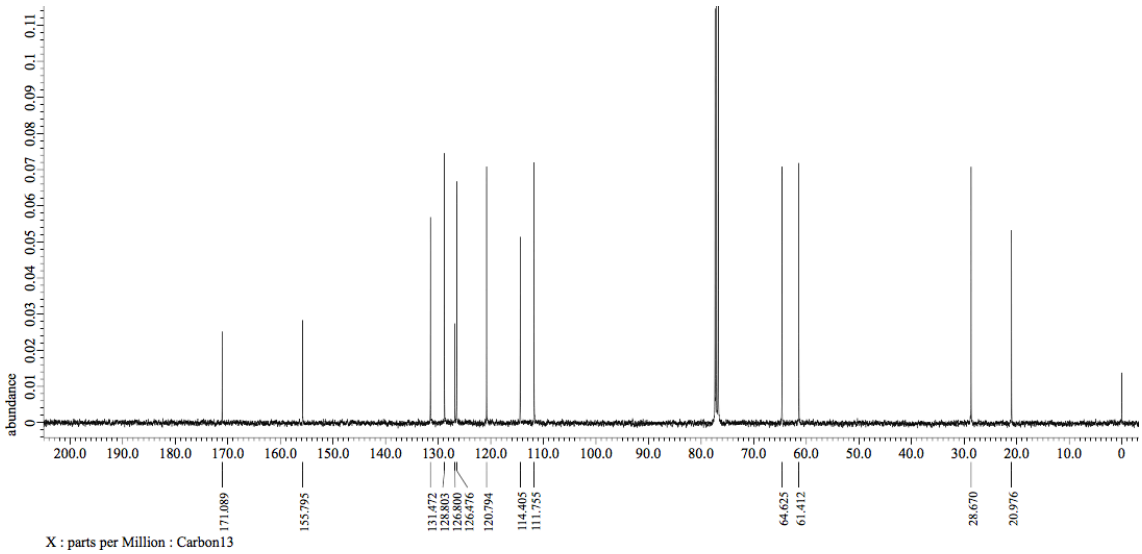


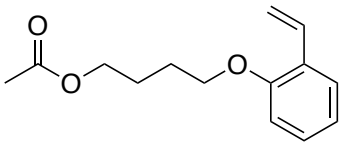


^{1}H-NMR (400 MHz, $CDCl_3$)

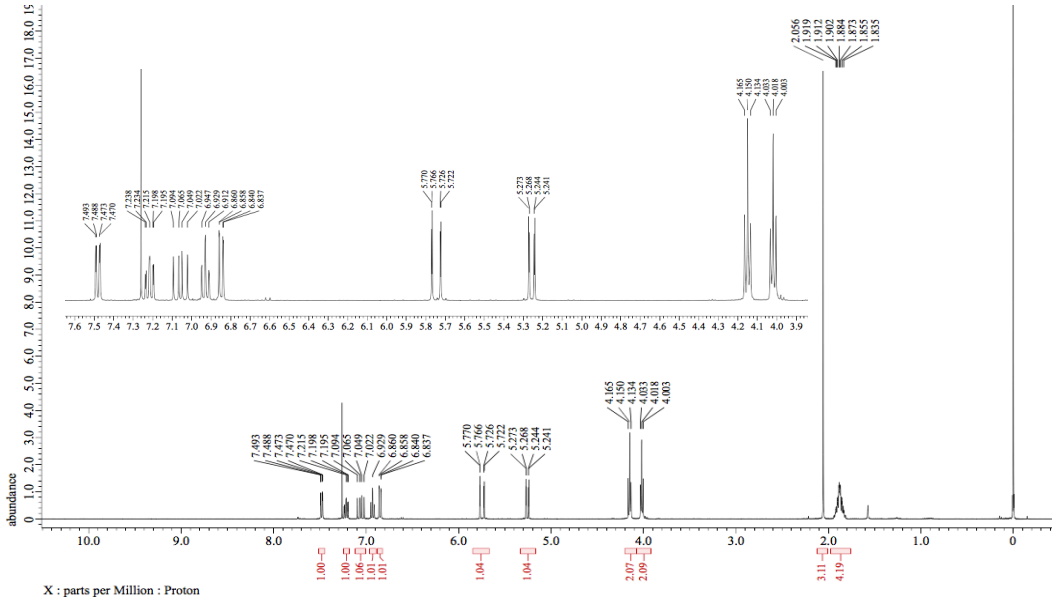


^{13}C-NMR (100 MHz, $CDCl_3$)

