Supporting Information

Activation of olefin metathesis complexes containing unsymmetrical unsaturated N-heterocyclic carbenes by copper and gold transmetalation

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1. General Information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques unless otherwise noticed. Toluene, diethyl ether, dichloromethane and tetrahydrofuran were purified using MBraun Solvent Purification Systems. Toluene was also degazed for kinetic studies. All commercial chemicals were used as received unless otherwise noted. Diethyl diallylmalonate (DEDAM) was used as received. Mesitylene was distilled over calcium hydride. 1-dodecene and 11-bromoundecene were distilled over sodium and filtrated over basic alumina prior to used. All scope substrats were dried over basic alumina. Imidazolium salt 3-cyclooctyl-1-mesitylimidazolium tetrafluoroborate[1] and catalyst bis(1-cyclooctyl-3-mesityl-imidazol-2-ylidene)(3-phenyl-1H-inden-1-ylidene)ruthenium dichloride (Ru-**1a**) [2] were synthesized according to the literature. The 0.5 M solution of potassium bis(trimethylsilyl)amid in toluene was purchased from Acros Organics with AcroSeal packaging. Flash chromatography was performed on silica gel 60 (230-400 mesh). NMR spectra were recorded on a Bruker ARX400 spectrometer (^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (376 MHz) and ^{11}B (128 MHz)) with complete proton decoupling for nucleus other than ^{1}H. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard ($CDCl_3$, ^{1}H: δ 7.26 ppm, ^{13}C: δ 77.16 ppm; CD_2Cl_2, ^{1}H: δ 5.32 ppm, ^{13}C: δ 53.84 ppm; C_6D_6, ^{1}H: 7.16 ppm, ^{13}C: 128.06 ppm; Toluene-d_8, ^{1}H: δ 2.08 ppm, ^{13}C: δ 20.43 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tt = triplet of triplets, q = quartet, sept = septuplet, m = multiplet, br = broad, bs = broad signal, Cq = quaternary carbon. High Resolution Mass Spectrometry (HRMS) were recorded on a Waters QTof-I spectrometer using electrospray ionization at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Melting points were measured on a Stuart Melting Point Apparatus SMP3 and are uncorrected.

[1] P. Queval, C. Jahier, M. Rouen, I. Artur, J.-C. Legeay, L. Falivene, L. Toupet, C. Crévisy, L. Cavallo, O. Baslé, M. Mauduit. *Angew. Chem. Int. Ed.* **2013**, *52*, 14103-14107

2 A. Dumas, S. Colombel-Rouen, I. Curbet, G. Forcher, F. Tripoteau, F. Caijo, P. Queval, M. Rouen, B. Baslé and M. Mauduit. *Cat. Sci. Techn*. **2019**, *9*, 436

2. GC method

Instrument: Shimadzu GC-2014

Column: TR5, 25 m x 0.25 mm x 0.25 µm.

GC and column conditions: Injector temperature: 250°C, FID: 250°C.

Oven temperature: Starting temperature: 60°C, hold time: 5 minutes.
Ramp rate 2°C/min to 120°C, hold time: 0 minute.
Ramp rate 5°C/min to 180°C, hold time: 0 minute.
Ramp rate 10°C/min to 280°C, hold time: 0 minute.
Ramp rate 15°C/min to 340°C, hold time: 9 minutes.

Carrier gas: Helium, u = 40 cm/sec.

Injection volume: 1 µl.

Split ratio: 20:1.

Run time: 70 minutes.

Calibration curves :

A GC method was developed to separate Docosene **P12** and tetradecane as the internal standard *(see **Figure S1**)*.

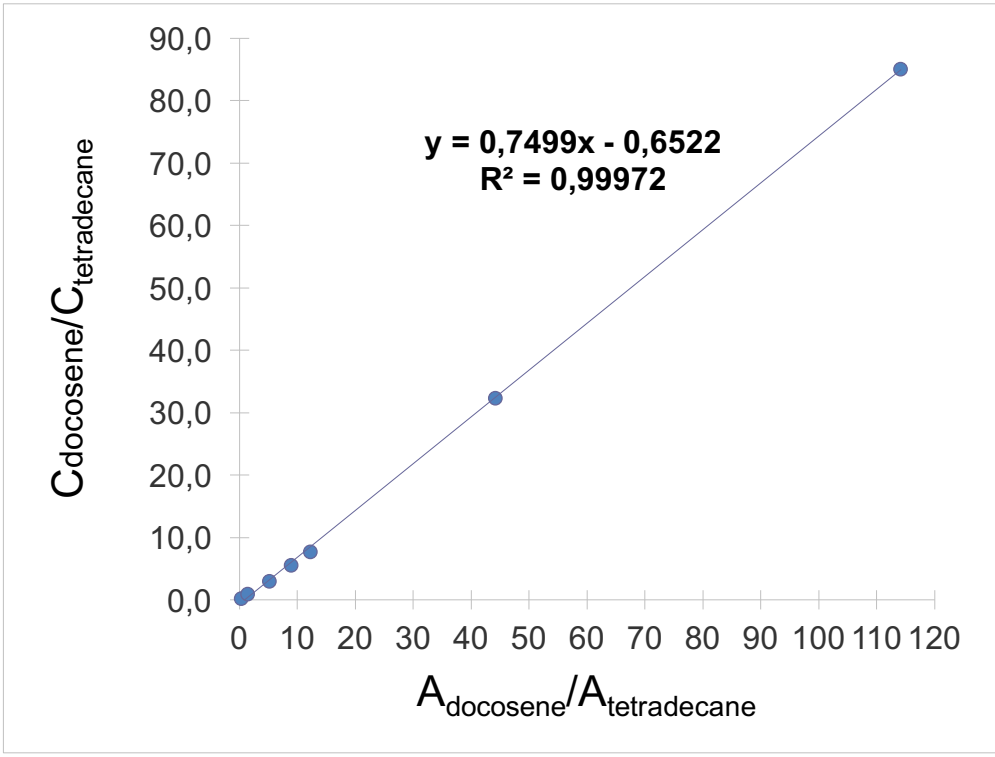


Figure S1 : *Calibration curve*

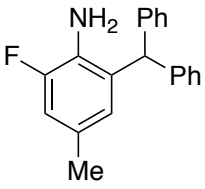
Determination of GC yield:

$$Yield = \frac{\left[0{,}7499 \times \frac{[A_{Docosene}]}{[A_{Tetradecane}]} - 0{,}6522\right] \times \left[\frac{m_{Aliquot} \times m_{Tetradecane}}{m_{overall\ mass}}\right] \times \left[\frac{m_{Dodecene}}{m_{Aliquot}}\right]}{\frac{M_{Docosene}}{\frac{m_{Dodecene}}{2 \times M_{Dodecene}}}} \times 100$$

	Retention time (min)
tetradecane	32.30
1-dodecene	18.66
docosene	52.53

3. Synthesis of Imidazolium Salts

3.1. Synthesis of 2-benzhydryl-6-fluoro-4-methylaniline (**3a**)



3a

$C_{20}H_{18}FN$

291,14 g.mol^{-1}

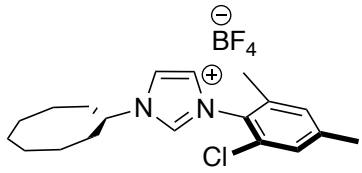
A mixture of $ZnCl_2$ (735 mg, 5.37 mmol, 0.5 equiv.) and concentred aqueous HCl (35% w/w, 0.98 mL 32.4 mmol, 3.0 equiv.) was added at 100 °C to 2-fluoro-4-methylaniline (1.22 mL, 10.7 mmol, 1.0 equiv.) and benzhydrol (1.98 g, 10.7 mmol, 1.0 equiv.). The resulting mixture was stirred and heated to 160 °C for 30 minutes. DCM (25 mL) and saturated $NaHCO_3$ solution (25 mL) were added to create a biphasic mixture which was stirred overnight. Organic layer was extracted and washed with water (2 x 40 mL) and dried over magnesium sulfate then the solvents were evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (Pentane/AcOEt : 80/20) to yield the aniline as a white solid (2.79 g, **89% yield**).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34-7.30 (m, 4H), 7.28-7.23 (m, 2H), 7.14-7.11 (m, 4H), 6.76 (dd, *J* = 11.4 and 1.9 Hz, 1H), 6.27 (s, 1H), 5.50 (s, 1H), 3.26 (br, 2H), 2.14 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 153.4, 151.0, 142.1, 136.8, 131.6, 131.6, 129.8, 129.7, 129.5, 128.6, 127.7, 127.6, 126.8, 125.6, 125.5, 113.7, 52.1, 20.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -135.8.

3.2. General procedure for synthesis of imidazolium salts:

The reaction was performed in open vessel under air atmosphere. In a round-bottomed flask were placed alkylamine (1.0 mmol, 1.0 equiv.), cyclooctylamine (1.0 mmol, 1.0 equiv.) and acetic acid (4.5 or 9.0 mmol, 4.5 or 9.0 equiv.) then the mixture was heated at 60 °C for 20 minutes (mixture A). In another round-bottomed flask were placed $ZnCl_2$ (1.5 or 1.2 mmol, 1.5 or 1.2 equiv.), glyoxal (40% w/w, 1.0 mmol, 1.0 equiv.), formaldehyde (37% w/w, 1.0 mmol, 1.0 equiv.) and acetic acid (4.5 or 9.0 mmol, 4.5 or 9.0 equiv.) then the mixture was heated at 60 °C for 20 minutes (mixture B). At the same temperature, mixture B was added to mixture A and the resulting mixture was stirred at 60 °C for 30 minutes then cooled down to room temperature. An aliquot of the crude reaction mixture was taken and a ^{1}H NMR was recorded to determine the selectivity of the reaction, which was calculated by integration of characteristic signals of the different compounds. Dichloromethane (50 mL) was added and the organic layer was successively washed with water (100 mL) then brine (2 x 50 mL). The combined aqueous layers were extracted with dichloromethane (50 mL). Water (20 mL) and KBF_4 (1.0 mmol, 1.0 equiv.) was added and the resulting mixture was stirred at room temperature for 1 hour. The organic layer was separated, dried over magnesium sulfate, filtered and the solvents were evaporated under reduced pressure. The desired imidazolium salt was isolated by recristallization in AcOEt.

3-(2-choloro-4,6-dimethylphenyl)-1-cyclooctyl-1*H*-imidazol-3-ium tetrafluoroborate (4a)



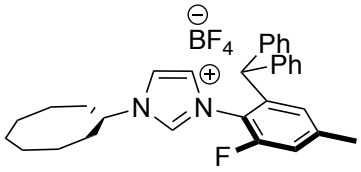
4a
$C_{19}H_{26}ClN_2BF_4$
404,68 g.mol^{-1}

Following the general procedure for the synthesis of imidazolium salts, with 2-chloro-4,6-dimethylaniline (1.00 g, 6.43 mmol), cyclooctylamine (880 µL, 6.43 mmol), $ZnCl_2$ (1.05 g, 7.70 mmol), glyoxal (740 µL, 6.43 mmol), formaldehyde (480 µL, 6.43 mmol), acetic acid (3.30 mL, 57.8 mmol, 9.0 equiv.) (selectivity **imidazolium salt-OAc/bisC_8-OAc/bisaniline-OAc** = 97/03/00) and KBF_4 (809 mg, 6.43 mmol) the desired product was isolated as a white solid (1.64 g, **63% yield**, mp = 158 °C) after recristallization in AcOEt.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.04 (s, 1H), 7.58 (s, 1H), 7.23 (s, 1H), 7.12 (s, 1H), 4.96-4.89 (m, 1H), 2.38 (s, 3H), 2.17-2.05 (m, 7H), 1.84-1.59 (m, 11H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 142.9, 137.1, 136.4, 130.9, 130.7, 128.5, 123.9, 120.8, 122.9, 62.3, 33.9, 33.4, 26.3, 25.4, 23.8, 21.2, 17.7. **^{11}B NMR (128 MHz, $CDCl_3$)** δ (ppm) -0.9. **^{19}F NMR (376 MHz,**

$CDCl_3$) δ (ppm) -151.7, -151.8. **HRMS (ESI)** calcd. for $C_{19}H_{26}N_2{}^{35}Cl$ [M^+]: m/z 317.1779, found : 317.1781 (1 ppm).

3-(2-benzhydryl-6-fluoro-4-methylphenyl-1-cyclooctyl-1*H*-imidazol-3-ium tetrafluoroborate (4b)



4b
$C_{31}H_{34}FN_2BF_4$
540,43 g.mol^{-1}

Following the general procedure for the synthesis of imidazolium salts, 2-benzhydryl-6fluoro-4-methylaniline (1.00 g, 3.43 mmol), cyclooctylamine (470 µL, 3.43 mmol), $ZnCl_2$ (701 mg, 5.14 mmol), glyoxal (400 µL, 3.43 mmol), formaldehyde (260 µL, 3.43 mmol), acetic acid (7.00 mL, 61.7 mmol, 18.0 equiv.) (selectivity **imidazolium salt-OAc/bisC_8-OAc/bisaniline-OAc** = 97/03/00) and KBF_4 (432 mg, 3.43 mmol) the desired product was isolated as a white solid (1.14 g, **62% yield**, mp = 185 °C) after recristallization in AcOEt.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.77 (t, *J* = 1.7 Hz, 1H), 7.28-7.19 (m, 7H), 7.04-6.99 (m, 5H), 6.72 (t, *J* = 1.7 Hz, 1H), 6.57 (s, 1H), 5.54 (s, 1H), 4.75-4.67 (sept, 1H), 2.31 (s, 3H), 2.04-1.87 (m, 4H), 1.75-1.58 (m, 10H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 158.4, 155.9, 143.7, 142.9, 140.9, 136.4, 129.5, 129.2, 128.8, 128.2, 127.3, 127.2, 126.3, 124.5, 119.6, 119.1, 119.0, 115.7, 115.6, 62.0, 51.6, 33.6, 26.2, 25.4, 23.8, 21.9. **^{11}B NMR (128 MHz, $CDCl_3$)** δ (ppm) -0.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -123.4, -129.8, -151.2, -151.2. **HRMS (ESI)** calcd. for $C_{31}H_{34}N_2F$ [M^+]: m/z 453.27005, found : 453.2704 (1 ppm).
Single-crystals of **4b** were obtained by slow diffusion between dichloromethane and pentane. CCDC 19378686

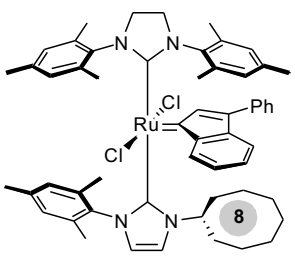
4. Synthesis of bis-NHC complexes

4.1. General procedure for synthesis of bis-NHC complexes:

To a suspension of imidazolium salt (1.5 or 2.5 equiv.) in dry toluene (0.1 M) stored in a schlenk was added a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (1.4 or 2.5 equiv.). The mixture was stirred 30 minutes at room temperature. Commercial Dichloro(3-phenyl-1H-inden-1-ylidene)bis(triphenylphosphine)ruthenium(II) **M10** or [1,3-Bis(2,4,6-trimethylphenyl)

-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine) ruthenium(II) **M2** ruthenium complexes (1.0 equiv.) was then added in one portion to the schlenk and the resulting mixture was stirred at 40 °C or 100 °C under argon atmosphere until TLC analysis showed complete conversion. After evaporation of the solvents, the crude material was purified by flash chromatography on silica gel using a mixture of Pentane/Et_2O (9/1 to 7/3). The desired complex was collected as a red solid.

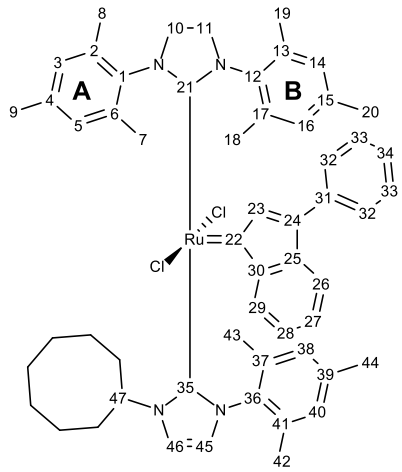
(Cyclooctyl-IMes)(SIMes)$RuCl_2$(3-phenylindenylid-1-ene) (Ru-1b)



Ru-1b
$C_{56}H_{64}Cl_2N_4Ru$
965.13 g.mol

Following the general procedure for the synthesis of bis-carbene complexes with 3-cyclooctyl-1-mesitylimidazolium tétrafluoroborate (308 mg, 0.80 mmol, 1.5 equiv.), 0.5 M KHMDS solution in toluene (1.60 mL, 0.80 mmol, 1.5 equiv.) and commercial **M2** (505 mg, 0.53 mmol, 1.0 equiv.) in toluene (4.40 mL, c = 0.1 M) at 100 °C, the desired product was obtained as a red solid (281 mg, **55% yield**).

^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) 8.31 (dd, *J* = 7.4, 1.3 Hz, 1H, H_{29}), 7.76 (dd, *J* = 8.3, 1.2 Hz, 2H, H_{32}), 7.57 (tt, *J* = 7.4, 1.2 Hz, 1H, H_{34}), 7.46 (tt, *J* = 7.5, 1.4 Hz, 2H, H_{33}), 7.18 (d, *J* = 1.8 Hz, 1H, H_{46}), 7.17 (s, 1H, H_5), 7.16 (s, 1H, H_3), 7.15 (td, *J* = 7.4, 1.3 Hz, 1H, H_{27}), 7.05 (s, 1H, H_{23}), 7.08 (td, *J* = 7.4, 1.4 Hz, 1H, H_{28}), 6.88 (dd, *J* = 7.4 and 1.4 Hz, 1H, H_{26}), 6.51 (d, *J* = 1.8 Hz, 1H, H_{45}), 6.25 (s, 1H, H_{14}), 6.21 (s, 1H, H_{38}), 5.83 (s, 1H, H_{16}), 5.81 (s, 1H, H_{40}), 4.94-4.87 (m, 1H, H_{47}), 3.91-3.82 (m, 2H, H_{11}), 3.72 (t, *J* = 9.5 Hz, 1H, H_{10}), 3.62 (t, *J* = 9.5 Hz, 1H, H_{11}), 2.72 (s, 3H, H_8), 2.71 (s, 3H, H_7), 2.48 (s, 3H, H_9), 2.17-1.97 [m, 4H: 2.09 (s, 3H, H_{19}) and 1H, CH_2 of cyclooctyl], 1.89-1.74 [m, 18H: 1.89 (s, 3H, H_{18}), 1.77 (s, 3H, H_{44}), 1.76 (s, 3H, H_{20}),1.74 (s, 3H, H_{43}), and 6H, CH_2 of cyclooctyl], 1.59-1.45 [m, 9H: 1.53 (s, 3H, H_{42}) and 6H, CH_2 of cyclooctyl], 1.33-1.18 (m, 1H, CH_2 of cyclooctyl).



Ru-1b

^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm) 292.2 (Cq, C_{22}), 220.0 (Cq, C_{21}), 183.2 (Cq, C_{35}), 143.9 (Cq, C_{30}), 140.0 (Cq, C_{25}), 139.0 (Cq, C_2, C_6), 138.2 (Cq, C_4), 137.6 (Cq, C_{31}), 137.3 (Cq, Mesityl), 137.1 (Cq, C_{39}), 137.0 (Cq, Mesityl), 136.4 (Cq, Mesityl), 136.3 (Cq, Mesityl), 136.2

(CH, C_{23}), 136.2 (Cq, C_{41}), 136.1 (Cq, Mesityl), 136.0 (Cq, C_{36}), 135.8 (Cq, C_{37}), 134.2 (Cq, C_{24}), 130.4 (CH, C_5), 130.3 (CH, C_3), 128.7 (CH, C_{14}), 128.7 (CH, C_{33}), 128.4 (CH, C_{16}), 128.0 (CH, C_{38}), 127.8 (CH, C_{29}), 127.8 (CH, C_{40}), 126.9 (CH, C_{28}), 126.7 (CH, C_{34}), 126.5 (CH, C_{32}), 125.7 (CH, C_{27}), 123.9 (CH, C_{45}), 119.7 (CH, C_{46}), 114.9 (CH, C_{26}), 60.5 (CH, C_{47}), 53.9-53.2 (bs, 3C, CH_2 of cyclooctyl), 52.9 (CH_2, C_{11}), 52.4 (CH_2, C_{10}), 30.4-23.6 (8C, CH_2 of cyclooctyl), 21.0 (CH_3, C_9), 20.6 (CH_3, C_{44}), 19.9 (CH_3, C_7, C_8), 18.5 (CH_3, C_{18}), 18.1 (CH_3, C_{19}), 18.0 (CH_3, C_{42}), 17.9 (CH_3, C_{20}), 17.9 (CH_3, C_{43}).

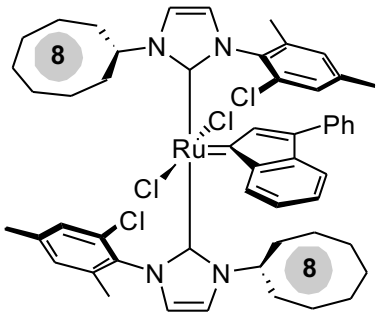
HRMS (ESI) calcd. for $C_{56}H_{64}N_4{}^{35}Cl_2{}^{102}Ru$ [$M^{+\cdot}$]: m/z 964.3546, found : 964.3559 (1 ppm).

Single-crystals of Ru-**1b** were obtained by slow diffusion with CD_2Cl_2. CCDC 1938684

Both Methyl 7 and 8 of Mesityl A as well as Methyl 18 and 19 of Mesityl B show dipolar coupling with proton H_{23} by ROESY. This can be explained by a rotation around the Ru-C_{21} axis. This hypothesis is confirmed by the existing exchange cross peak between the Methyl 7 and 8 of Mesityl A and Methyl 18 and 19 of Mesityl B (*see Figure S42 and S43*).