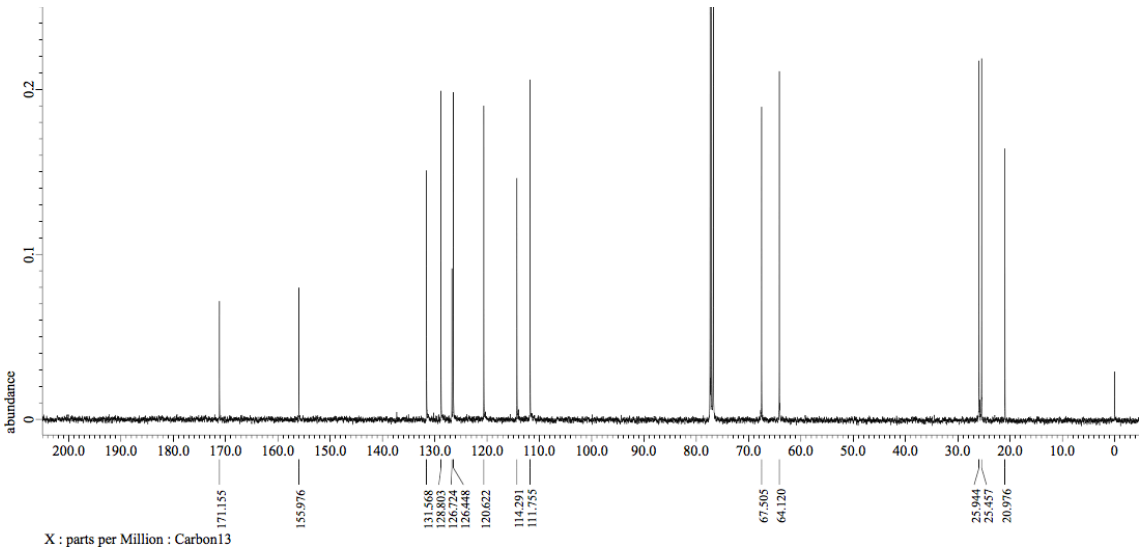


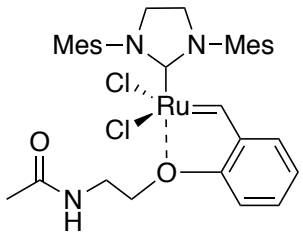


^{1}H-NMR (400 MHz, $CDCl_3$)

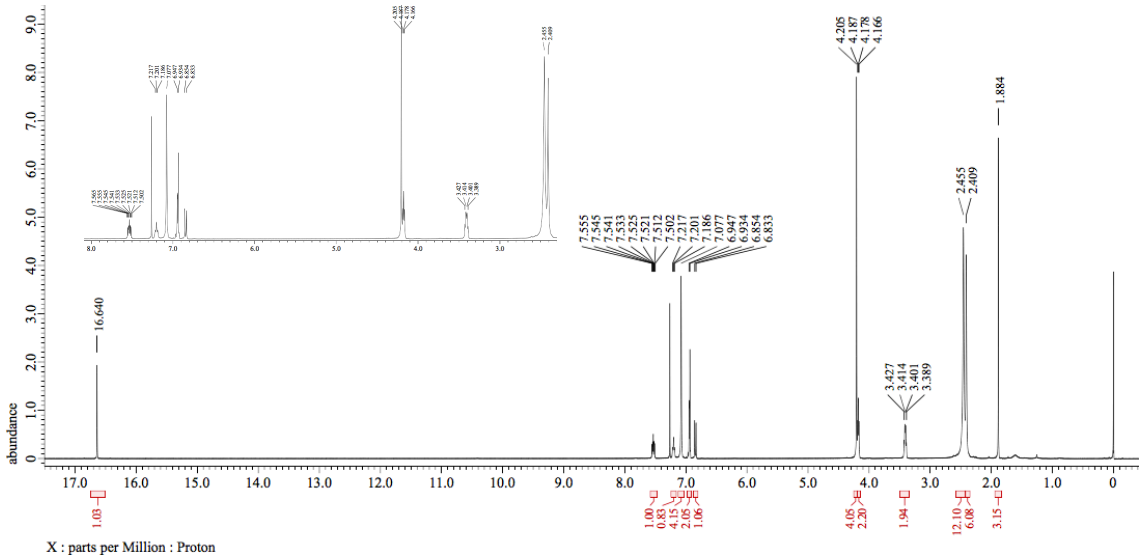


^{13}C-NMR (100 MHz, $CDCl_3$)

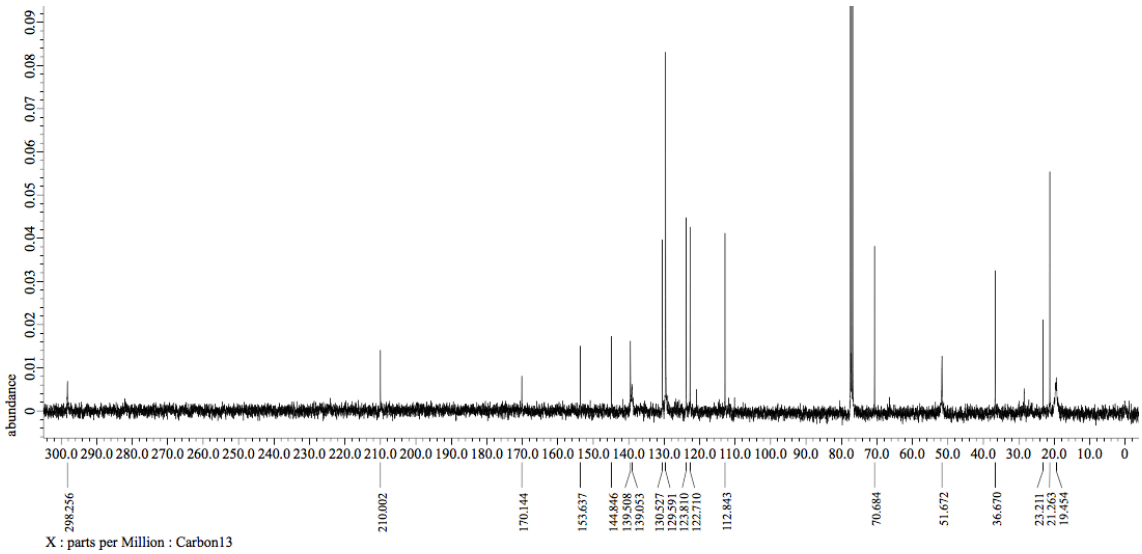


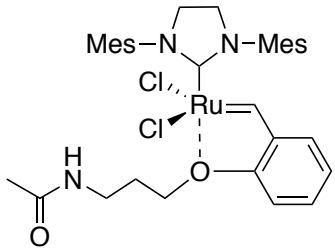


^{1}H-NMR (400 MHz, $CDCl_3$)

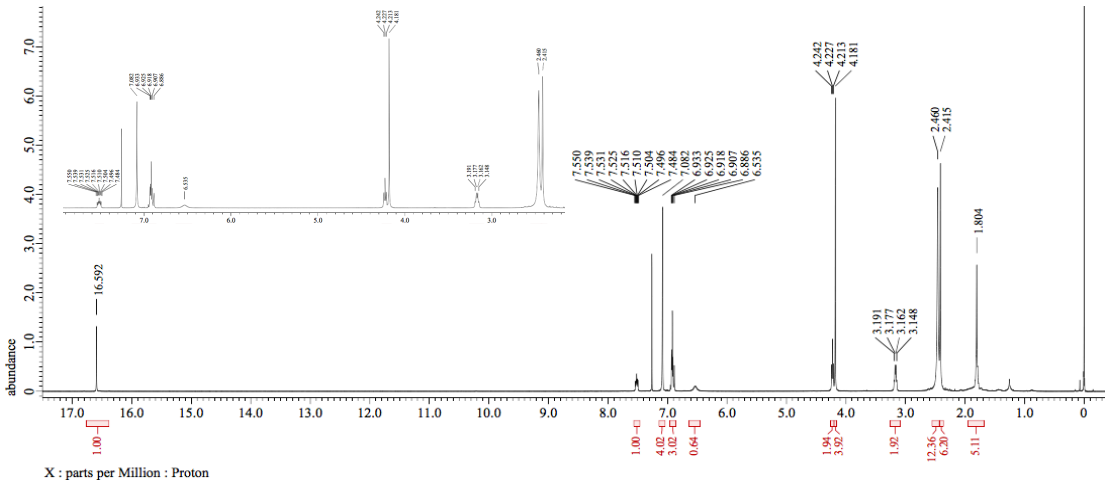


^{13}C-NMR (100 MHz, $CDCl_3$)