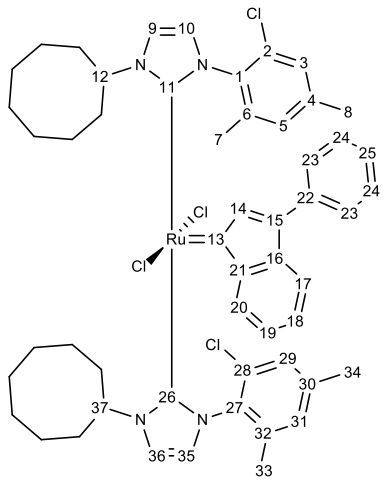
(Cyclooctyl-chloromesityl)$_2$RuCl$_2$(3-phenylindenylid-1-ene) (Ru-1c)

Following the general procedure for the synthesis of bis-carbene complexes with imidazolium salt **4a** (567 mg, 1.40 mmol, 2.5 equiv.), 0.5 M KHMDS solution in toluene (2.80 mL, 1.40 mmol, 2.5 equiv.) and commercial **M10** (503 mg, 0.57 mmol, 1.0 equiv) in toluene (5.60 mL, c = 0.1 M) at 40 °C, the desired product was obtained as a red solid (320 mg, **57% yield**).



Ru-1c
$C_{53}H_{60}Cl_4N_4Ru$
995.96 g.mol^{-1}

^{1}H NMR (500 MHz, CD_2Cl_2, 250 K) δ (ppm) 8.23-8.01 [1H, H_{20}, 2 major forms: 8.21 (d, *J* = 7.4 Hz), 8.15 (d, *J* = 7.4Hz) and 2 minor forms: 8.10 (d, J = 7.4 Hz), 8.02 (d, *J* = 7.4 Hz)], 7.97-7.88 (m, 2H, H_{23}), 7.63-7.55 (m, 1H, H_{25}), 7.54-7.48 (m, 1H, H_{18}), 7.47-7.39 (m, 2H, H_{24}), 7.39-7.11 (m, 6H, H_{19}, H_{17}, H_3, H_5, H_{29}, H_{31}), 6.96-6.71 (m, 5H, H_{14}, H_9, H_{10}, H_{30}, H_{35}), 3.35-3.17 (m, 2H, H_{12}, H_{37}), 2.72-2.40 (m, 9H, CH_3 of Mesityl), 2.10-1.95 (m, 1H, CH_2 of cyclooctyl), 1.89-1.71 (bs, 3H, CH_3 of Mesityl), 1.5-0.5 (m, 29H, CH_2 of cyclooctyl).

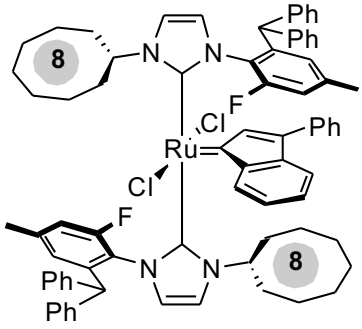


Ru-1c

^{13}C NMR (126 MHz, CD_2Cl_2, 250 K) δ (ppm) 294.8-294.1 (4Cq, C_{13}, 2 major forms: 294.6, 294.1 and 2 minor forms: 294.8 and 294.5), 177.6-174.5 (8Cq, C_{11}, C_{26}, 2 major: 177.3, 176.6, 175.7, 175.3 and 2 minor forms: 177.6, 177.5, 174.6, 174.5), 144.6-144.3 (4Cq, C_{15}, 2 major forms: 144.6, 144.5 and 2 minor forms: 144.4, 144.3), 141.6-140.7 (8Cq, C_{16}, 2 major forms: 141.1, 141.08, 140.9, 140.7 and 2 minor forms: 141.6, 1415, 141.2, 141.06), 139.6-136.37 (28CH, Ar, 2 major and 2 minor forms: 139.6, 139.4, 139.39, 139.38, 139.2, 139.1, 138.8, 138.4, 138.38, 138.2, 138.0, 137.98 (C_{14}), 137.88 (C_{14}), 137.83 (C_{14}), 137.7 (C_{14}), 137.6, 137.33, 137.30, 137.27, 137.01, 136.99, 136.84, 136.82, 136.7, 136.58, 136.57, 136.45, 136.37), 134.6-133.8 (4Cq, C_{21}, 2 major and minor forms: 134.6, 134.4, 134.3, 133.8), 133.06-126.12 (56CH, Ar, 2 major and 2 minor forms: 133.06, 133.03, 132.91, 132.87, 132.2, 132.08, 132.06, 132.05, 131.97, 131.9, 131.8, 131.72, 130.70, 130.4, 130.0, 129.91, 129.86, 129.8, 129.54, 129.48, 129.45, 129.37, 129.35, 129.32, 129.29, 129.23, 129.21, 129.04, 129.03, 128.97, 128.7, 128.6, 128.5, 128.41, 128.37, 128.29, 128.28, 128.2, 127.9, 127.8, 127.7, 127.53, 127.47, 127.45, 127.21, 127.19, 127.15, 127.07, 126.3, 126.22, 126.18, 126.12), 123.0-122.5 (8CH, C_9, C_{36}, 2 major and 2 minor: 123.0, 122.9, 122.89, 122.85, 122.84, 122.83, 122.7, 122.5), 118.1-117.5 (8CH, C_{10}, C_{35}, 2 major and 2 minor: 118.1, 118.0, 117.9, 117.8, 117.77, 117.7, 117.6, 117.5), 58.5 (bs, C_{12}), 58.2 (bs, C_{37}), 37.0-36.3 (bs, CH_2 of cyclooctyl), 33.25 (bs, CH_2 of cyclooctyl), 27.3-22.9 (bs, CH_2 of cyclooctyl), 21.1-21.0 (CH_3 of Mesityl), 20.1-19.9 (CH_3 of Mesityl).

HRMS (ESI) calcd. for $C_{53}H_{60}N_4{}^{35}Cl_4{}^{102}Ru$ [$M^{+\cdot}$]: m/z 994.26101, found : 994.2614 (0 ppm).

(Cyclooctyl-fluorobenzhydrylmesityl)$_2$RuCl$_2$(3-phenylindenylid-1-ene) (Ru-1d)



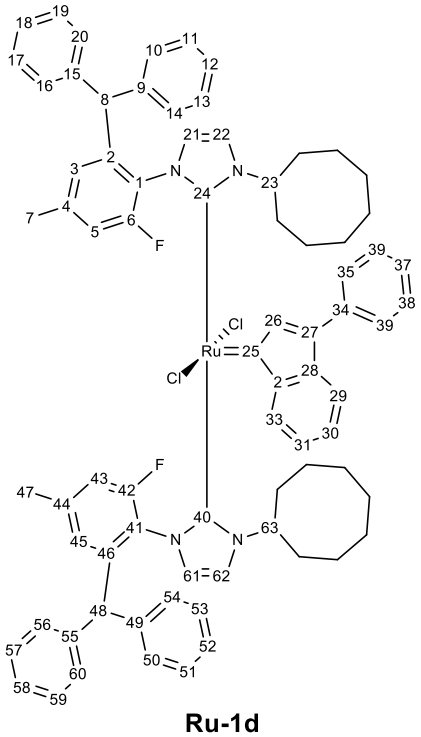
Ru-1d

$C_{77}H_{76}Cl_2F_2N_4Ru$

1267.45 g.mol^{-1}

Following the general procedure for the synthesis of bis-carbene complexes with imidazolium salt **4b** (764 mg, 1.41 mmol, 2.5 equiv.), 0.5 M KHMDS solution in toluene (2.82 mL, 1.41 mmol, 2.5 equiv.) and commercial **M10** (500 mg, 0.56 mmol, 1.0 equiv.) in toluene (5.60 mL, c = 0.1 M) at 40 °C, the desired product was obtained as a red solid (350 mg, **52% yield**).

^{1}H NMR (500 MHz, C_2D_6, 300 K) δ (ppm) 9.14-8.84 [1H, H_{32}, 1 major form: 9.14 (d, J = 7.2 Hz) and 1 minor form: 8.84 (d, J = 7.3 Hz)], 8.18-5.50 [39H, Ar, insaturated protons: H_{21}, H_{22}, H_{61}, H_{62} and H_{26}, H_{30}, H_{31}, H_8, H_{48}, $H_{23\ or\ 63}$], 3.75-3.64 (m, 1H, CH, H_{23}, H_{63}), [3.30-3.15 (CH_2), 2.56-2.47 (m, CH_2): 1H], 2.29-0.52 (34H, CH_2 of cyclooctyl and CH_3).



Ru-1d

^{13}C NMR (126 MHz, C_6D_6, 300 K) δ (ppm) 293.2 (Cq, C_{25}, major form), 286.4 (Cq, C_{25}, minor form), [180.1, 177.7 (Cq, C_{24}, C_{40}, major form)], [178.1, 176.4 (Cq, C_{24}, C_{40}, minor form)], 160.1, 160.0, 159.8, 158.1, 158.0, 157.7, 156.2, 156.1, 145.5, 144.6, 144.5, 144.2, 144.1, 144.0, 143.8, 143.7, 143.6, 143.1, 142.8, 142.6, 141.8, 140.7, 141.6, 141.2, 139.2, 139.1, 139.0, 138.9, 137.9, 137.7, 137.6, 137.5, 132.1, 132.0, 131.7, 131.2, 130.9, 130.8, 130.7, 130.4, 130.1, 130.0, 129.9, 129.8, 129.4, 129.3, 128.8, 128.6, 128.5, 128.4, 128.1, 127.3, 127.1, 126.6, 126.5, 126.4, 125.8, 125.4, 125.3, 125.1, 125.0, 123.9, 123.8, 118.1, 117.8, 117.2, 116.4, 116.0, 115.0, 114.8, 114.7, [61.3, 59.0, 58.1, 57.9 58.9 (CH, C_{23}, C_{63})], [52.5, 52.4, 52.4, 48.5 (CH, C_8, C_{48})], [38.6, 36.7, 36.5, 36.1, 36.0, 35.4, 33.2, 31.3, 31.1, 29.8, 28.8, 28.7, 27.2, 27.7, 27.6, 26.4, 26.3, 26.1, 25.9, 25.4, 25.3, 25.1, 24.8, 24.6, 24.4, 24.0, 23.8, 23.6, 23.5, 23.3 (CH_2 of cyclooctyl)], 21.0 (CH_3), 20.9 (CH_3). Many carbons under C_6D_6 can be observed and many others are overlaps.

^{19}F NMR (471 MHz, C_6D_6, 300 K) δ (ppm), -119.8 (s, major form), -121.5 (s, major form), -121.8 (d, J = 13.3, minor form), -121.9 (d, J = 13.3, minor form).

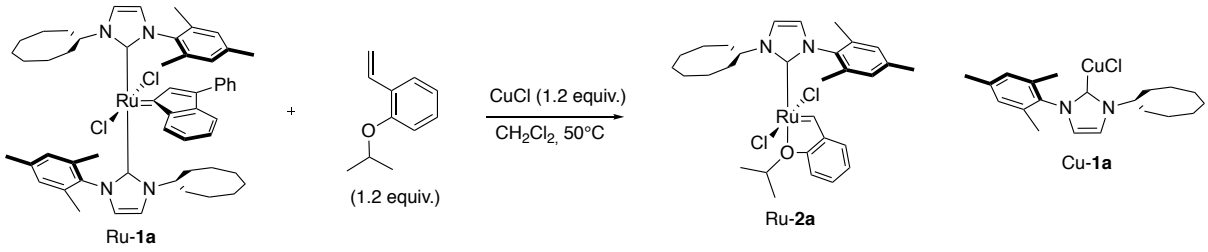
HRMS (ESI) calcd. for $C_{77}H_{76}N_4F_2{}^{35}Cl_2{}^{102}Ru$ [$M^{+\cdot}$]: m/z 1266.44531, found : 1266.4462 (1 ppm).

4.2. General procedure for transmetalation

To a Schlenk apparatus was introduced 1-isopropoxy-2-vinylbenzene (0.07 mmol), activator (0.07 mmol), trimethoxybenzene (0.002 mmol) and dichloromethane (0.7 mL, c = 0.1M) under argon. The complex (0.06 mmol) was added and the mixture was heated at 50 °C. The reaction was monitored by ^{1}H NMR (CD_2Cl_2) until complete conversion. After evaporations of the solvents, the crude material was purified on SiO_2 using the gradient of eluent : Pentane/Acetone = 90/10 to 70/10.

4.2.1. Transmetalation process using Copper(I) chloride.

4.2.1.1. *Transmetalation process between Cu(I)Cl and Ru-**1a***



Following the general procedure at 50 °C for transmetalation reactions with the Ru-**1a** complex (57.8 mg, 0.06 mmol, 1 equiv.), 1-isopropoxy-2-vinylbenzene (12.3 mg, 0.07 mmol, 1.2 equiv.), CuCl (6.9 mg, 0.07 mg, 1.2 equiv.) in dichloromethane**,** conversion was determined by ^{1}H-NMR (>95% after 5h of reaction). Ru-**2a** was isolated as a brown solid (33.8 mg, **91% yield**) and Cu-**1a** was isolated as a white solid (20.6 mg, **86% yield**).

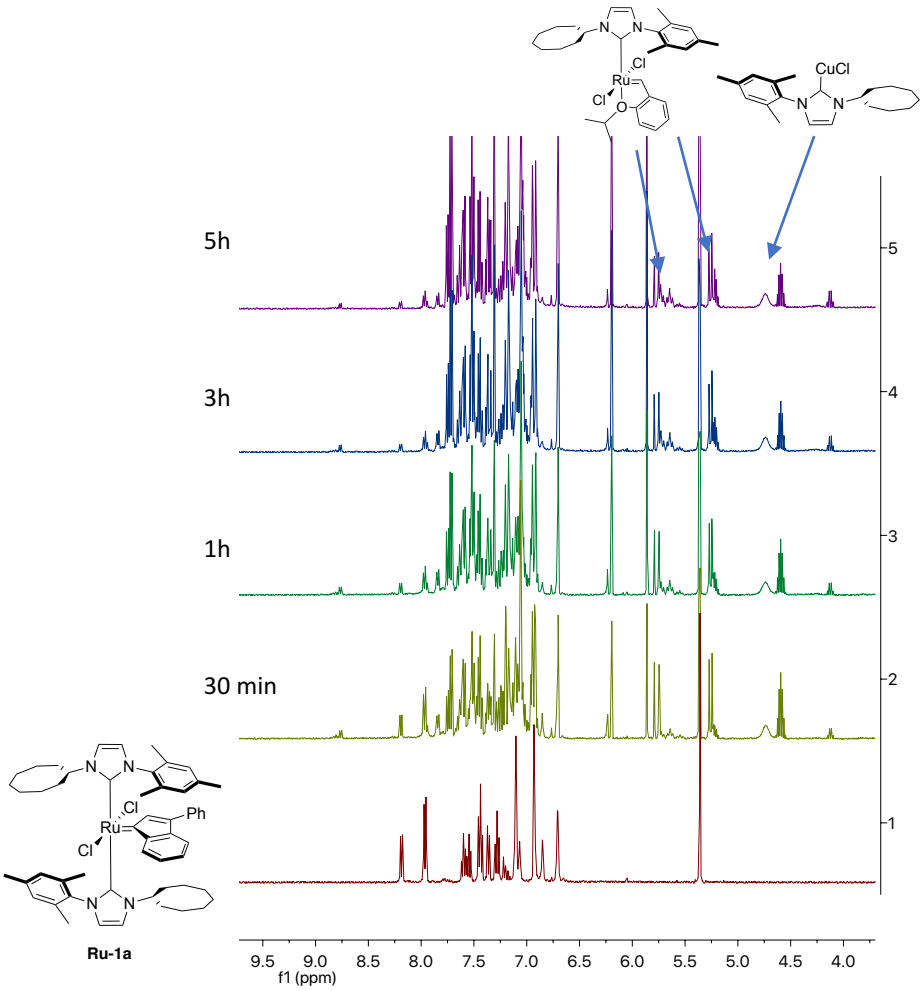
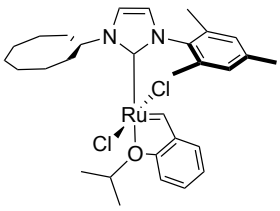


***Figure S2**: [1]H-NMR monitoring of Ru-**1a** Copper (I) transmetalation*

(1-cyclooctyl-3-mesityl-2,3-dihydro-1*H*-imidazol-2-ylidene)(2-isopropoxybenzylidene) ruthenium(V) chloride (Ru-2a)



Ru-**2a**
$C_{30}H_{40}Cl_2N_2ORu$
616,16 g.mol^{-1}

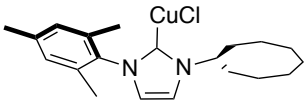
^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 16.35 (s, 1H), 7.58 (ddd, *J* = 8.5, 7.0, 2.0 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.13 (br. s, 2H), 7.04-6.96 (m, 3H), 6.91-6.89 (m, 1H), 5.68 (tt, *J* = 10.1, 3.3 Hz, 1H), 5.18 (sep., *J* = 6.1 Hz, 1H), 2.51 (s, 3H), 2.49-2.40 (m, 2H), 2.10-2.03 (m, 2H), 1.97 (s, 6H), 1.94-1.82 (m, 6H), 1.78 (d, *J* = 6.1 Hz, 6H), 1.75-1.68 (m, 4H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 287.4, 170.0, 152.8, 144.8, 140.2, 138.0, 129.6, 129.3, 125.5, 123.2, 122.2, 119.5, 113.5, 75.6, 62.9, 36.0, 27.5, 26.6, 25.3, 22.5, 21.6, 18.2.

HRMS (ESI) : m/z : $M^{+\cdot}$ ($C_{30}H_{40}N_2OCl_2Ru$) calc.: 616.15557; found: 616.1557 (1 ppm).

Single-crystals of Ru-**2a** were obtained by slow diffusion between dichloromethane and pentane. CCDC 1937863

(1-cyclooctyl-3-mesityl-2,3-dihydro-1*H*-imidazol-2-ylidene)copper(II) chloride (Cu-1a)

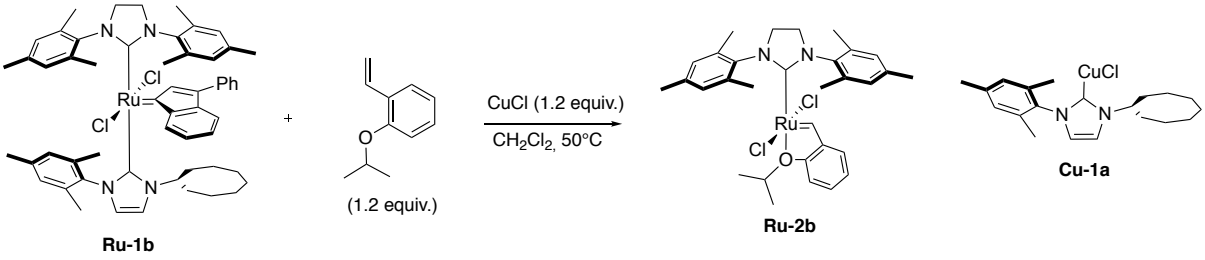


Cu-**1a**
$C_{20}H_{28}ClCuN_2$
394,13 g.mol^{-1}

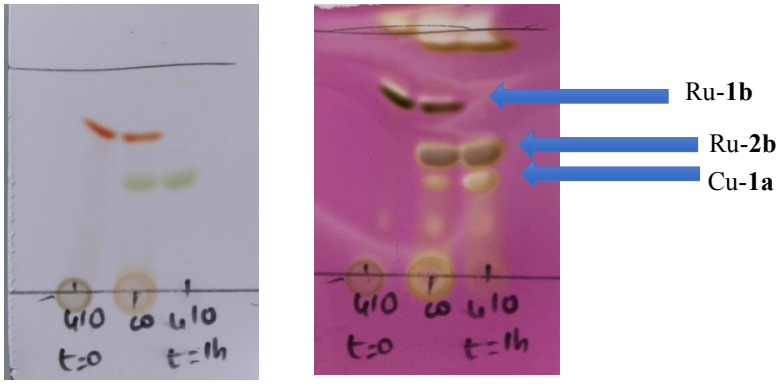
^{1}H NMR (400 MHz, *CD_2Cl_2*): δ (ppm) 7.15 (s, 1H), 7.00 (s, 2H), 6.88 (s, 1H), 4.68 (sep., *J* = 4.1 Hz, 1H), 2.34 (s, 3H), 2.17-2.03 (m, 4H), 1.99 (s, 6H), 1.90-1.79 (m, 2H), 1.76-1.52 (m, 8H).

^{13}C NMR (101 MHz, *CD_2Cl_2*): δ (ppm) 139.9, 136.3, 135.4, 129.7, 122.5, 118.8, 63.0, 35.5, 27.2, 26.4, 25.0, 21.4, 18.1.

*4.2.1.2. Transmetalation process between Cu(I)Cl and Ru-**1b***

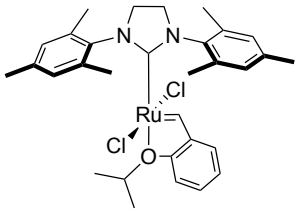


Following the general procedure at 50 °C for transmetalation reactions with the Ru-**1b** complex (59.4 mg, 0.06 mmol 1 equiv.), 1-isopropoxy-2-vinylbenzene (12.9 mg, 0.07 mmol, 1.2 equiv.), CuCl (7.4 mg, 0.07 mg, 1.2 equiv.) in dichloromethane**,** conversion was determined by ^{1}H-NMR (>95% after 1h of reaction). Ru-**2b** was isolated as a green solid (37.0 mg, **95% yield**) and Cu-**1a** was isolated as a white solid (18.4 mg, **75% yield**).



Eluent : Pentane/Acetone 8/2
Stain : $KMnO_4$

(1,3-Bismesityl-2-imidazolidin-2-yl)(2-isopropoxybenzylidene)ruthenium dichloride (Ru-2b)



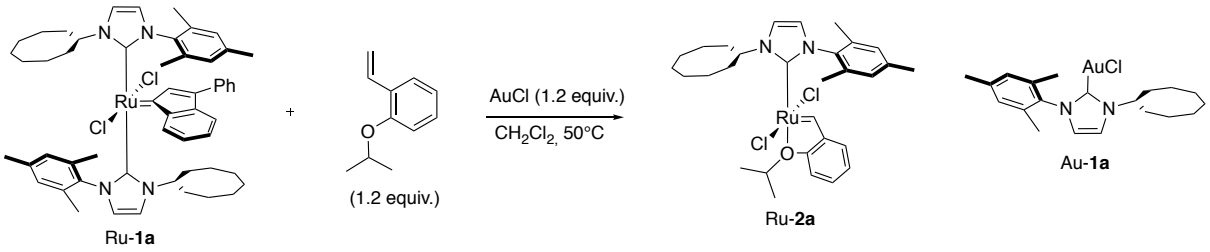
Ru-**2b**
$C_{31}H_{38}Cl_2N_2ORu$
627,15 g.mol^{-1}

^{1}H NMR (400 MHz, *CD_2Cl_2*): δ (ppm) 16.51 (s, 1H), 7.55 (ddd, *J* = 7.2, 1.8, 0.8 Hz, 1H), 7.07 (s, 4H), 6.96 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.93-6.88 (m, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.88 (sep., *J* = 6.2 Hz, 1H), 4.16 (s, 4H), 2.55-2.30 (m, 18H), 1.23 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (101 MHz, *CD_2Cl_2*): δ (ppm) 296.2, 211.3, 152.5, 145.7, 139.4, 130.0, 129.8, 122.9, 122.7, 113.5, 75.7, 52.1, 21.4, 21.3, 19.7.