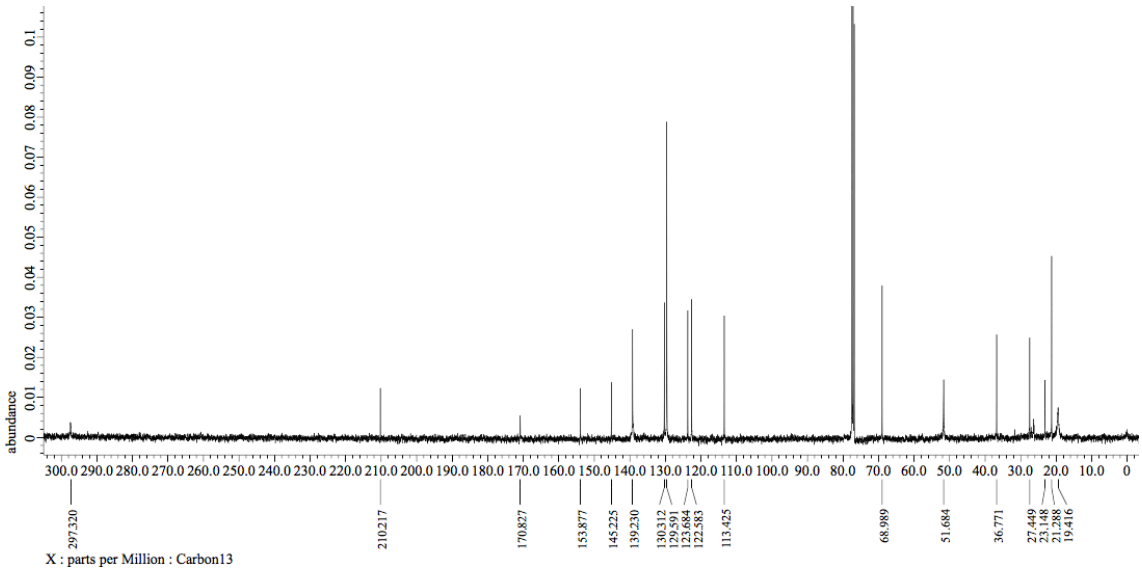


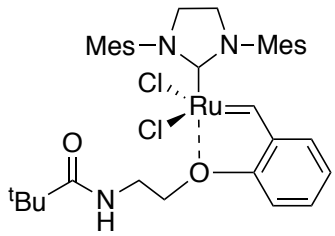


^{1}H-NMR (400 MHz, $CDCl_3$)

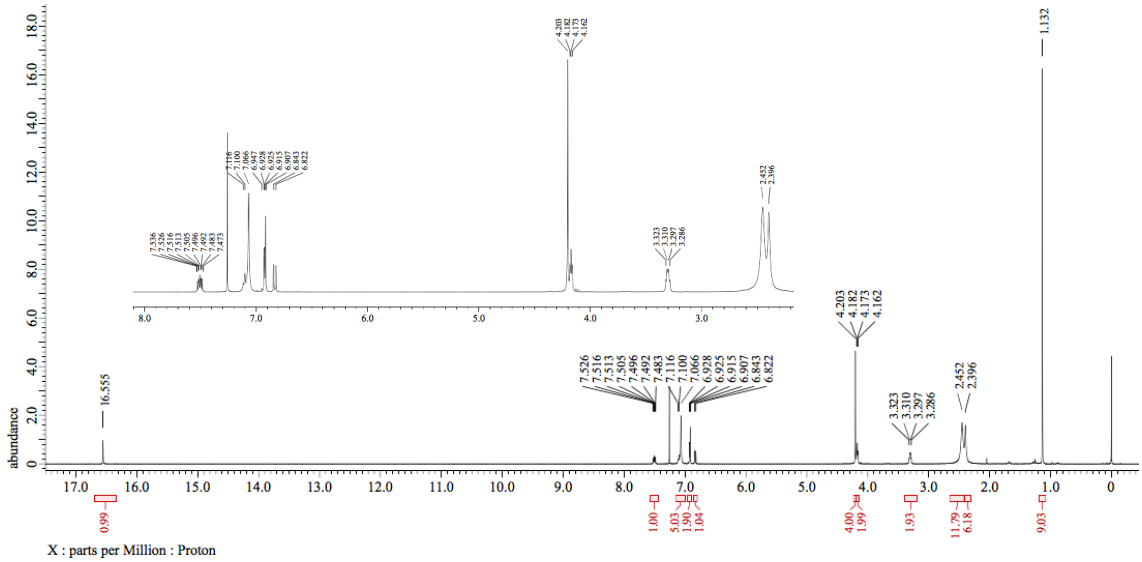


^{13}C-NMR (100 MHz, $CDCl_3$)

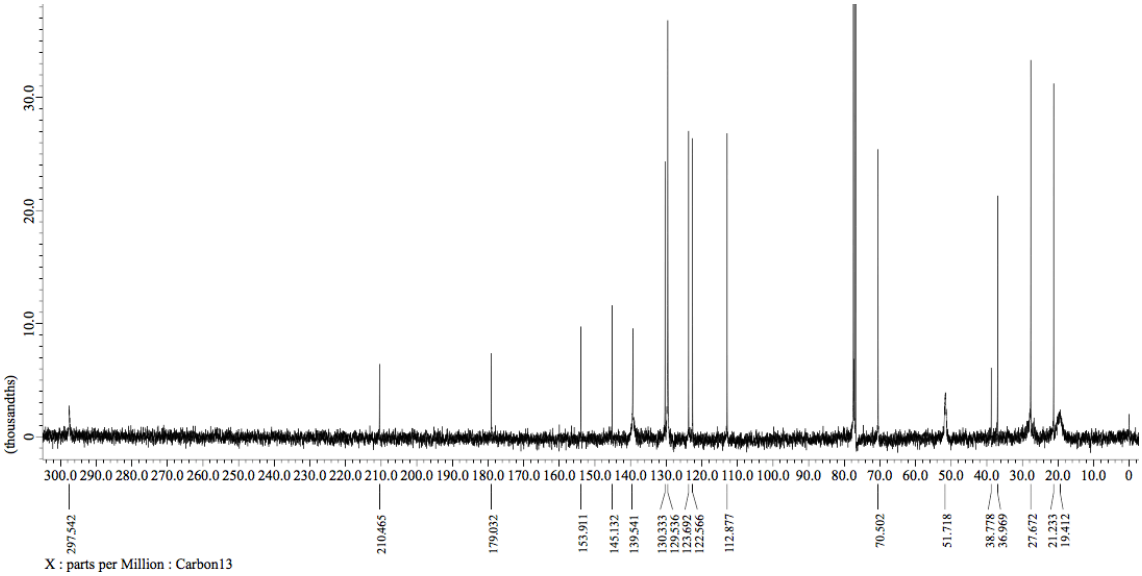


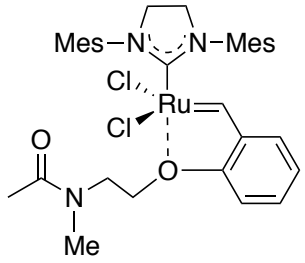


^{1}H-NMR (400 MHz, $CDCl_3$)

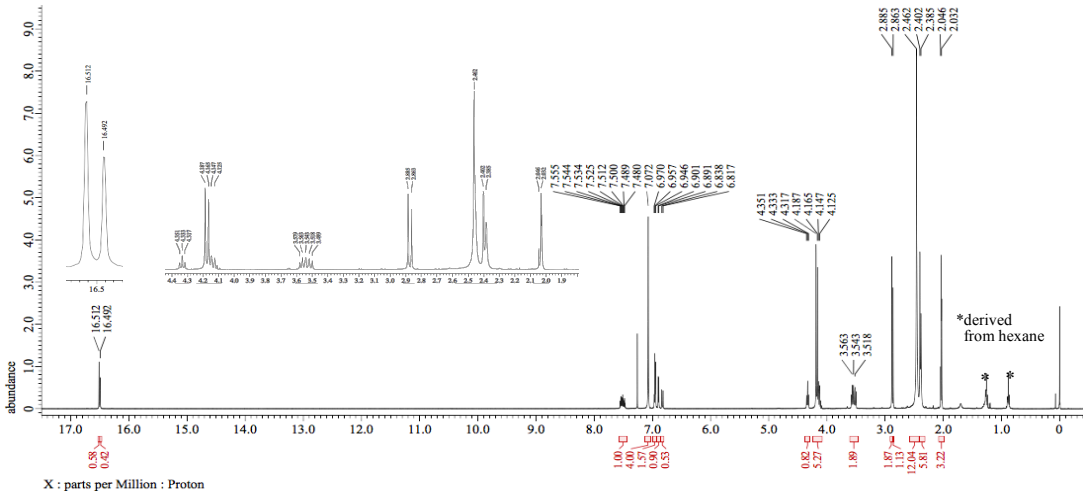


^{13}C-NMR (100 MHz, $CDCl_3$)