Analytical data for this compound are consistent with the previously reported data[3]

4.2.2. Transmetalation process using Gold(I) chloride.



Following the general procedure at 50 °C for transmetalation reactions with the Ru-**1a** complex (56.7 mg, 0.06 mmol 1 equiv.), 1-isopropoxy-2-vinylbenzene (11.4 mg, 0.07 mmol, 1.2 equiv.), AuCl (17.2 mg, 0.07 mg, 1.2 equiv.) in dichloromethane**,** conversion was determined by ^{1}H-NMR (>69% after 24h of reaction). Ru-**2a** was isolated as a brown solid (16.2 mg, **45% yield**) and Au-**1a** was isolated as a white solid (12.2 mg, **39% yield**).

[3] Gessler, S.; Randl, S.; Blechert, S. *Tetrahedron Lett.,* **2000,** *41*, 9973–9976.

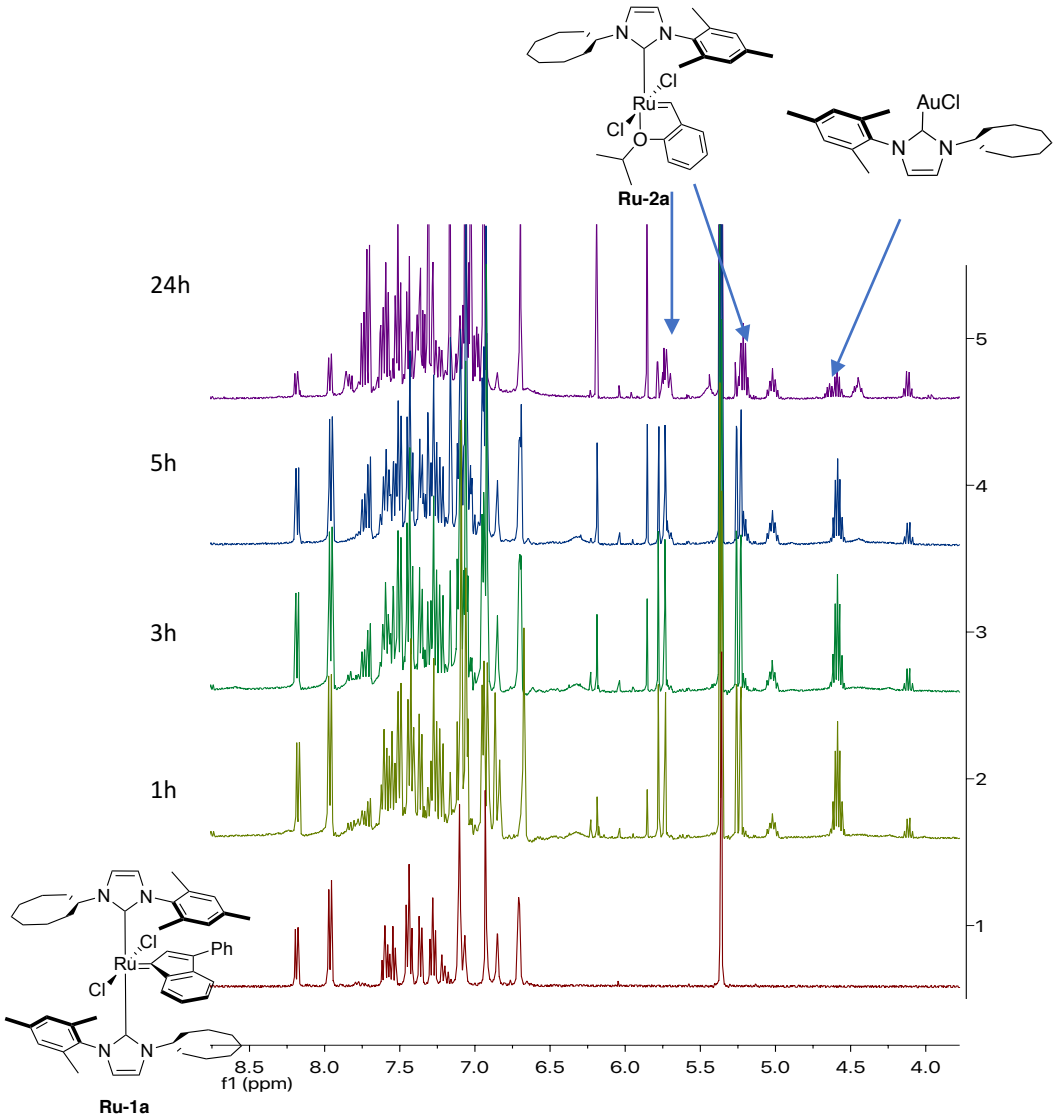
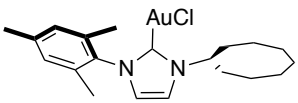


***Figure S3**: [1]H-NMR monitoring of Ru-**1b** Gold (I) transmetalation*



Au-**1a**
$C_{20}H_{28}AuClN_2$
528,17 g.mol^{-1}

^{1}H NMR (400 MHz, *CD_2Cl_2*): δ (ppm) 7.21 (d, *J* = 2.0 Hz, 1H), 7.02 (br. s, 2H), 6.90 (d, *J* = 2.0 Hz, 1H), 4.68 (sep., *J* = 4.8 Hz, 1H), 2.36 (s, 3H), 2.12-2.05 (m, 4H), 2.01 (s, 6H), 1.90-1.79 (m, 2H), 1.79-1.56 (m, 8H).

^{13}C NMR (101 MHz, *CD_2Cl_2*): δ (ppm) 171.1, 140.3, 135.8, 135.6, 129.8, 122.7, 118.4, 62.7, 34.7, 27.2, 26.4, 24.9, 22.9, 21.5, 18.1, 14.4.

HRMS (ESI) : m/z : $[M+Na]^+$ ($C_{20}H_{28}N_2ClNaAu$) calc.: 551.14988; found: 551.1502 (1 ppm).

Single-crystals of Au-**1a** were obtained by slow evaporation of a saturated solution in dichloromethane/Pentane. CCDC 1937862

5. General procedure for kinetic studies

Diethyldiallylmalonate (DEDAM) **S1** (48.5 µL, 0.2 mmol), trimethoxybenzene (5.6 mg, 0.033 mmol) as the internal standard and toluene (1.8 mL) were added in a Schlenk tube under argon. The solution was equilibrated at 30 or 80 °C before the activator addition (0.1 mL of a 0.1 M solution of activator, 5 mol%) and catalyst addition (0.1 mL of a 0.02 M solution of catalyst, 1 mol%). Aliquots were taken and the conversion was calculated from ^{1}H NMR spectra by comparing the characteristic signal for allylic proton to the internal standard.

Example of ^{1}H-NMR spectra at 100 % conversion :

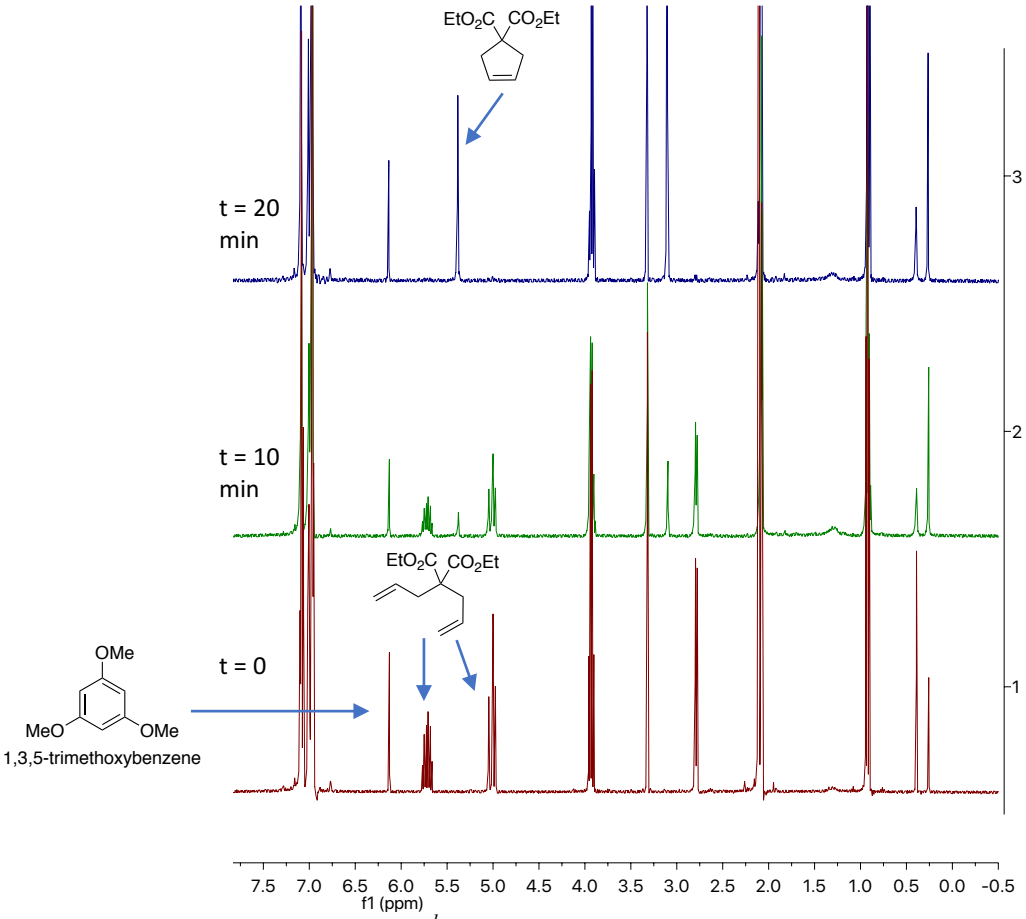
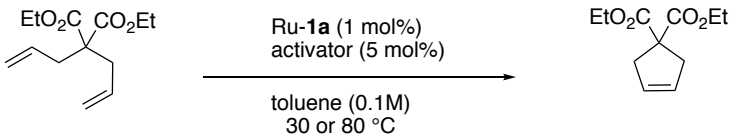


***Figure S4**: ^{1}H-NMR monitoring of DEDAM **S1** RCM*



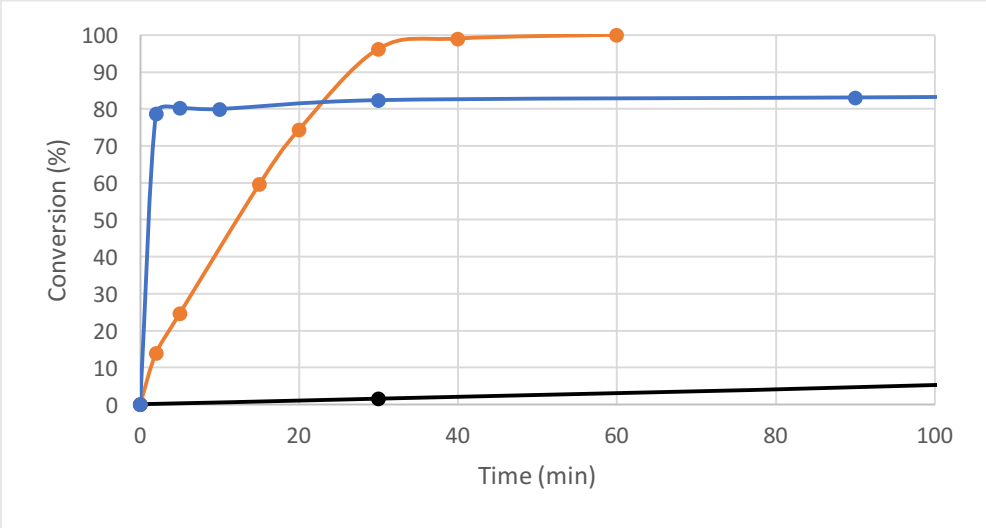


Figure S5: *Catalytic activity profiles of complexes Ru-**1a** (1 mol%)for RCM of DEDAM **S1** at 30 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue); **without activators** (black).*

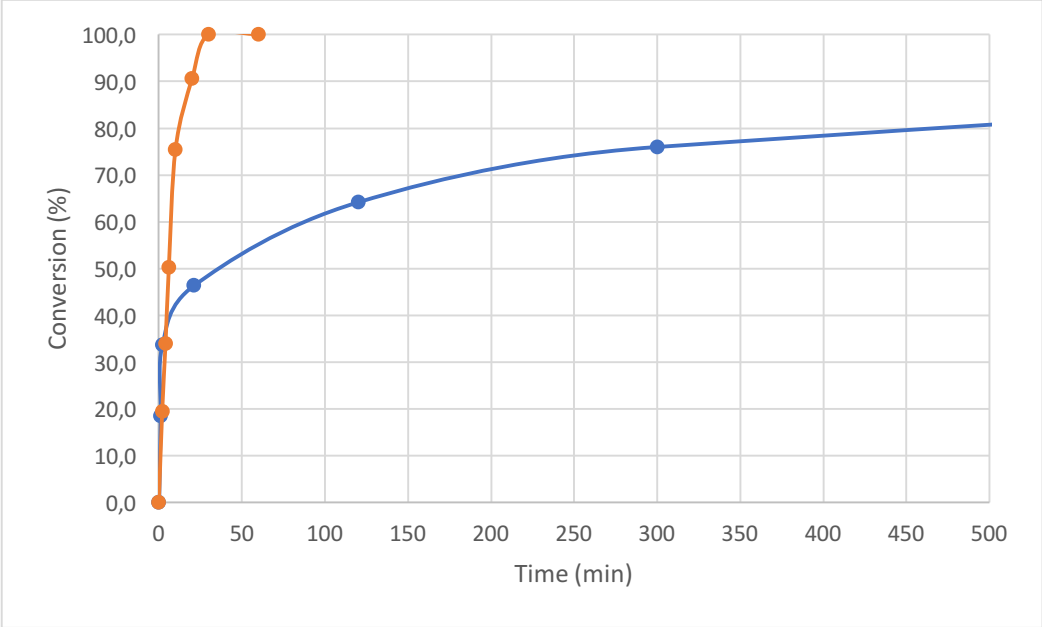


Figure S6: *Catalytic activity profiles of complexes Ru-**1a** (0.1 mol%) for RCM of DEDAM **S1** at 30 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 0.5 mol% (orange); **AuCl** – 0.5 mol% (blue).*

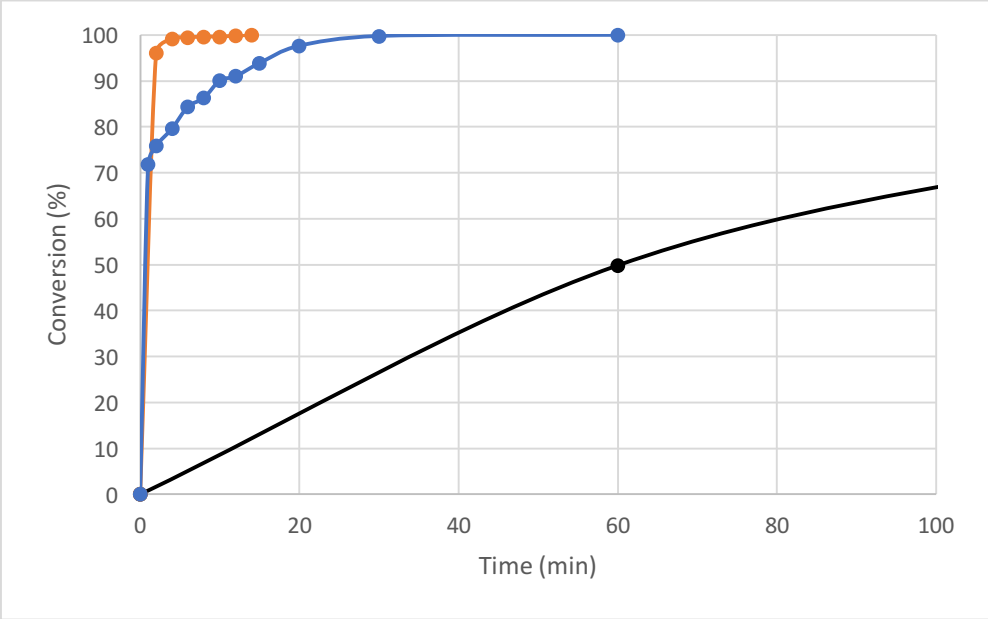
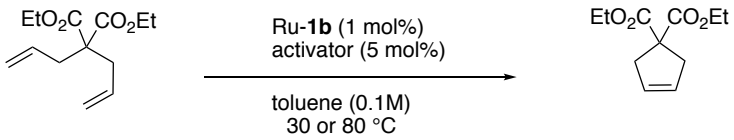


Figure S7: *Catalytic activity profiles of complexes Ru-**1a** (1mol%) for RCM of DEDAM **S1** at 80 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard.* ***CuCl*** – 5 mol% *(orange);* ***AuCl*** – 5 mol% *(blue);* ***without activators*** *(black).*



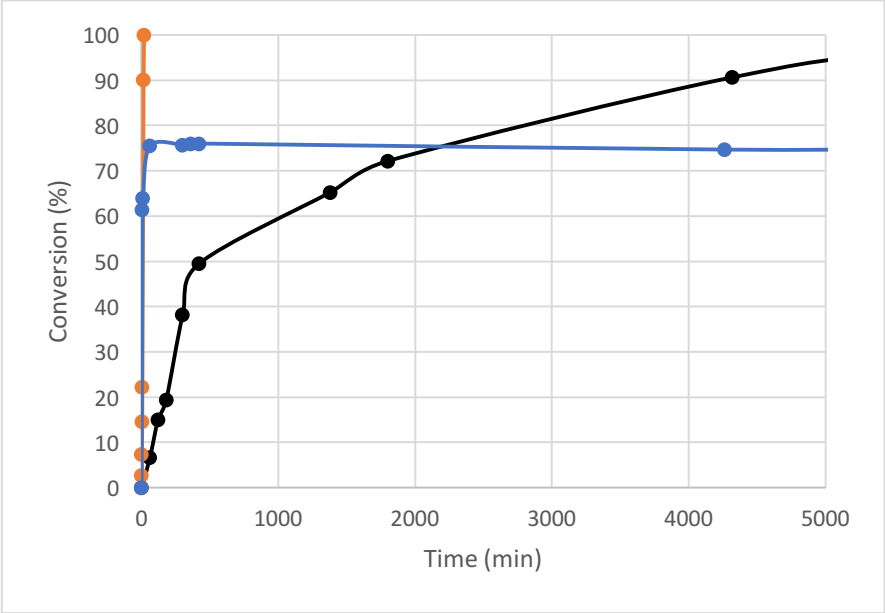


Figure S8: *Catalytic activity profiles of complexes Ru-**1b** (1 mol%) for RCM of DEDAM **S1** at 30 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue) ; **without activators** (black).*

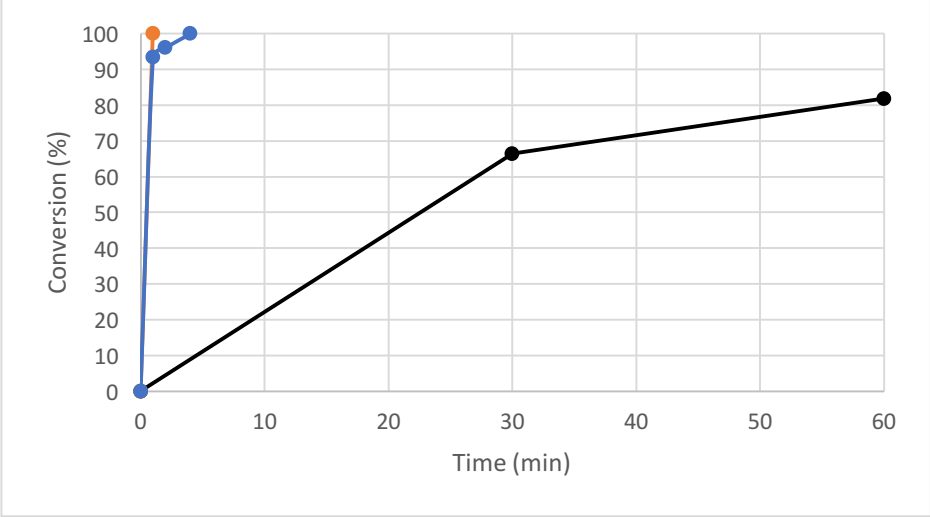
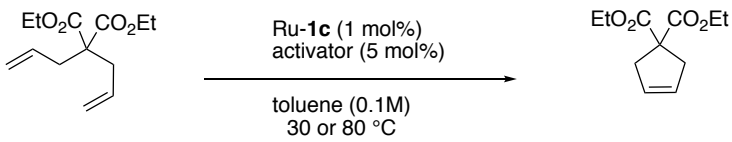


Figure S9: *Catalytic activity profiles of complexes Ru-**1b** (1 mol%) for RCM of DEDAM **S1** at 80 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue); **without activators** (black).*



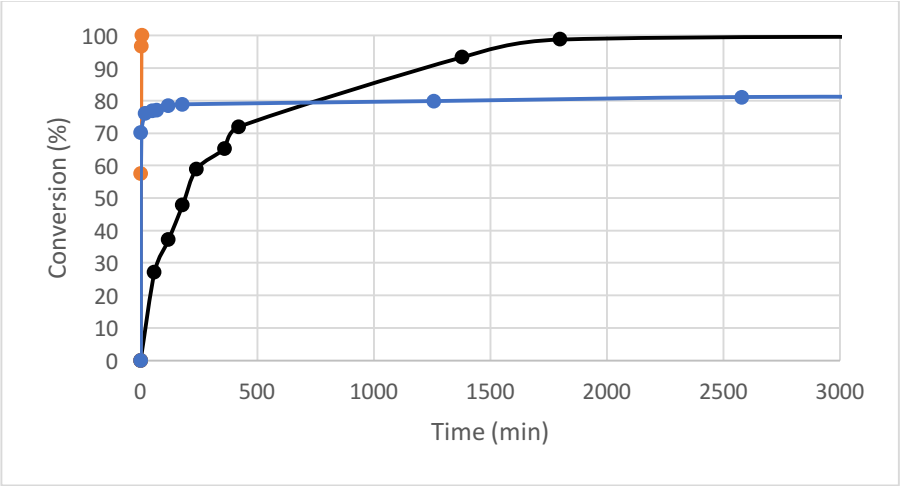


Figure S10: *Catalytic activity profiles of complexes Ru-**1c** (1 mol%) for RCM of DEDAM **S1** at 30 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue); **without activators** (black).*

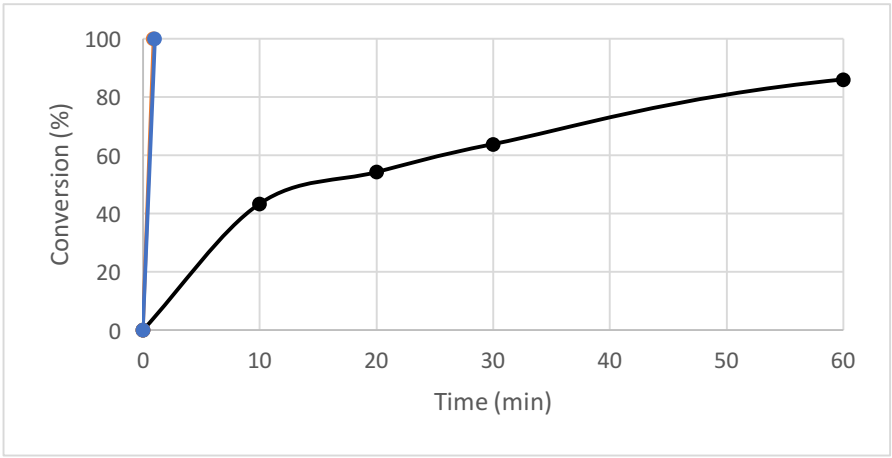
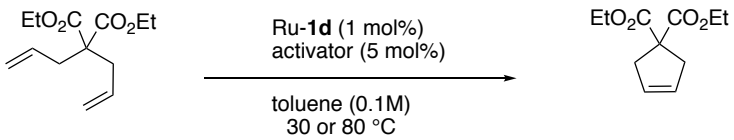


Figure S11: *Catalytic activity profiles of complexes Ru-**1c** (1 mol%) for RCM of DEDAM **S1** at 80 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue); **without activators** (black).*



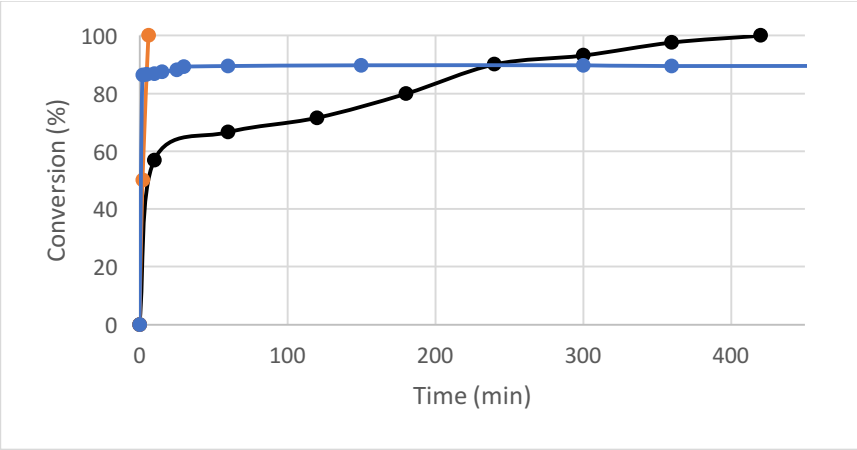


Figure S12: *Catalytic activity profiles of complexes Ru-**1d** (1 mol%) for RCM of DEDAM **S1** at 30 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue); **without activators** (black).*

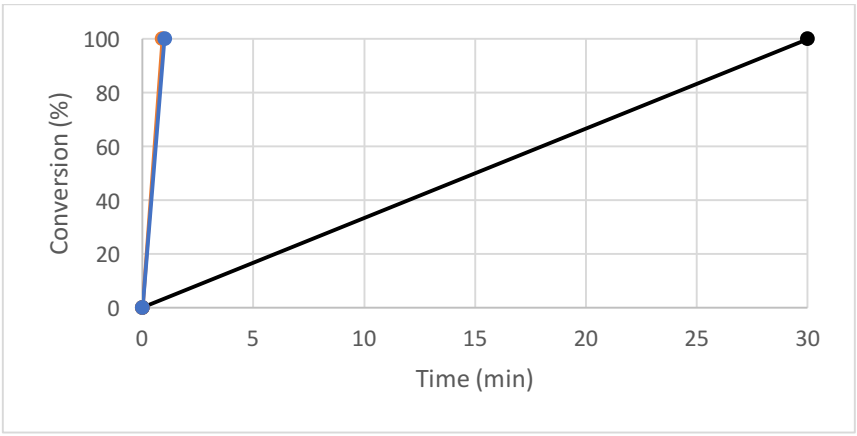


Figure S13: *Catalytic activity profiles of complexes Ru-**1d** (1 mol%) for RCM of DEDAM **S1** at 80 °C in toluene (1.8 mL). Conversions were monitored by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. **CuCl** – 5 mol% (orange); **AuCl** – 5 mol% (blue); **without activators** (black).*

6. Scope of Metathesis Transformations

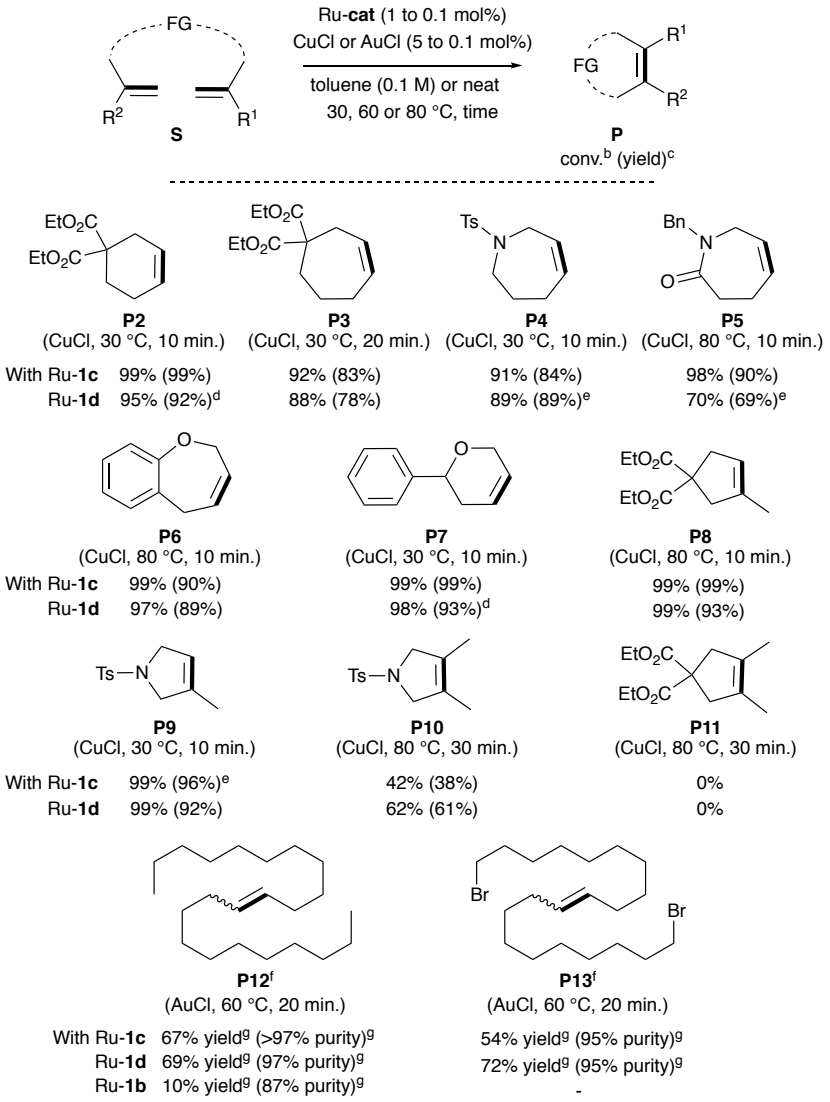


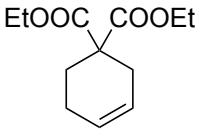
***Figure S14** : Scope of metathesis transformations catalyzed by Ru-**1b**, **1c** et **1d**/ CuCl or AuCl*

6.1. Ring Closing Metathesis (RCM)

General Procedure for RCM Reactions:

To a Schlenk apparatus was introduced substrate (0.2 mmol, 1.0 equiv.), 1,3,5-trimethoxybenzene (0.066 mmol, 0.33 equiv.), CuCl (0.01 mmol, 0.05 equiv.) and toluene (2 mL, c = 0.1M) under argon. Precatalyst (0.002 mmol, 0.01 equiv.) was added and the mixture was heated at 30 or 80 °C. Aliquots were taken, quenched with Ethylvinylether and concentrated. The reaction was monitored by ^{1}H NMR ($CDCl_3$) until complete conversion or catalyst death.

Diethyl cyclohex-3-ene-1,1-dicarboxylate (P2)



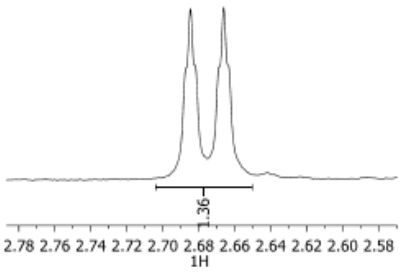
P2
$C_{12}H_{18}O_4$
226.27 g.mol^{-1}

With Ru-**1c** - Freshly made solutions in toluene were prepared:

- 60.3 mg of Diethyl 2-allyl-2-(but-3-en-1-yl)malonate in 0.12 mL of toluene.
- 33.1 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 5.3 mg of CuCl in 0.53 mL of toluene.
- 4.8 mg of Ru-**1c** in 0.24 mL of toluene.

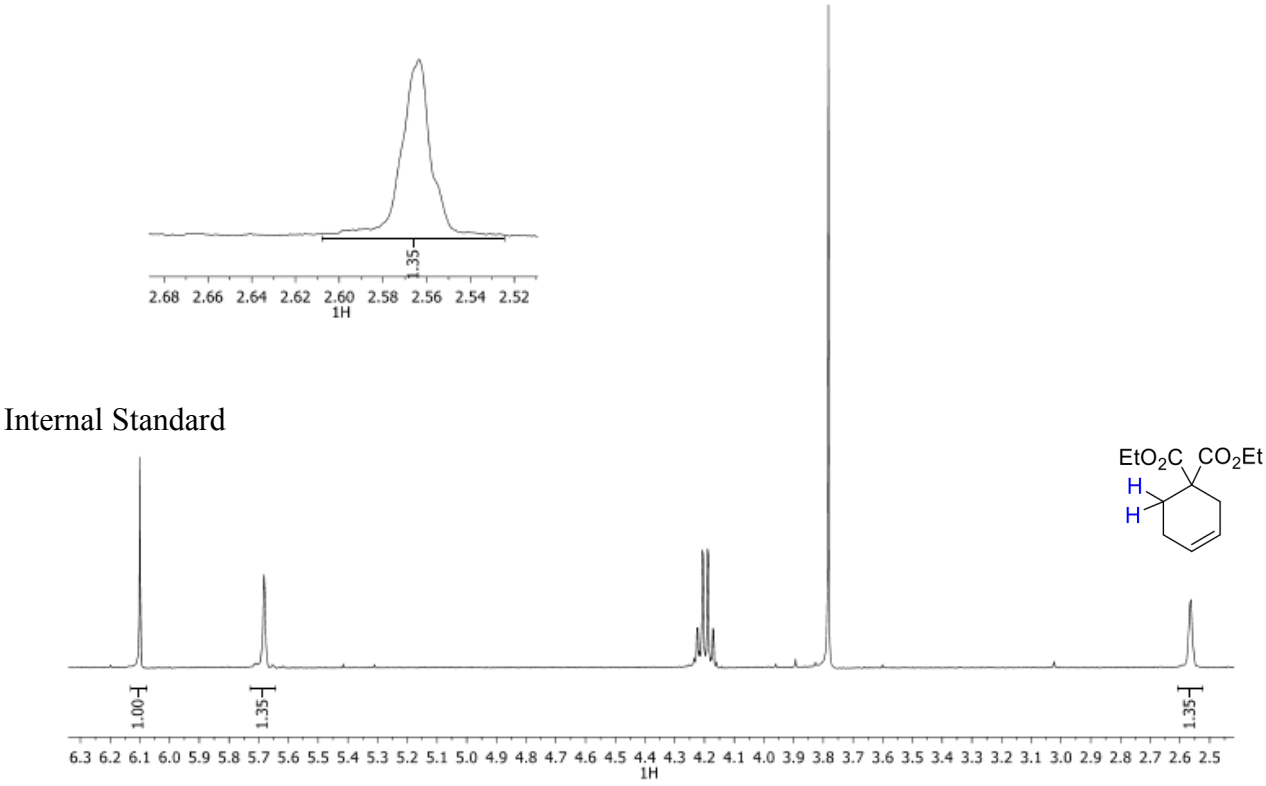
Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(but-3-en-1-yl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 99% yield with Ru-**1c** after 10 min of reaction.

^{1}H-NMR spectra with Ru-**1c** at T0 :



Internal Standard

^{1}H-NMR spectra with Ru-**1c** at 99% conversion and 99% NMR yield [(1.35/1.36) x 100 = 99%] after 10 min of reaction:

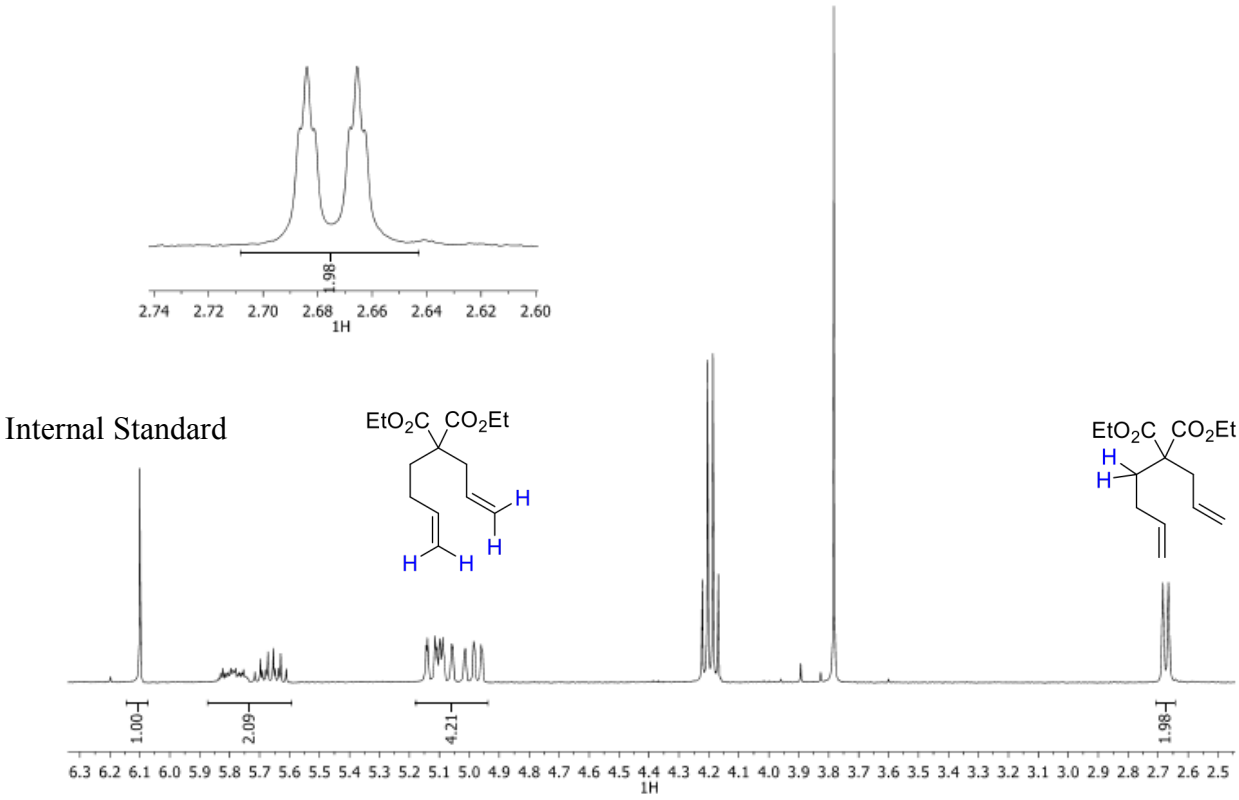


With **Ru-1d** - A freshly made solutions in toluene were preapared :

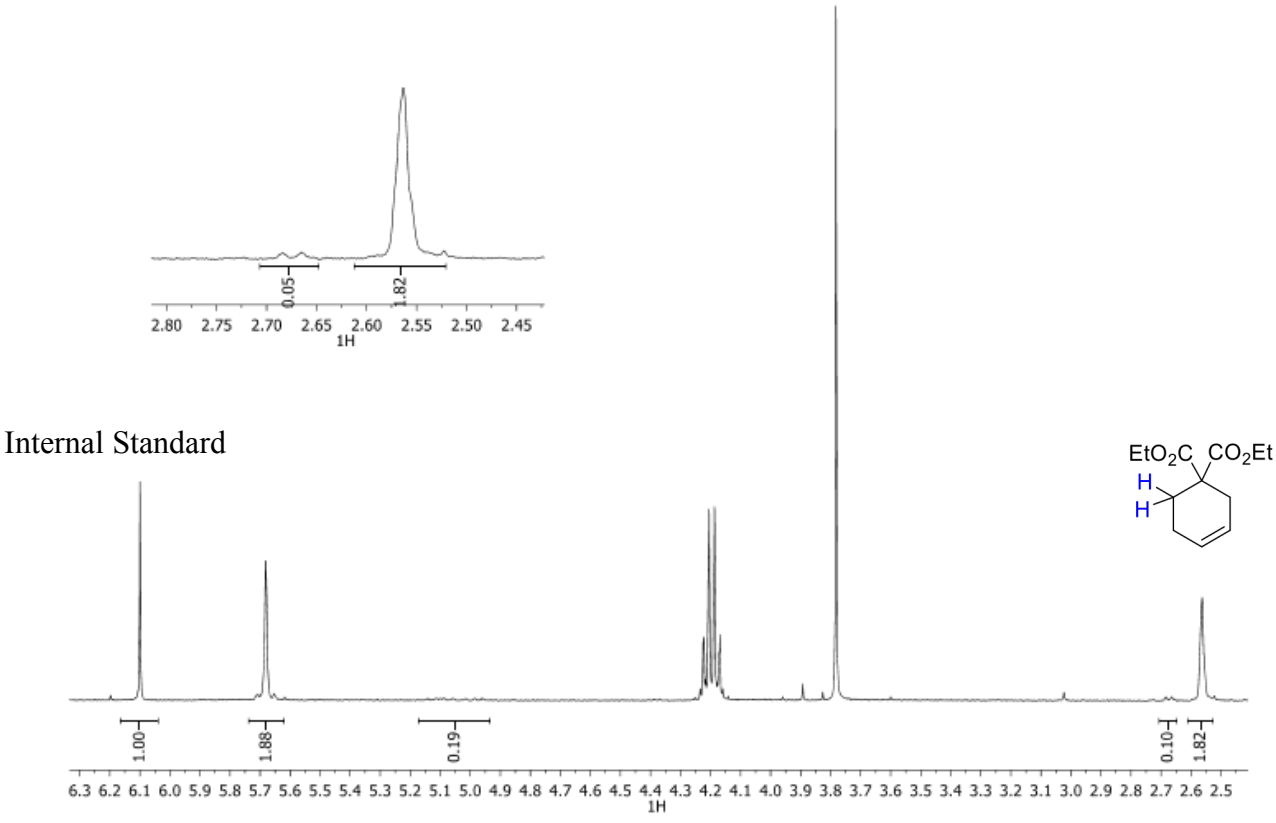
- 70.3 mg of Diethyl 2-allyl-2-(but-3-en-1-yl)malonate in 0.14 mL of toluene.
- 6.8 mg of CuCl in 0.68 mL of toluene.
- 6.0 mg of Ru-**1d** in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(but-3-en-1-yl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.063 mmol, 10.6 mg) in Toluene (1,7 mL), conversion was determined by ^{1}H-NMR comparing standard peak with internal olefin peak on the starting material. 95% conversion and 92% yield with Ru-**1d** after 30 min of reaction.

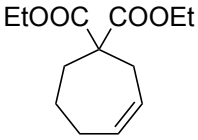
^{1}H-NMR spectra with Ru-**1d** at T0 :



[1]H-NMR spectra with Ru-**1d** at 95% conversion [100 - (0.19/4.21) x 100) = 95%] and 92% NMR yield [(1.82/1.98) x 100) = 92%] after 30 min of reaction:



Diethyl cyclohept-3-ene-1,1-dicarboxylate (P3)



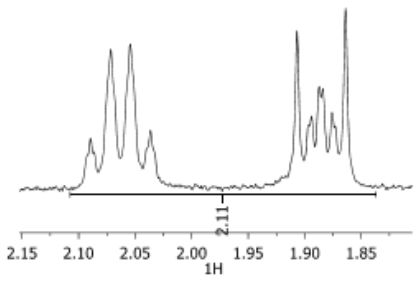
P3
$C_{13}H_{20}O_4$
240.30 g.mol^{-1}

With **Ru-1c** - Freshly made solutions in toluene were prepared:

- 61.0 mg of Diethyl 2-allyl-2-(pent-4-enyl)malonate in 0.11 mL of toluene.
- 33.1 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 5.3 mg of CuCl in 0.53 mL of toluene.
- 4.8 mg of Ru-**1c** in 0.24 mL of toluene.