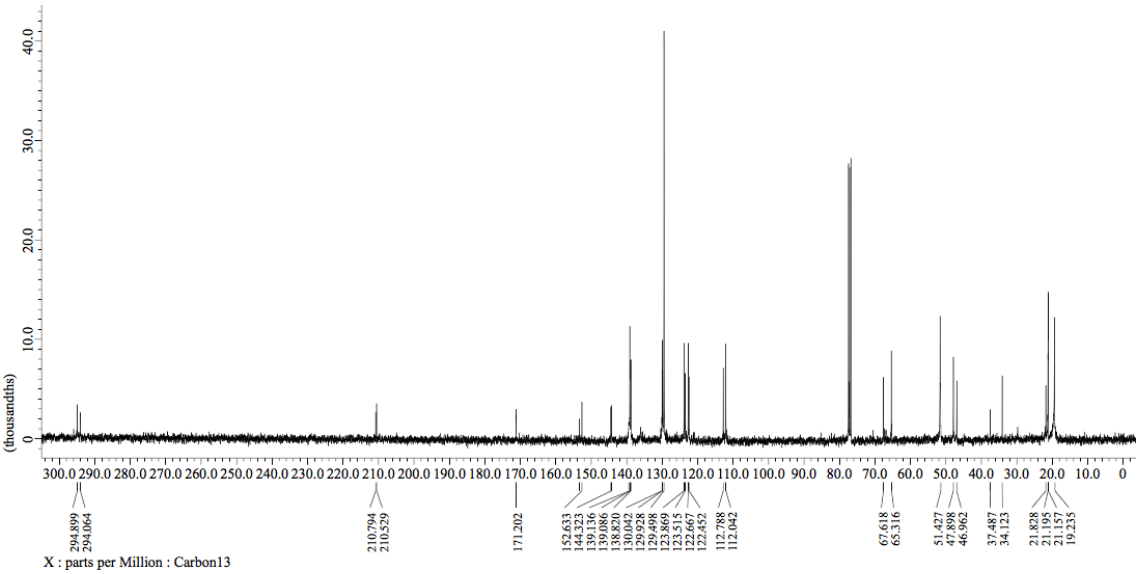


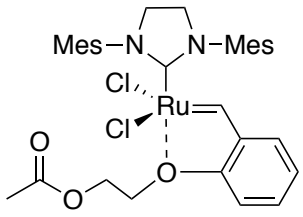


^{1}H-NMR (400 MHz, $CDCl_3$)

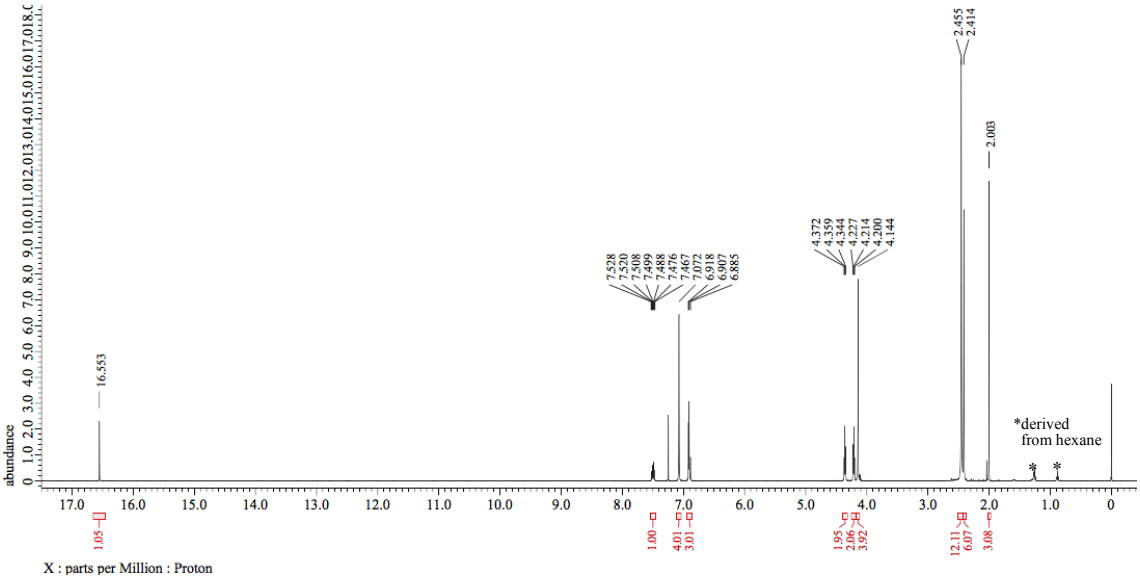


^{13}C-NMR (100 MHz, $CDCl_3$)