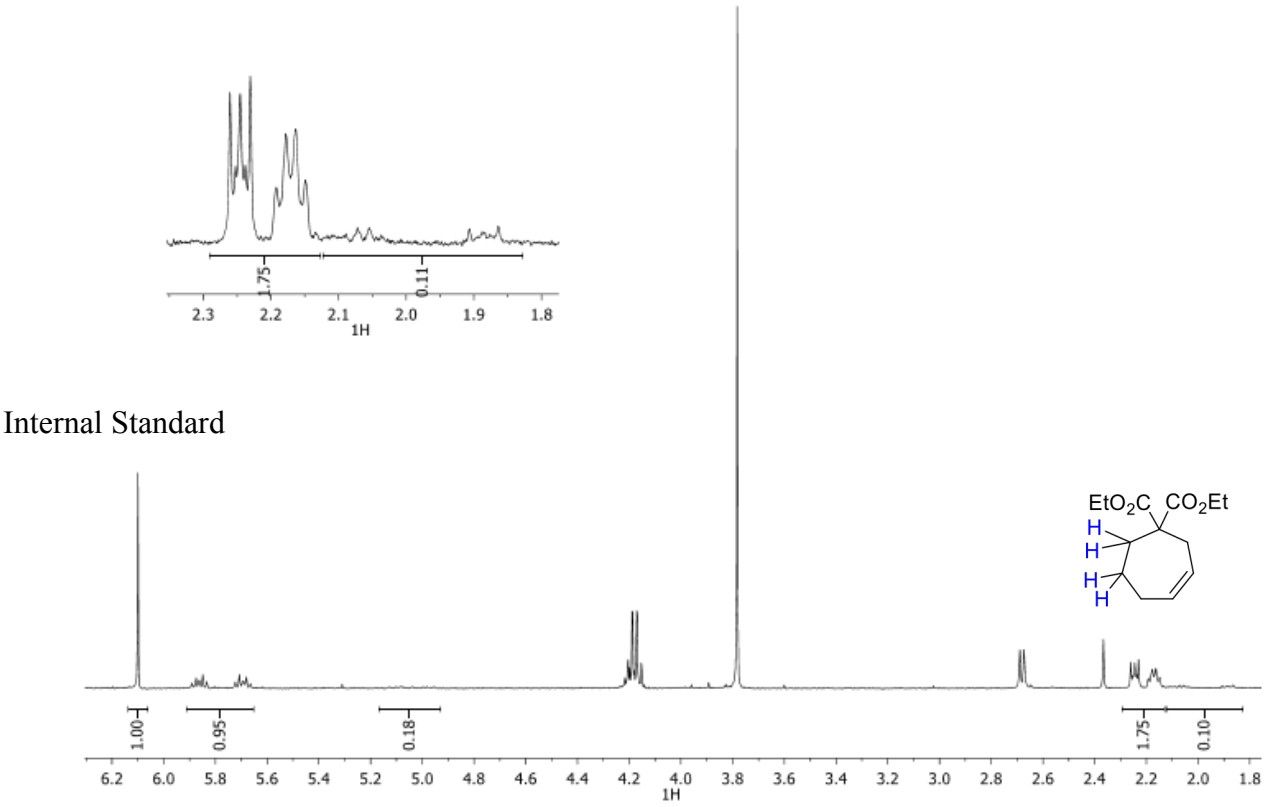
Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(pent-4-enyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1,6 mL), conversion was determined by ^{1}H-NMR comparing standard peak with internal olefin peak on the starting material. 92% conversion and 83% yield with Ru-**1c** after 20 min of reaction.

^{1}H-NMR spectra with Ru-**1c** at T0 :



Internal Standard

^{1}H-NMR spectra with Ru-**1c** at 92% conversion [100 - (0.18/2.14) x 100) = 92%] and 83% NMR yield [(1.75/2.11) x 100) = 83%] after 20 min of reaction:

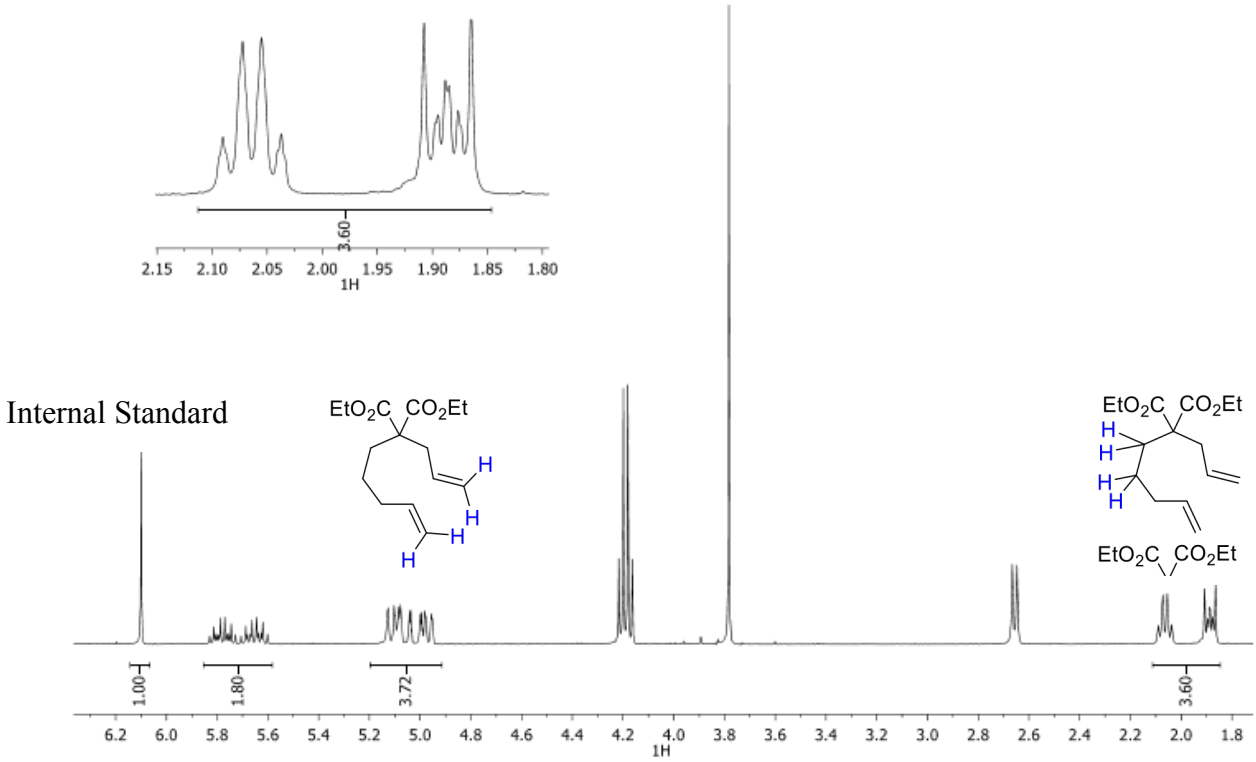


With Ru-1**d** - Freshly made solutions in toluene were prepared:

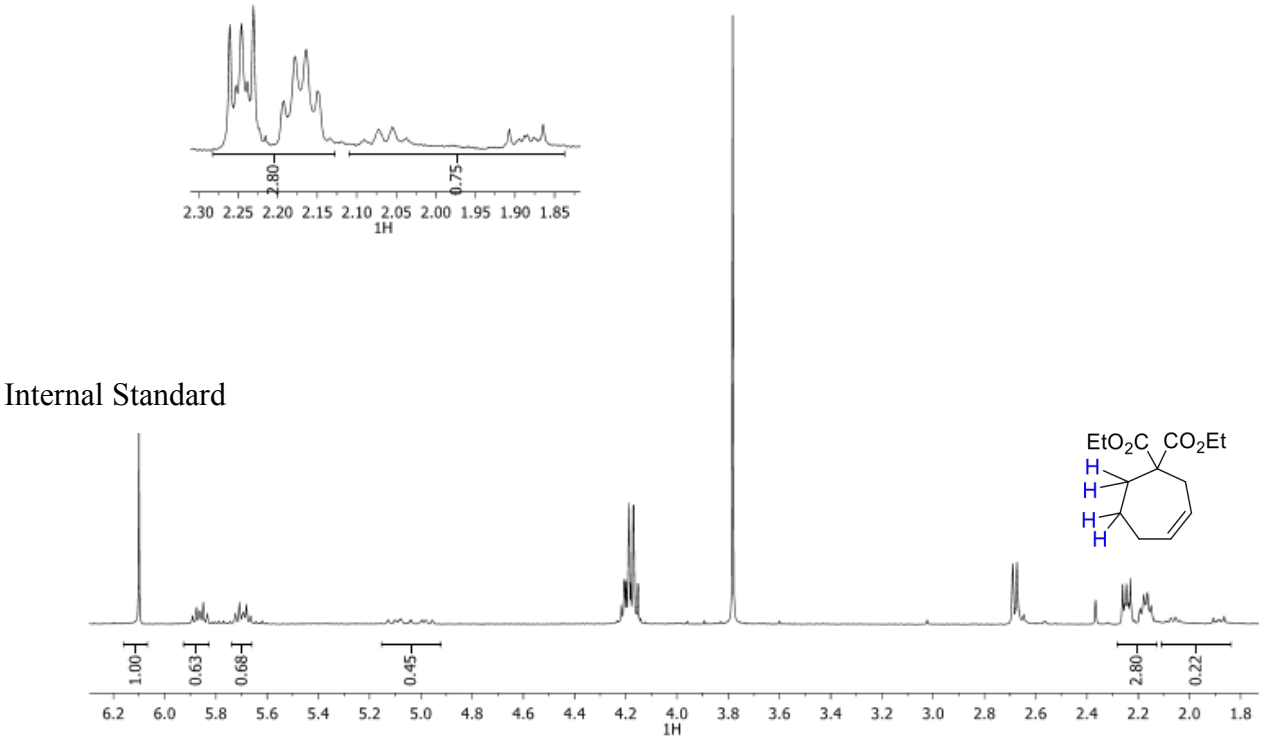
- 62.8 mg of Diethyl 2-allyl-2-(pent-4-enyl)malonate in 0.12 mL of toluene.
- 6.8 mg of CuCl in 0.68 mL of toluene.
- 6.0 mg of Ru-**1d** in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(pent-4-enyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.071 mmol, 12.0 mg) in Toluene (1,7 mL), conversion was determined by ^{1}H-NMR comparing standard peak with internal olefin peak on the starting material. 88% conversion and 78% yield with Ru-**1d** after 20 min of reaction.

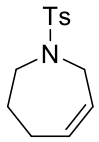
^{1}H-NMR spectra with Ru-**1d** at T0 :



^{1}H-NMR spectra with Ru-**1d** at 88% conversion [100 - (0.45/3.72) x 100) = 88%] and 78% NMR yield [(2.80/3.60) x 100) = 78%] after 20 min of reaction:



1-tosyl-2,3,4,7-tetrahydro-1*H*-azepine (P4)



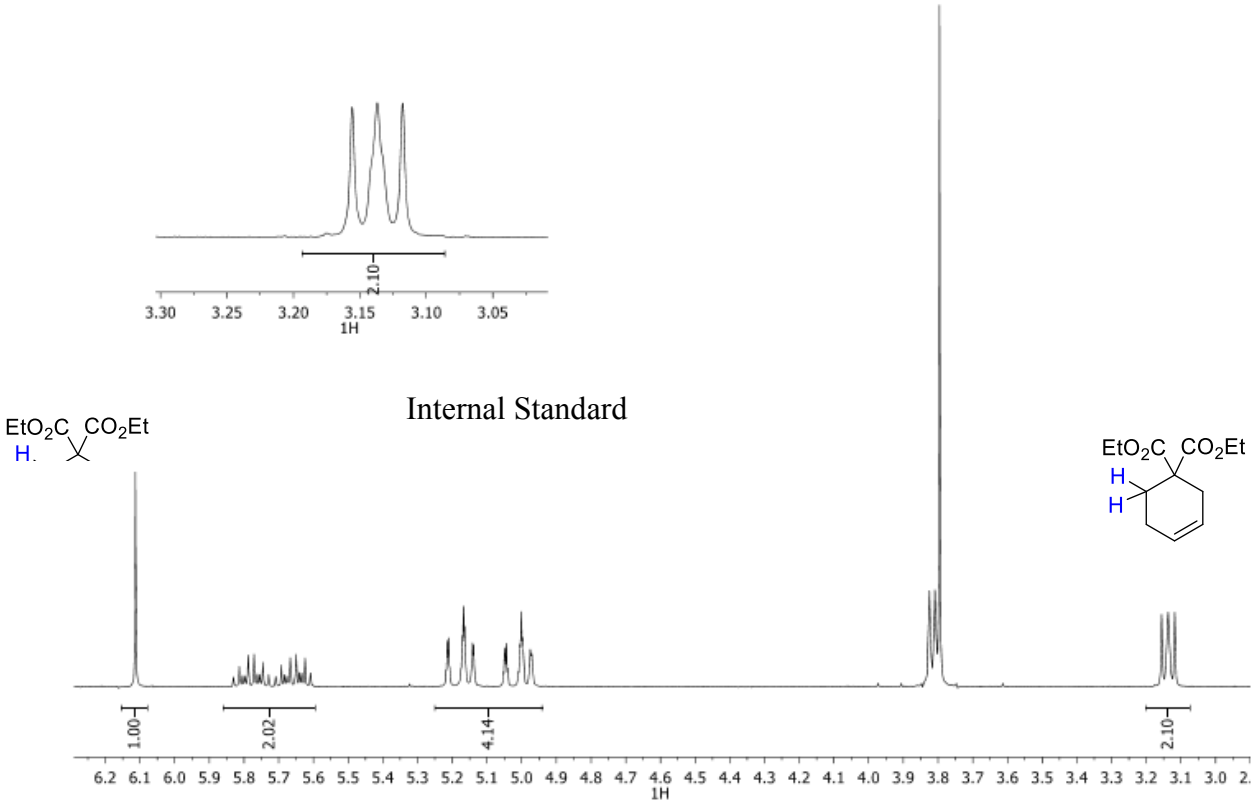
$C_{13}H_{17}NO_2S$
251.34 g.mol^{-1}

With Ru-**1c** - Freshly made solutions in toluene were prepared:

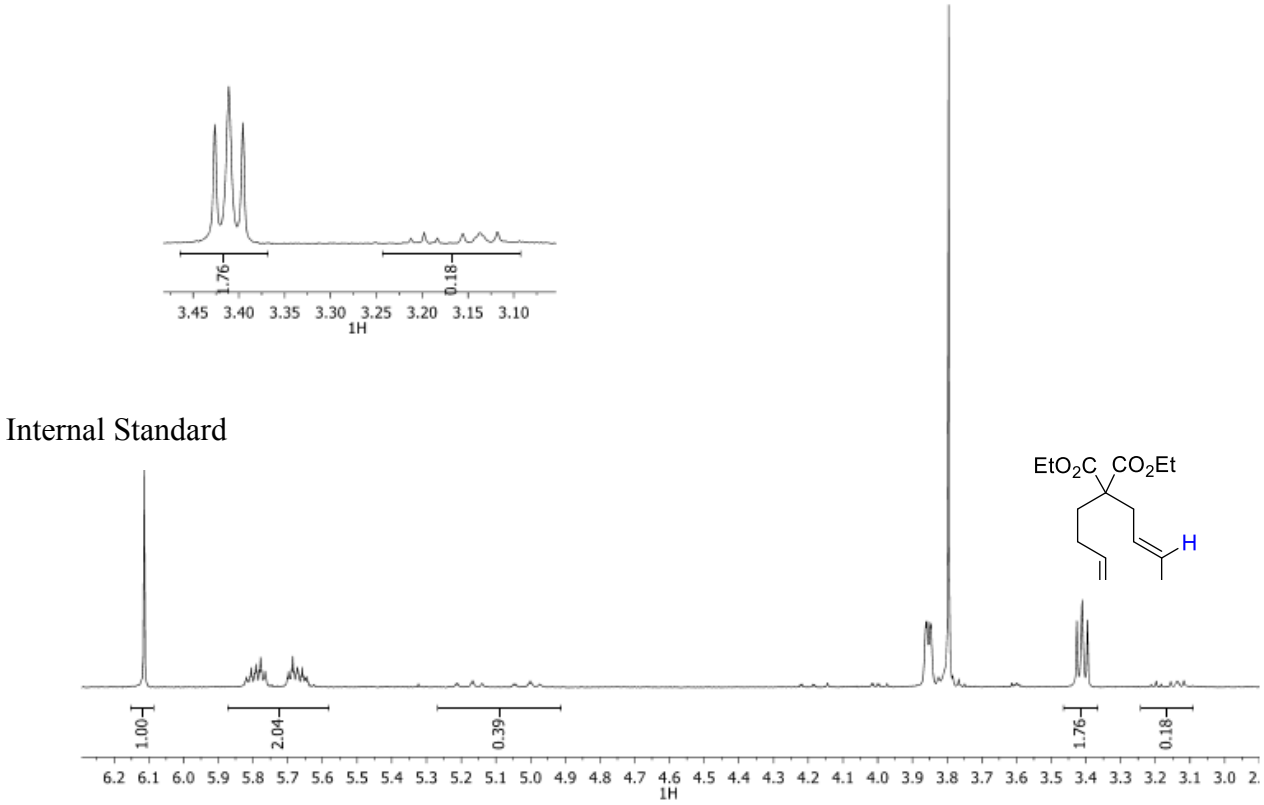
- 67.9 mg of N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide in 0.12 mL of toluene.
- 5.1 mg of CuCl in 0.51 mL of toluene.
- 5.4 mg of Ru-**1c** in 0.27 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 11.0 mg) in Toluene (1.7 mL), conversion was determined by ^{1}H-NMR comparing standard peak with internal olefin peak on the starting material. 91% conversion and 84% yield with Ru-**1c** after 10 min of reaction.

^{1}H-NMR spectra with Ru-**1c** at T0 :



^{1}H-NMR spectra with Ru-**1c** at 91% conversion [100 - (0.39/4.14) x 100) = 91%] and 84% NMR yield [(1.76/2.10) x 100) = 84%] after 10 min of reaction:

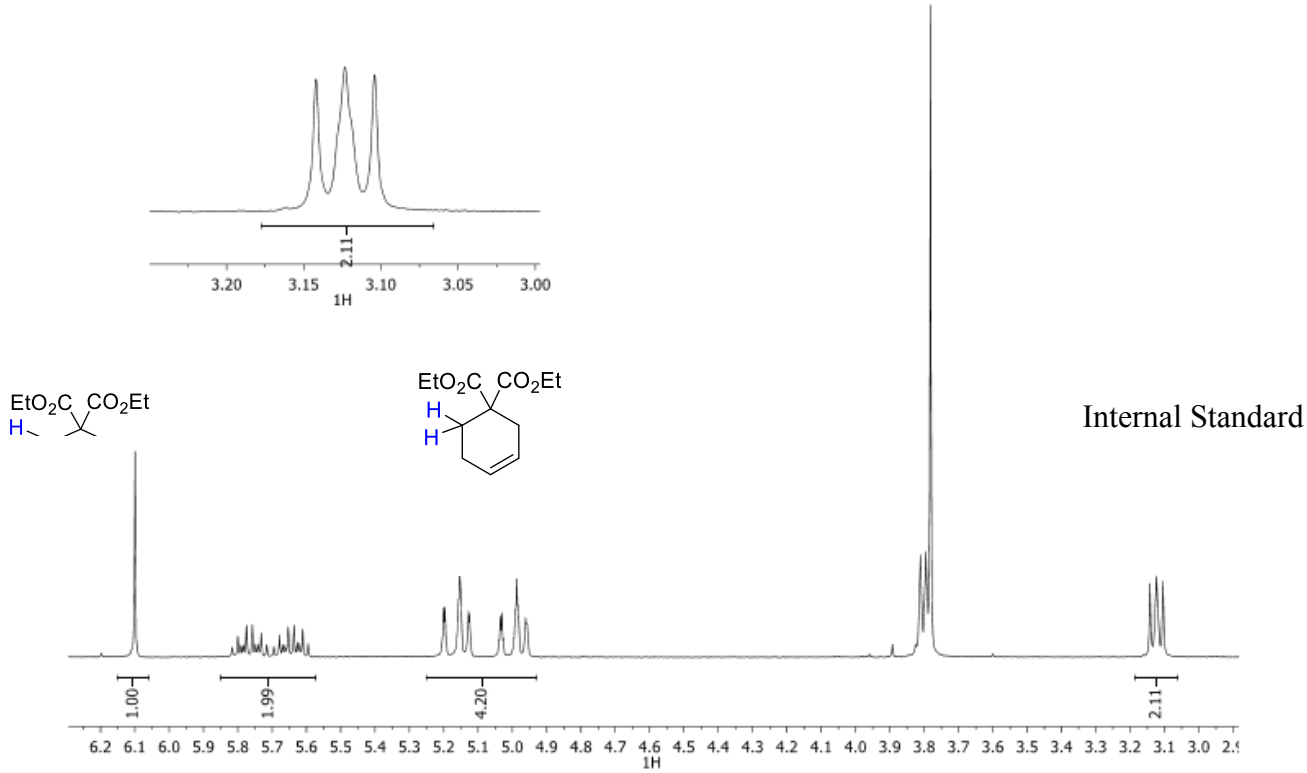


With Ru-**1d** - Freshly made solutions in toluene were prepared:

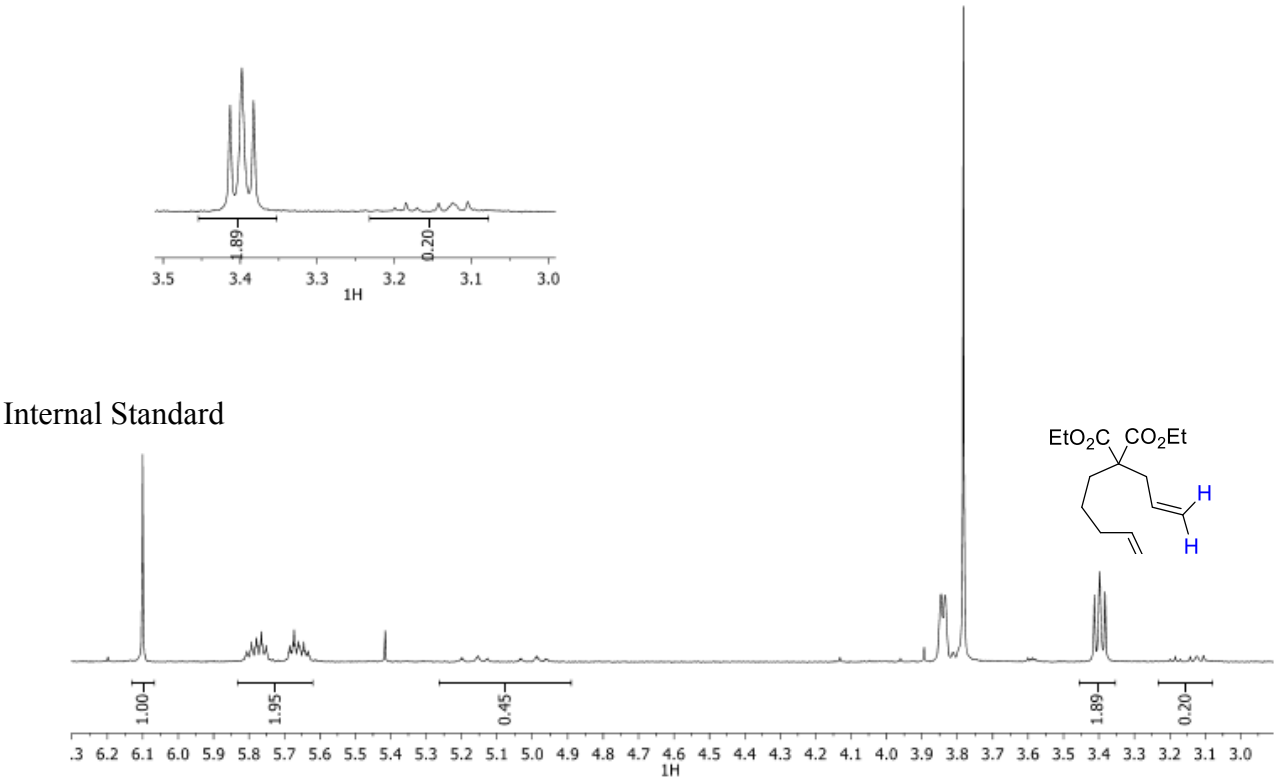
- 67.1 mg of N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide in 0.12 mL of toluene.
- 8.0 mg of CuCl in 0.80 mL of toluene.
- 6.1 mg of Ru-**1d** in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 11.1 mg) in Toluene (1.7 mL), conversion was determined by ^{1}H-NMR comparing standard peak with internal olefin peak on the starting material. 89% conversion and 89% yield with Ru-**1d** after 20 min of reaction.

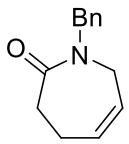
^{1}H-NMR spectra with Ru-**1d** at T0 :



^{1}H-NMR spectra with Ru-**1d** at 89% conversion [100 - (0.45/4.20) x 100) = 89%] and 89% NMR yield [(1.89/2.11) x 100) = 89%] after 20 min of reaction:



1-benzyl-1,3,4,7-tetrahydro-2*H*-azepin-2-one (P5)



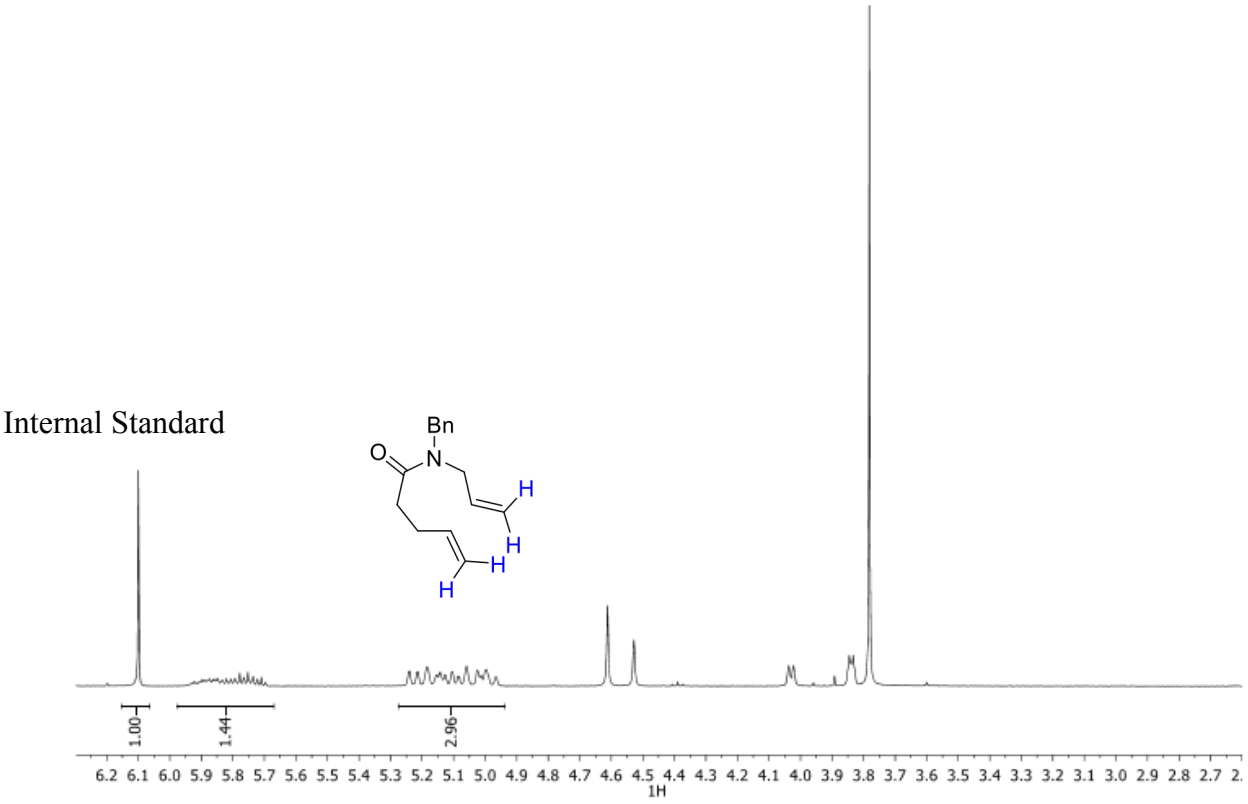
$C_{13}H_{15}NO$
201.27 g.mol^{-1}

With Ru-**1c** - Freshly made solutions in toluene were prepared:

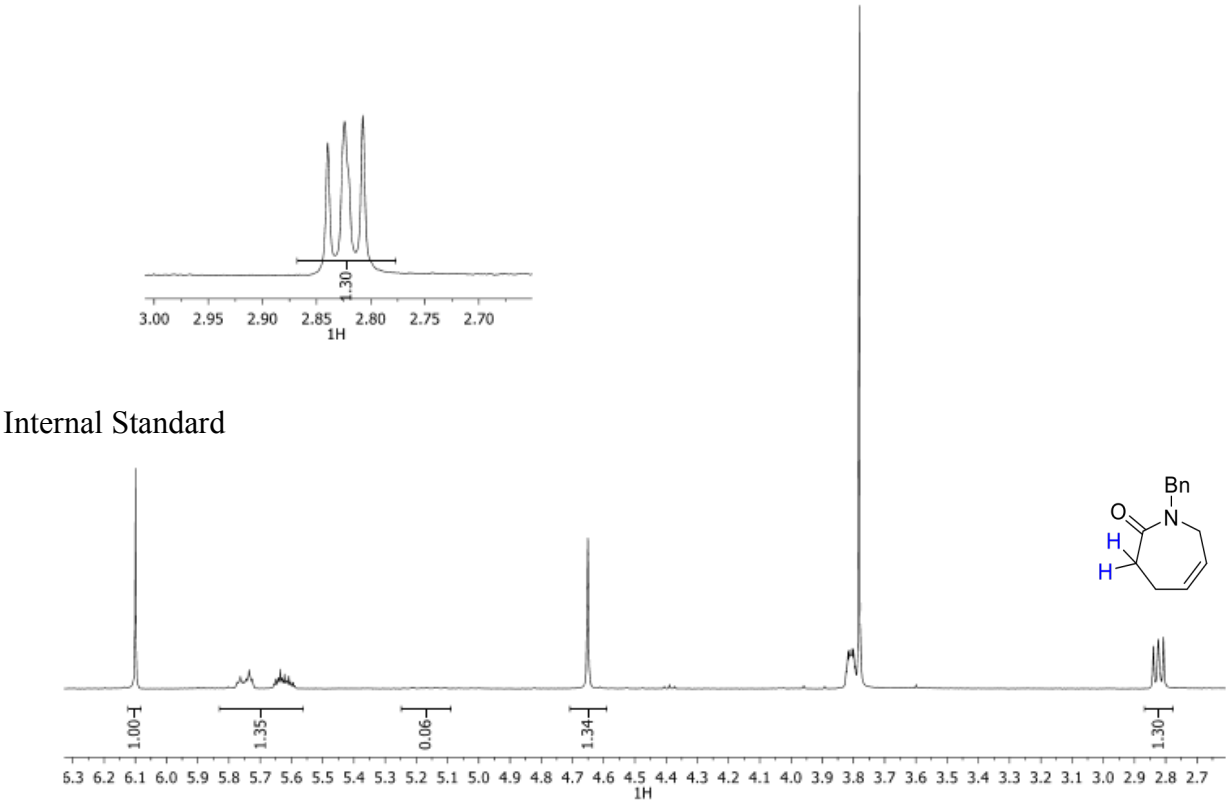
- 100.9 mg of N-allyl-N-benzylpent-4-enamide in 0.22 mL of toluene.
- 66.1 mg of 1,3,5-trimethoxybenzene in 0.60 mL of toluene.
- 9.1 mg of CuCl in 0.91 mL of toluene.
- 9.9 mg of Ru-**1c** in 0.50 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-benzylpent-4-enamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 98% conversion and 90% yield with Ru-**1c** after 10 min of reaction.

^{1}H-NMR spectra with Ru-**1c** at T0 :



[1]H-NMR spectra with Ru-**1c** at 98% conversion [100 - (0.06/2.96) x 100) = 98%] and % NMR yield [(1.30/1.44) x 100) = 90%] after 10 min of reaction:

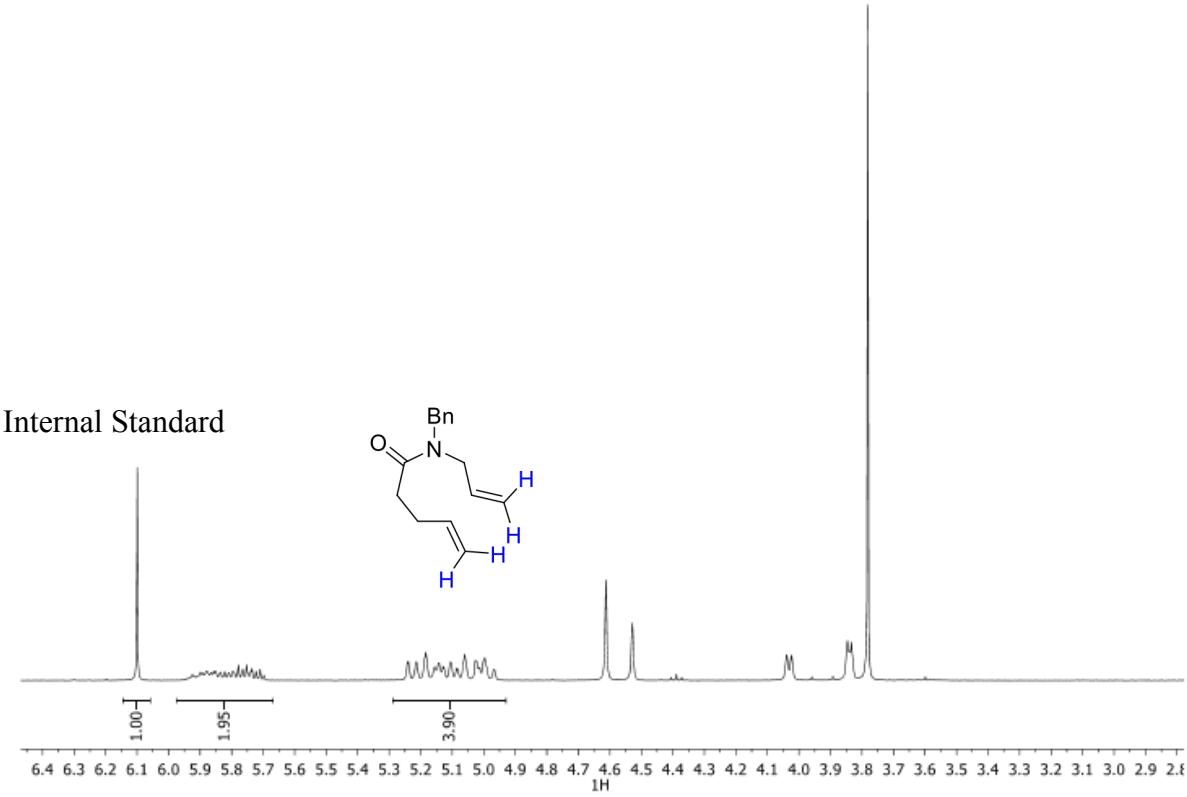


With Ru-**1d** - Freshly made solutions in toluene were prepared:

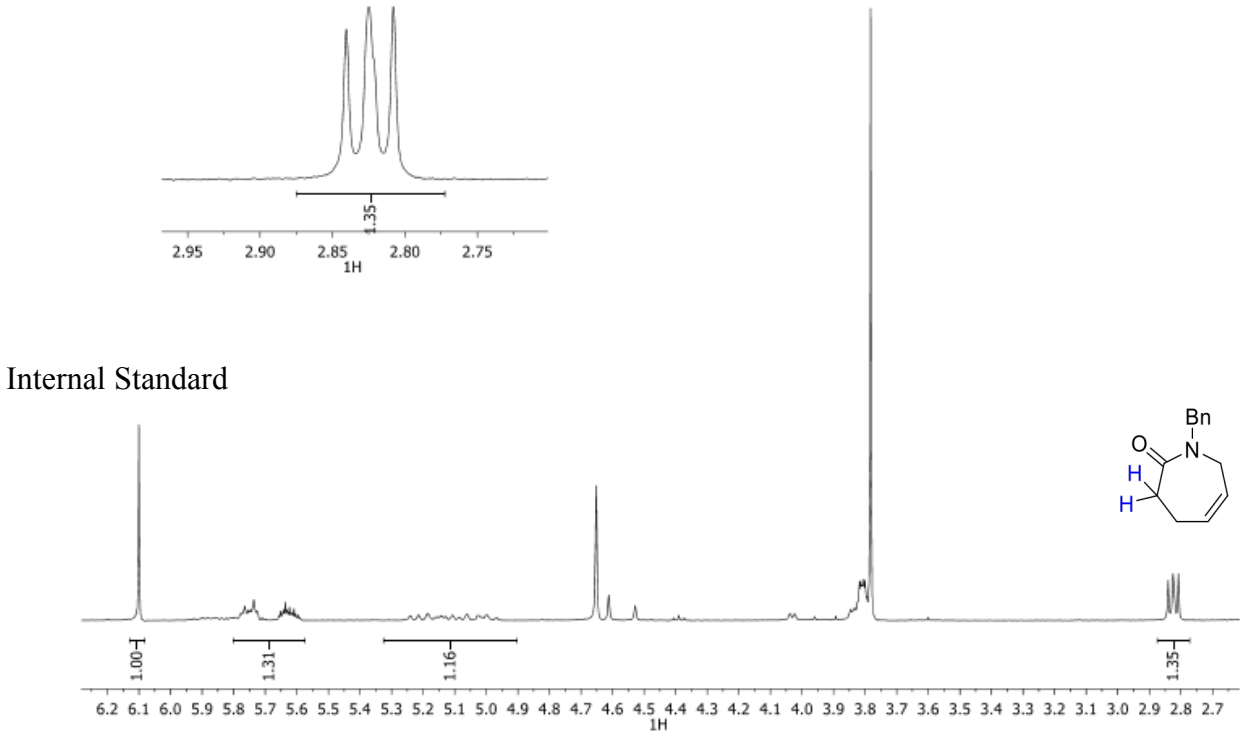
- 67.8 mg of N-allyl-N-benzylpent-4-enamide in 0.15 mL of toluene.
- 9.5 mg of CuCl in 0.95 mL of toluene.
- 7.2 mg of Ru-**1d** in 0.30 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-benzylpent-4-enamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.069 mmol, 11.6 mg) in Toluene (1.7 mL), conversion was determined by [1]H-NMR. 70% conversion and 69% yield with **Ru-1d** after 20 min of reaction.

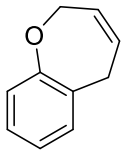
^{1}H-NMR spectra with **Ru-1d** at T0 :



^{1}H-NMR spectra with Ru-**1d** at 70% conversion [100 - (1.16/3.90) x 100) = 70%] and 69% NMR yield [(1.35/1.95) x 100) = 69%] after 20 min of reaction:



2,5-dihydrobenzo[*b*]oxepine (P6)



$C_{10}H_{10}O$
146.19 g.mol^{-1}

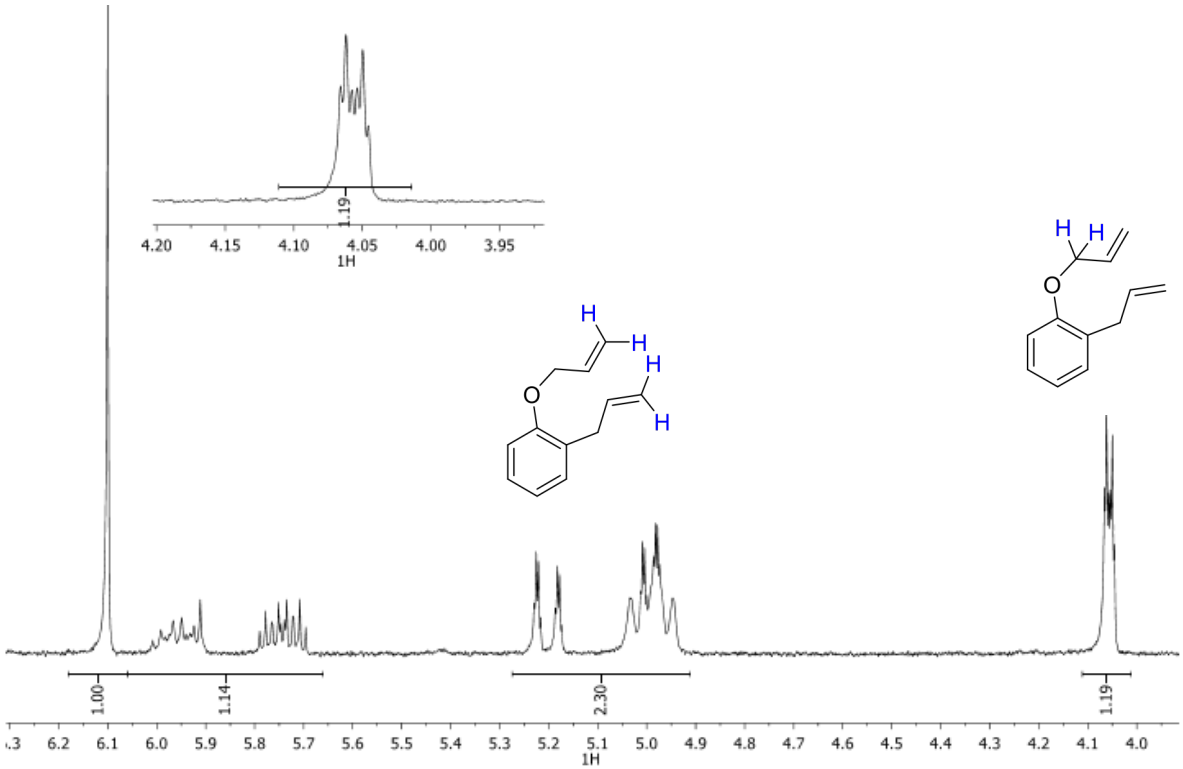
With Ru-**1c** - Freshly made solutions in toluene were prepared:

- 80.7 mg of 1-allyl-2-(allyloxy)benzene in 0.21 mL of toluene.
- 55.5 mg of 1,3,5-trimethoxybenzene in 0.50 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 5.6 mg of Ru-**1c** in 0.28 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), 1-allyl-2-(allyloxy)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 90% yield with Ru-**1c** after 10 min of reaction.