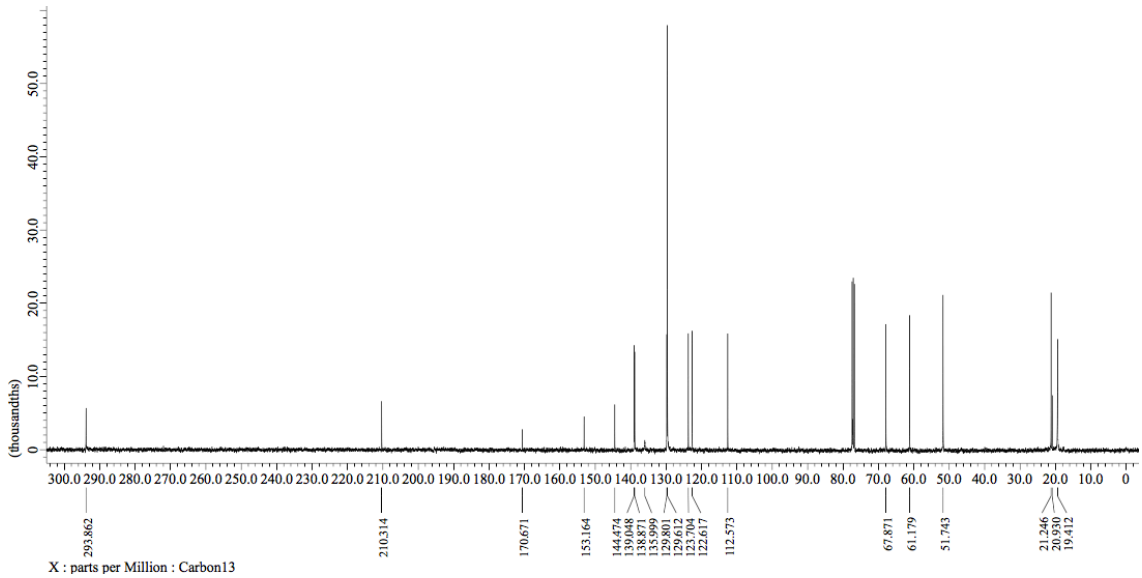


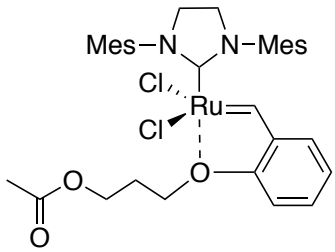


^{1}H-NMR (400 MHz, $CDCl_3$)

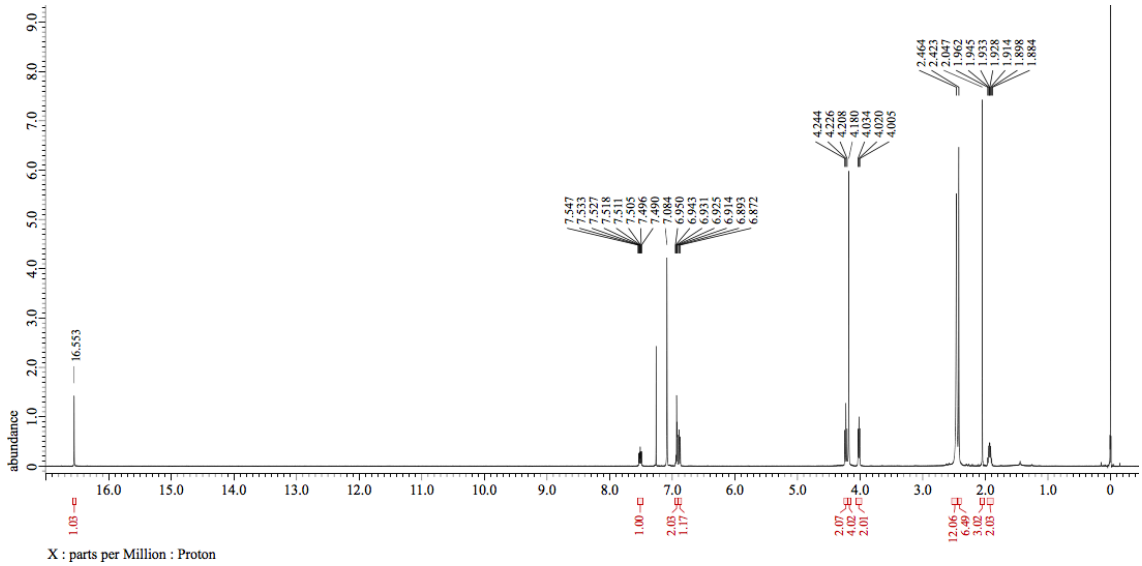


^{13}C-NMR (100 MHz, $CDCl_3$)