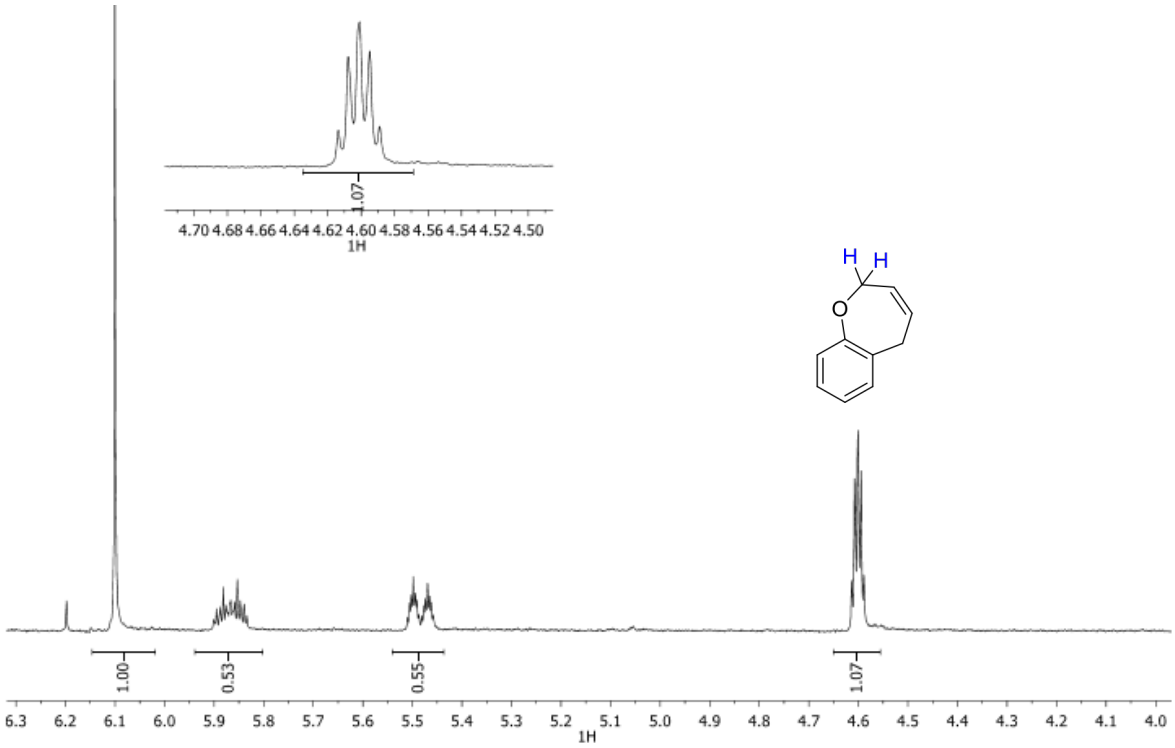
^{1}H-NMR spectra with Ru-**1c** at T0 :

Internal Standard



^{1}H-NMR spectra with Ru-**1c** at 99% conversion and 90% NMR yield [(1.07/1.19) x 100) = 90%] after 10 min of reaction:

Internal Standard



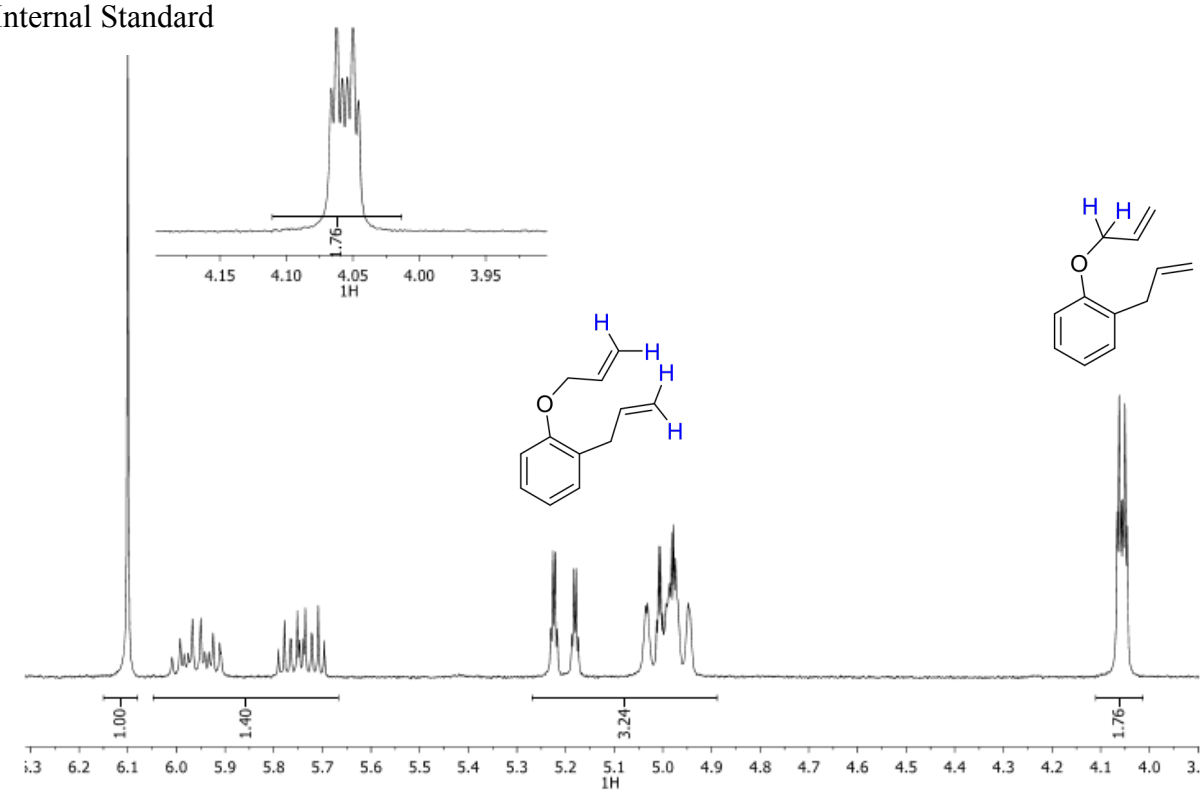
With Ru-**1d** - Freshly made solutions in toluene were prepared:

- 80.7 mg of 1-allyl-2-(allyloxy)benzene in 0.21 mL of toluene.
- 55.5 mg of 1,3,5-Trimethoxybenzene in 0.50 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 5.8 mg of **Ru-1d** in 0.24 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), 1-allyl-2-(allyloxy)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 97% conversion and 89% yield with Ru-**1d** after 10 min of reaction.

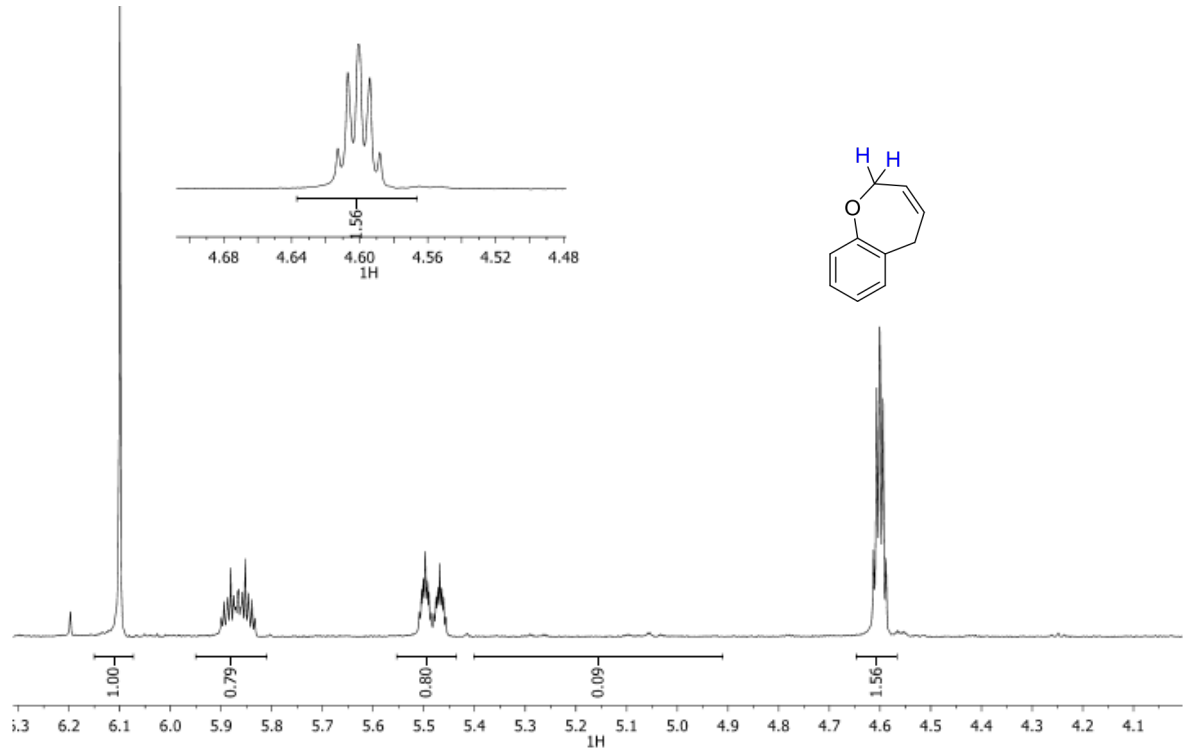
^{1}H-NMR spectra with Ru-**1d** at T0 :

Internal Standard

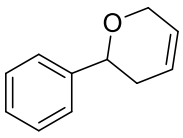


^{1}H-NMR spectra with Ru-**1d** at 97% conversion [100 - (0.09/3.24) x 100) = 97%] and 89% NMR yield [(1.56/1.76) x 100) = 89%] after 10 min of reaction:

Internal Standard



2-phenyl-3,6-dihydro-2*H*-pyran (P7)



$C_{11}H_{12}O$
160.22 g.mol^{-1}

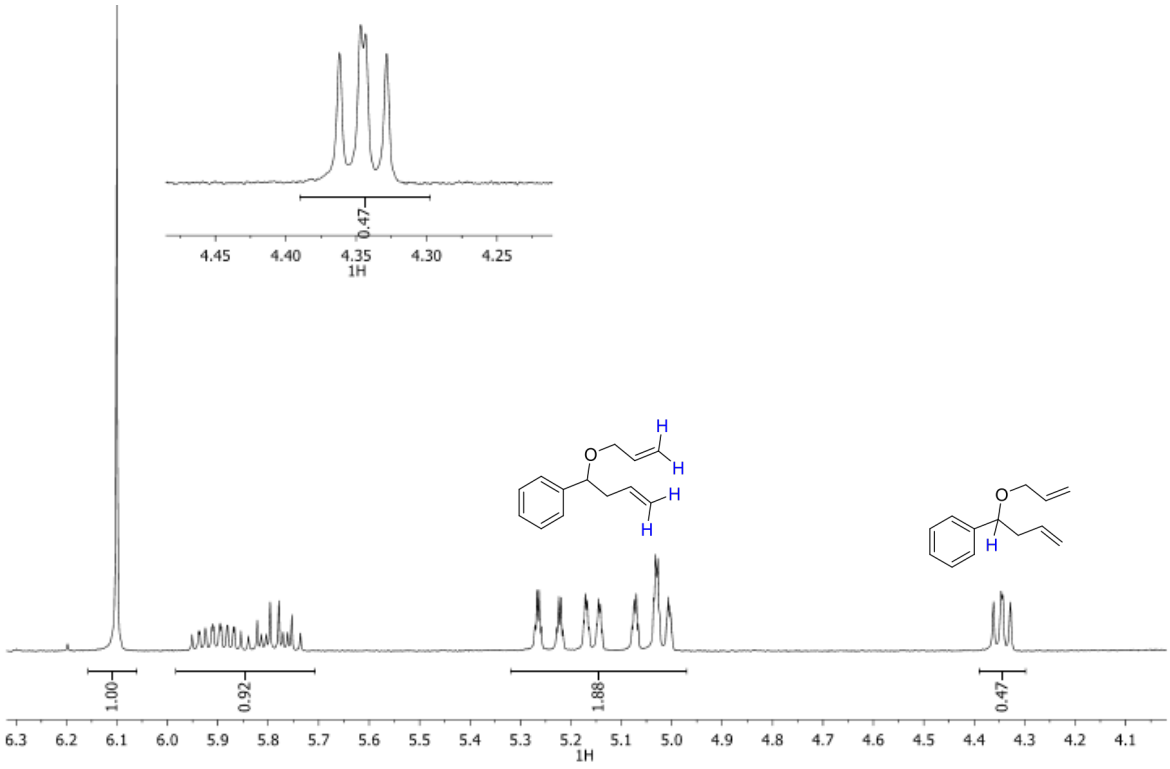
With Ru-**1c** - Freshly made solutions in toluene were prepared:

- 49.3 mg of (1-allyloxy)but-3-en-1yl)benzene in 0.13 mL of toluene.
- 5.1 mg of CuCl in 0.51 mL of toluene.
- 4.5 mg of Ru-**1c** in 0.23 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), (1-allyloxy)but-3-en-1yl)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.134 mmol, 22.6 mg) in Toluene (1.7 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 99% yield with Ru-**1c** after 10 min of reaction.

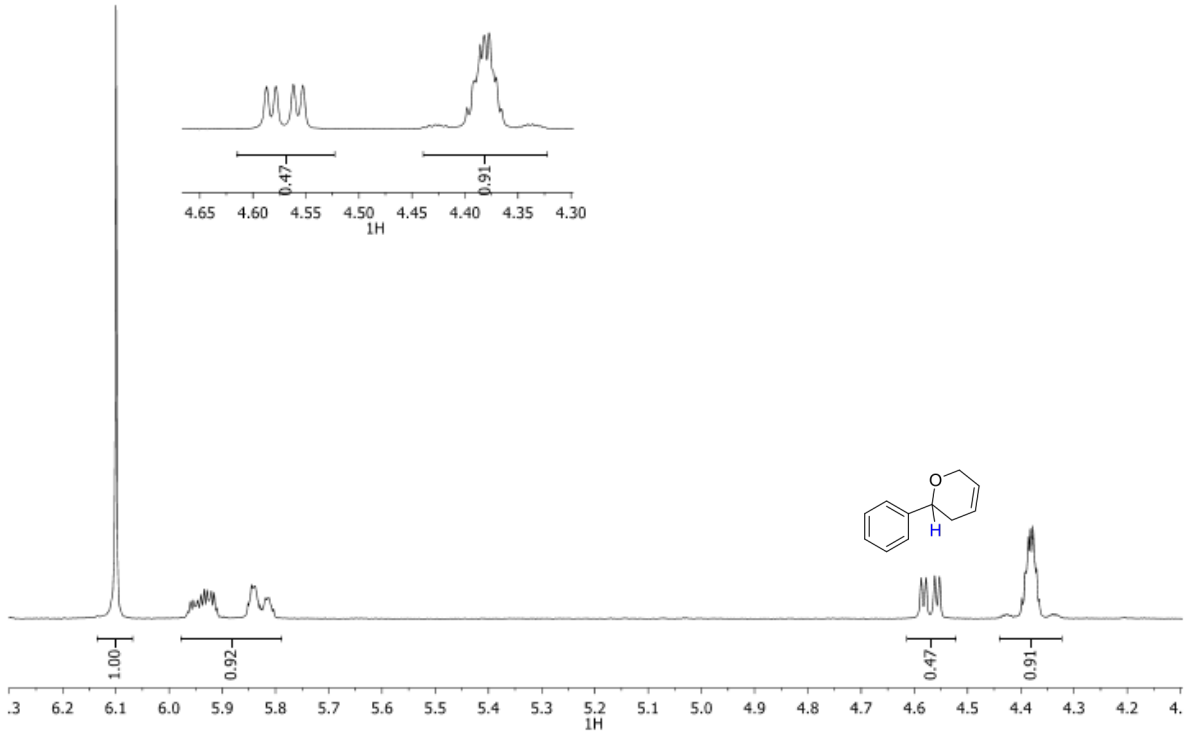
^{1}H-NMR spectra with Ru-**1c** at T0 :

Internal Standard



^{1}H-NMR spectra with Ru-**1c** at 99% conversion and 99% NMR yield [(0.47/0.47) x 100) = 99%] after 10 min of reaction:

Internal Standard



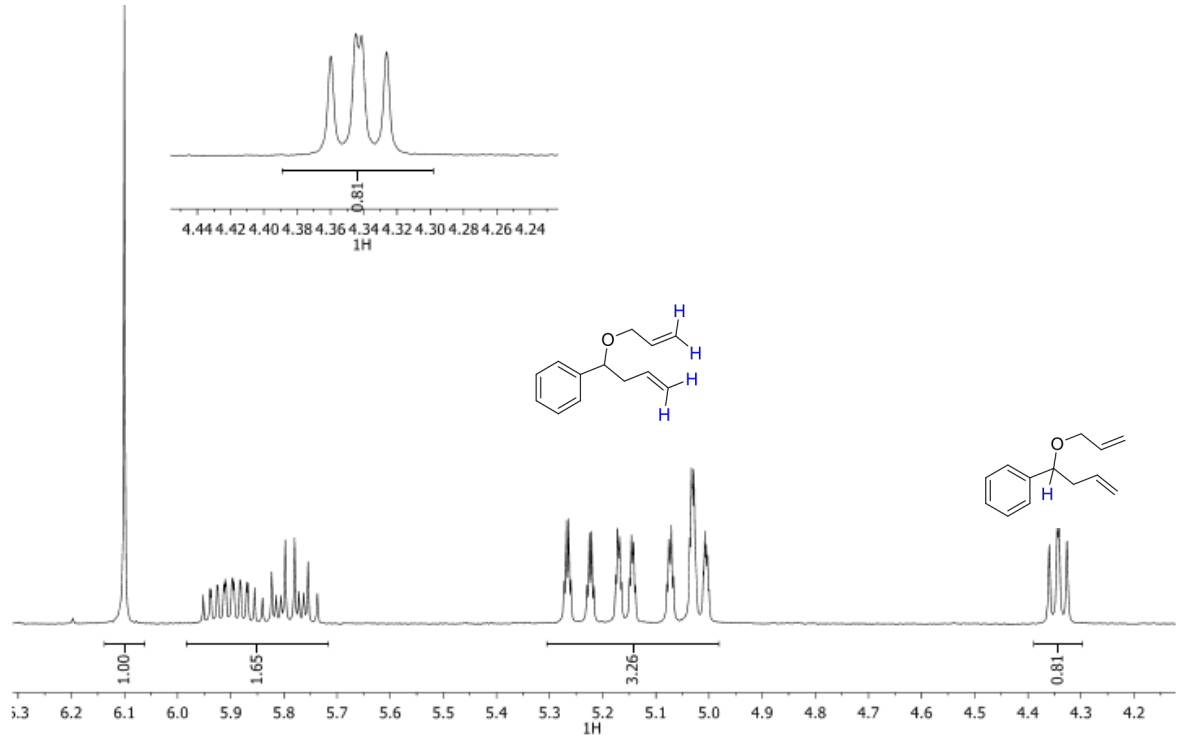
With Ru-**1d** - Freshly made solutions in toluene were prepared:

- 48.1 mg of (1-allyloxy)but-3-en-1yl)benzene in 0.13 mL of toluene.
- 8.0 mg of CuCl in 0.80 mL of toluene.
- 6.1 mg of Ru-**1d** in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), (1-allyloxy)but-3-en-1yl)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.074 mmol, 12.5 mg) in Toluene (1.7 mL), conversion was determined by ^{1}H-NMR. 98% conversion and 93% yield with Ru-**1d** after 30 min of reaction.

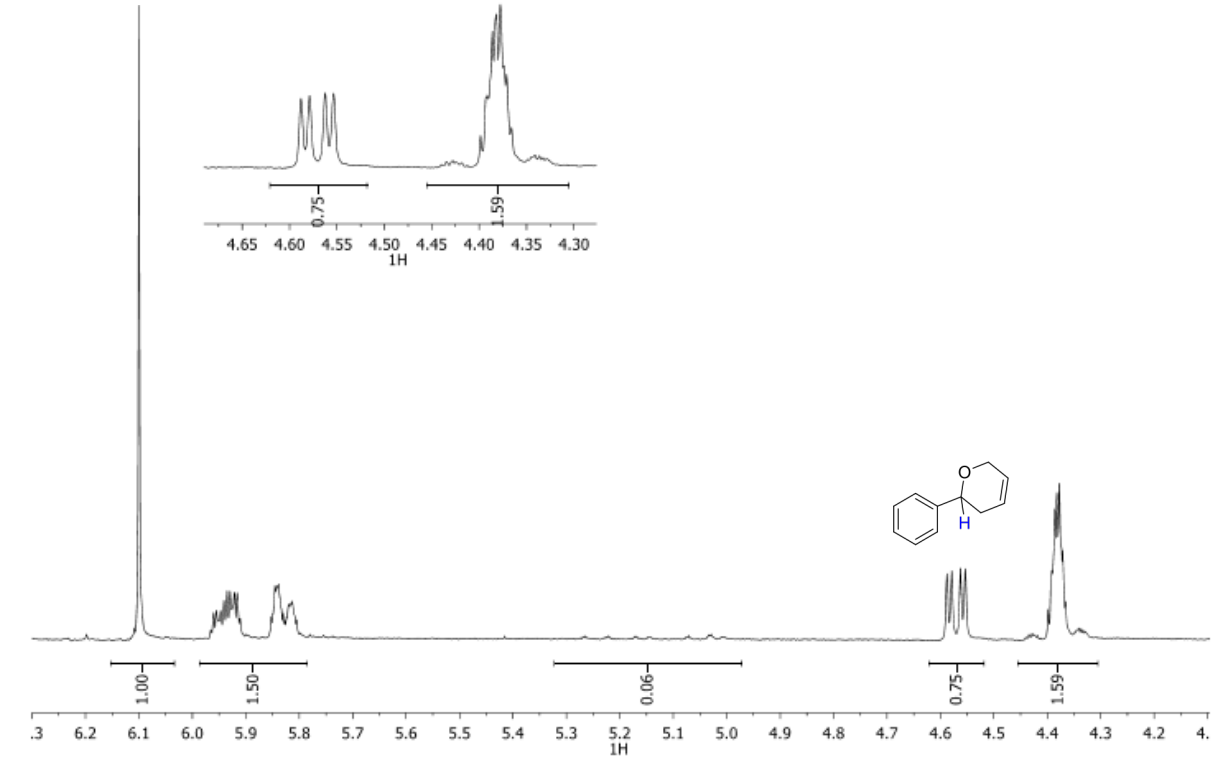
^{1}H-NMR spectra with Ru-**1d** at T0 :

Internal Standard

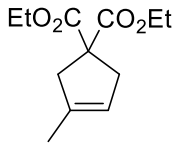


^{1}H-NMR spectra with Ru-**1d** at 98% conversion [100 - (0.06/3.26) x 100) = 98%] and 93% NMR yield [(0.75/0.81) x 100) = 93%] after 30 min of reaction:

Internal Standard



Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (P8)



$C_{12}H_{18}O_4$
226.27 g.mol^{-1}

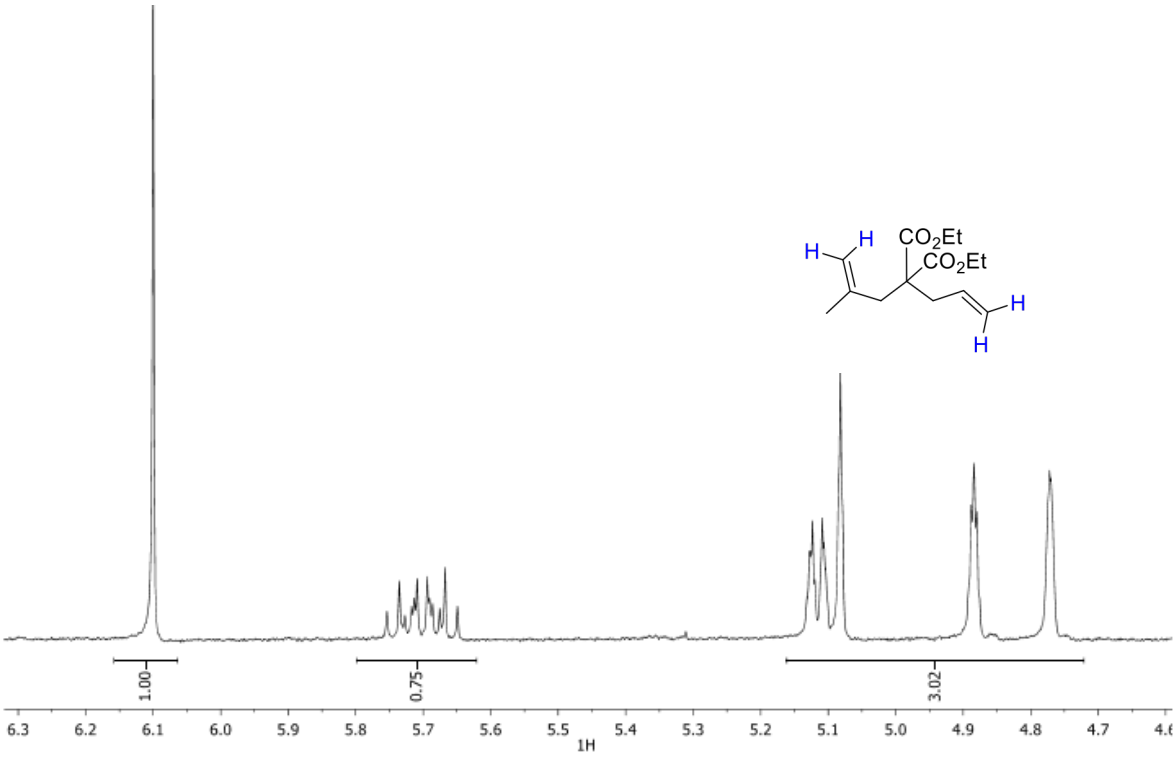
With Ru-**1c** - Freshly made solutions in toluene were prepared:

- 314.2 mg of diethyl 2-allyl-2-(2-methylallyl)malonate in 0.62 mL of toluene.
- 61.4 mg of 1,3,5-trimethoxybenzene in 0.55 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 6.4 mg of Ru-**1c** in 0.32 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 99% yield with Ru-**1c** after 10 min of reaction.