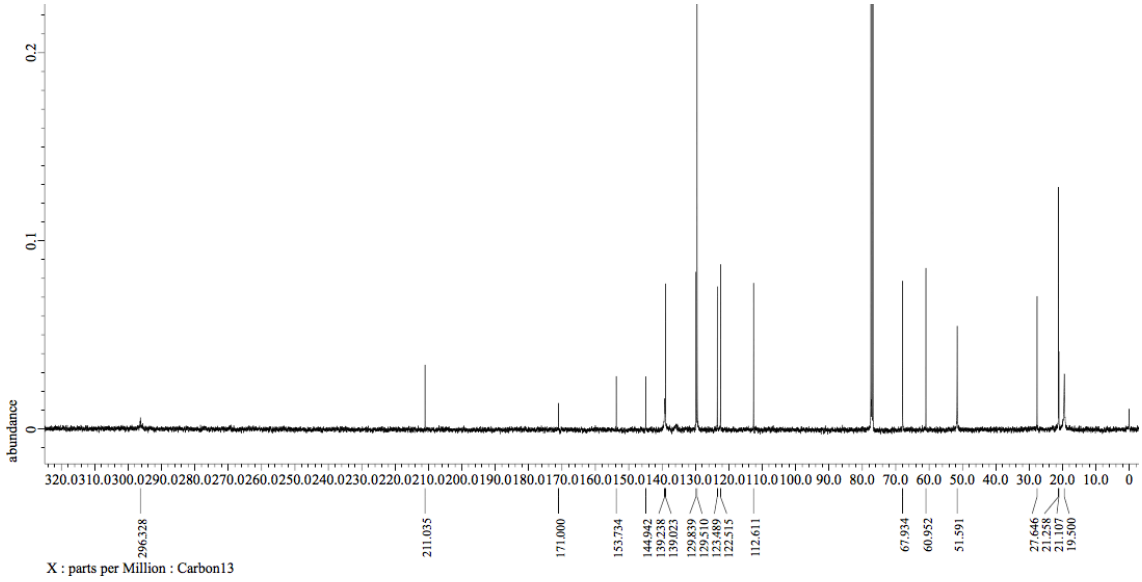


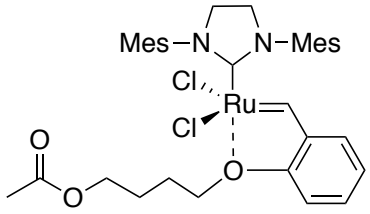


^{1}H-NMR (400 MHz, $CDCl_3$)

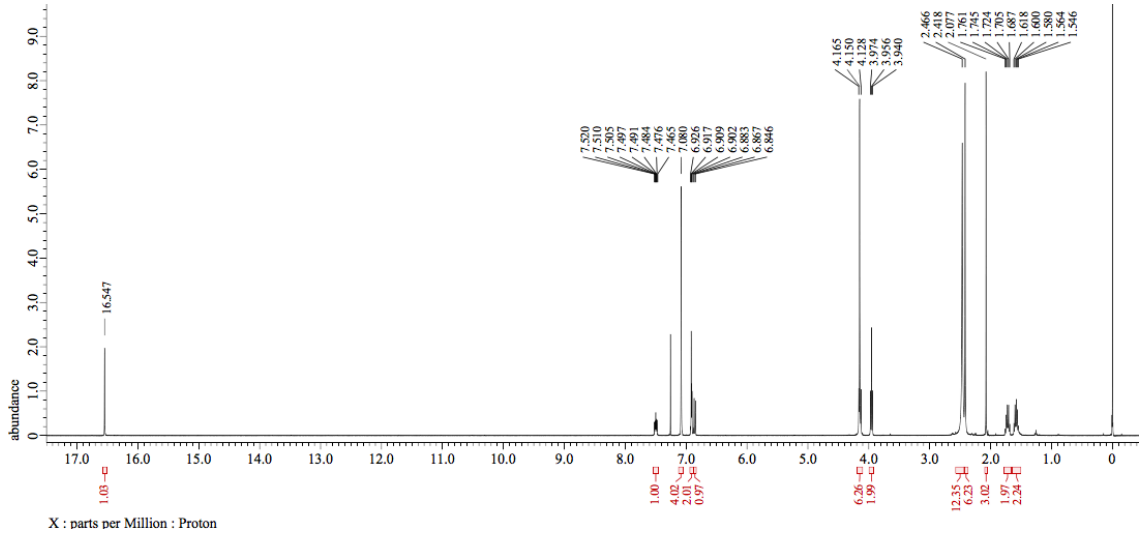


^{13}C-NMR (100 MHz, $CDCl_3$)





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



^{13}C-NMR (100 MHz, $CDCl_3$)