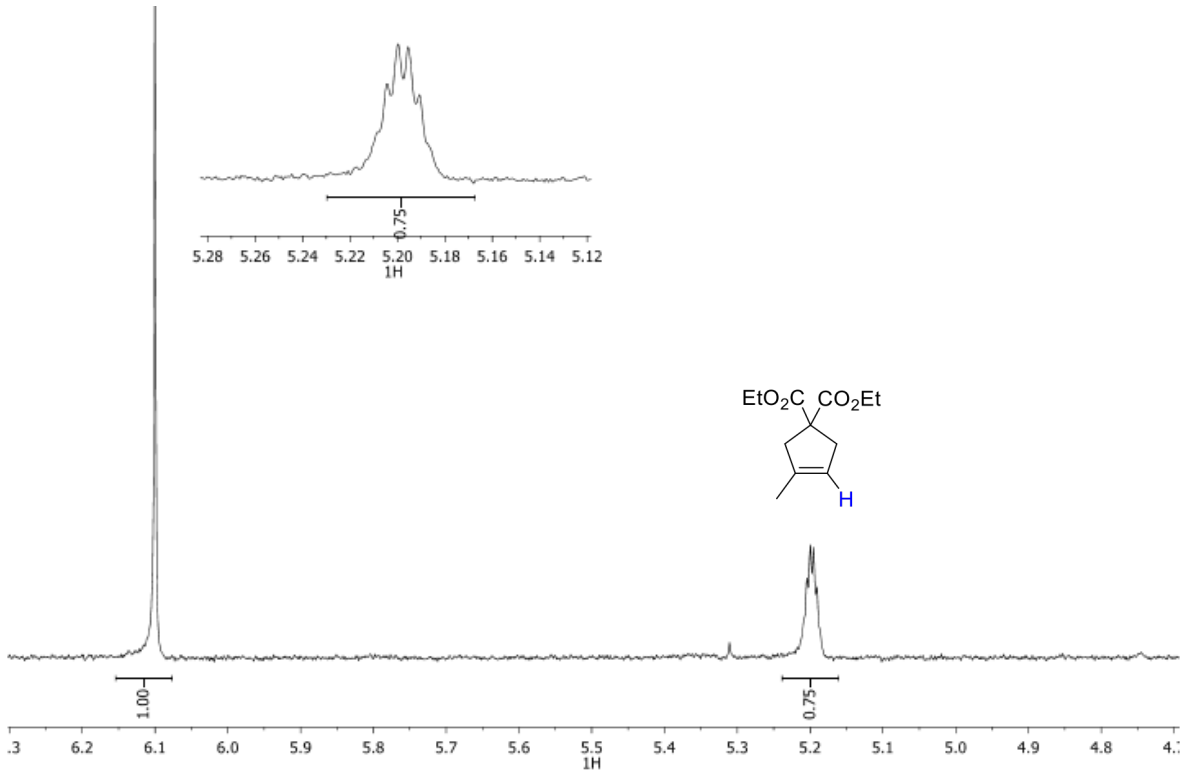
^{1}H-NMR spectra with Ru-**1c** at T0 :

Internal Standard



^{1}H-NMR spectra with Ru-**1c** at 99% conversion and 99% NMR yield [(0.75/0.75) x 100) = 99%] after 10 min of reaction:

Internal Standard



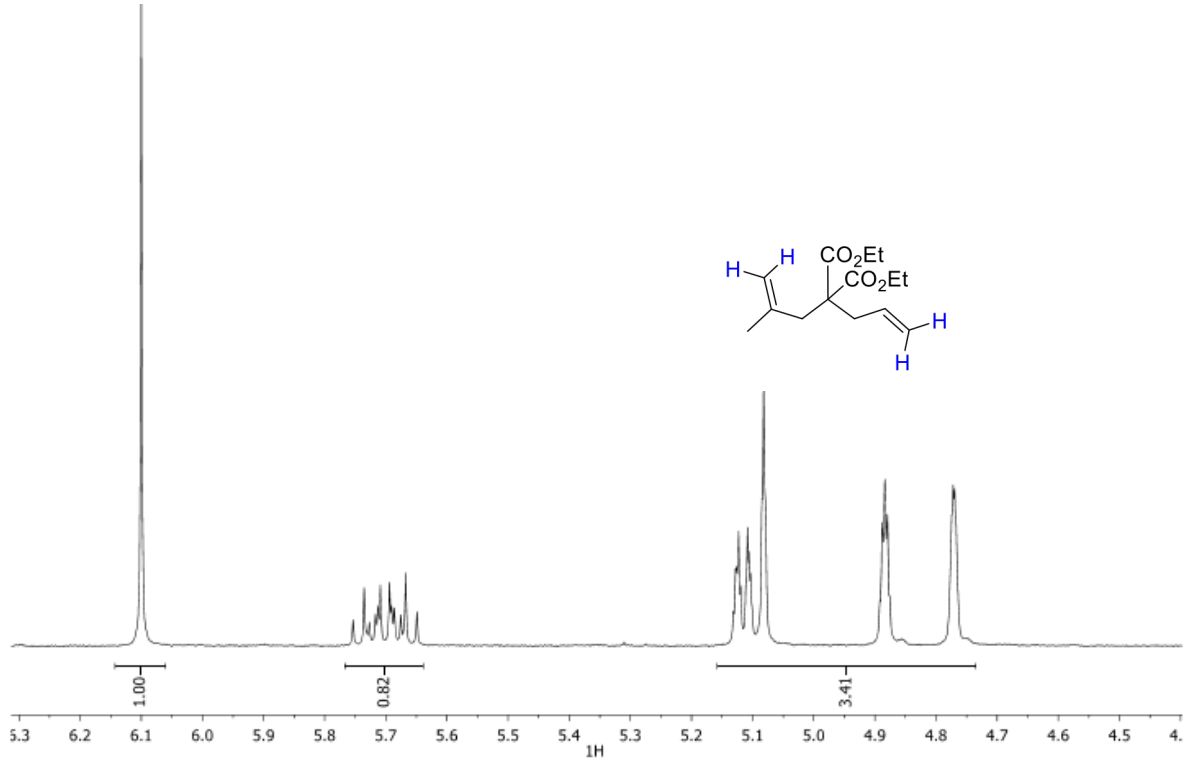
With Ru-**1d** - Freshly made solutions in toluene were prepared:

- 314.2 mg of diethyl 2-allyl-2-(2-methylallyl)malonate in 0.62 mL of toluene.
- 61.4 mg of 1,3,5-trimethoxybenzene in 0.55 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 7.3 mg of Ru-**1d** in 0.30 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 93% yield with Ru-**1d** after 10 min of reaction.

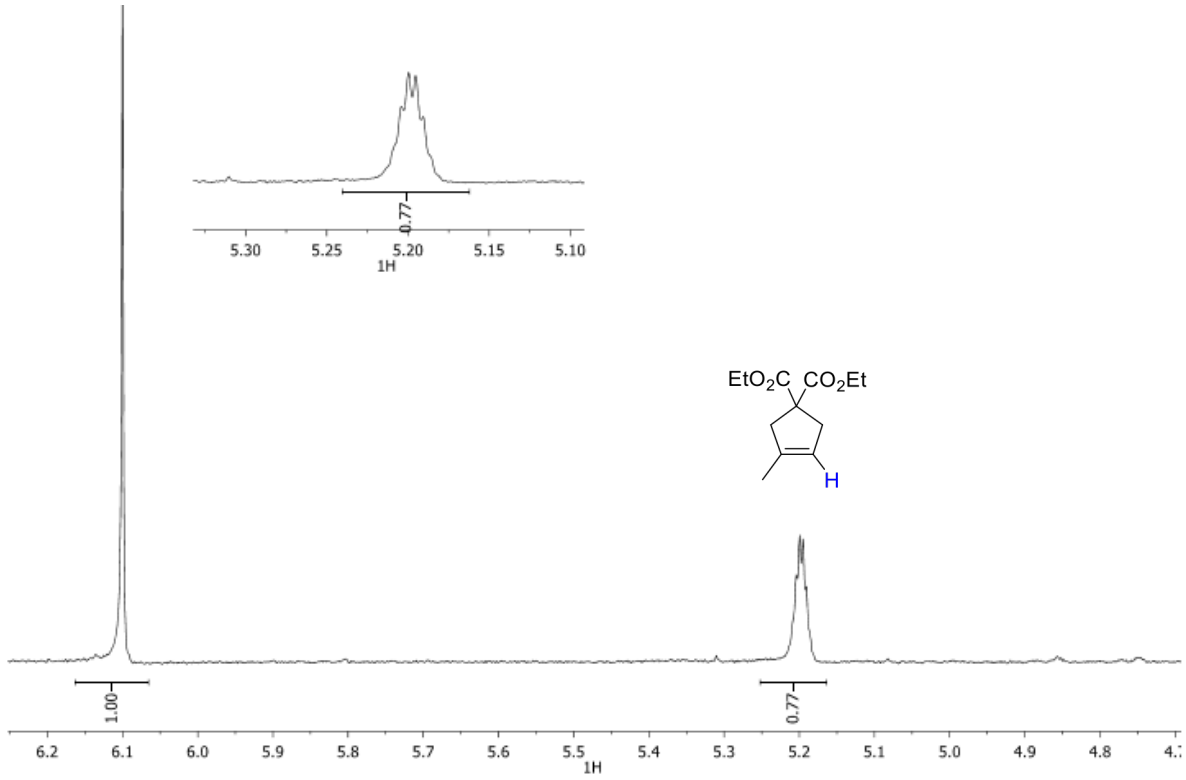
[1]H-NMR spectra with Ru-**1d** at T0 :

Internal Standard

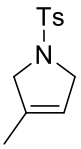


[1]H-NMR spectra with Ru-**1d** at 99% conversion and 93% NMR yield [(0.77/0.82) x 100) = 94%] after 10 min of reaction:

Internal Standard



3-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (P9)



$C_{21}H_{15}NO_2S$
237.32 g.mol^{-1}

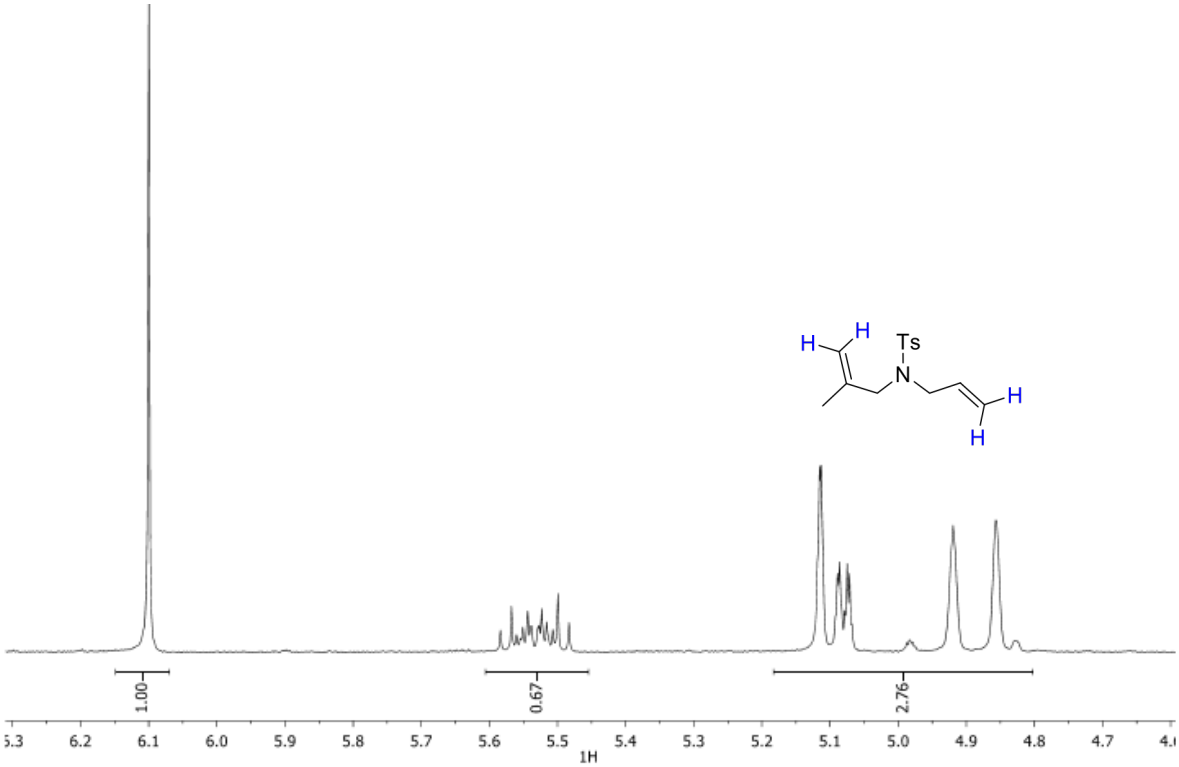
With Ru-**1c** - Freshly made solutions in toluene were prepared:

- 233.4 mg of N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide in 0.44 mL of toluene.
- 69.8 mg of 1,3,5-trimethoxybenzene in 0.63 mL of toluene.
- 9.6 mg of CuCl in 0.96 mL of toluene.
- 6.3 mg of Ru-**1c** in 0.32 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 96% yield with Ru-**1c** after 20 min of reaction.

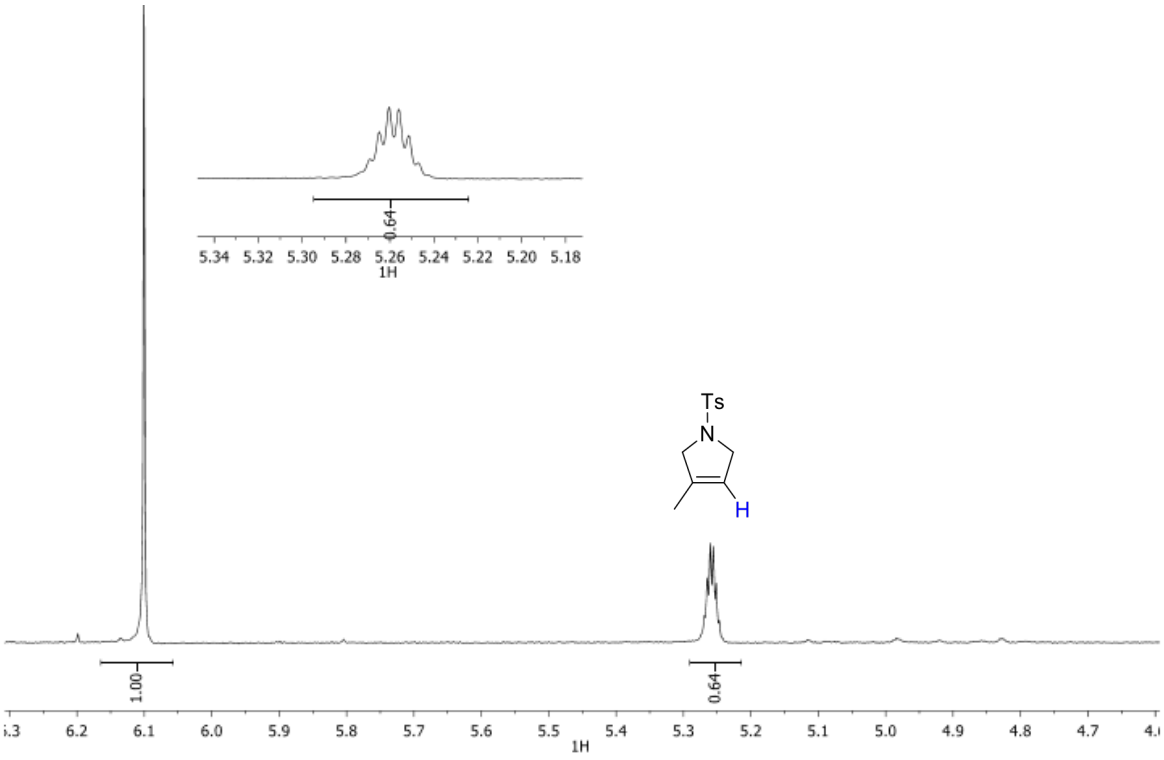
^{1}H-NMR spectra with Ru-**1c** at T0 :

Internal Standard



^{1}H-NMR spectra with Ru-**1c** at 99% conversion and 96% NMR yield [(0.64/0.67) x 100) = 96%] after 20 min of reaction:

Internal Standard



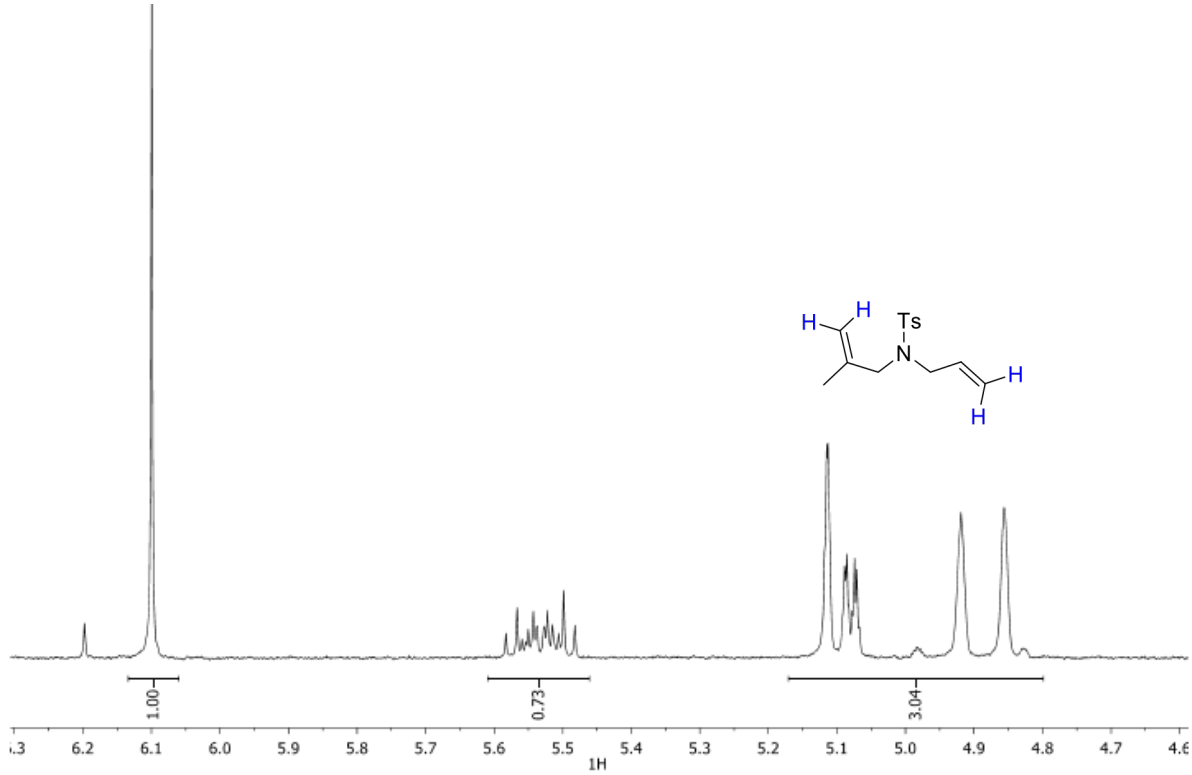
With Ru-**1d** - Freshly made solutions in toluene were prepared:

- 233.4 mg of N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide in 0.44 mL of toluene.
- 69.8 mg of 1,3,5-trimethoxybenzene in 0.63 mL of toluene.
- 9.6 mg of CuCl in 0.96 mL of toluene.
- 5.5 mg of Ru-**1d** in 0.23 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 99% conversion and 92% yield with Ru-**1d** after 10 min of reaction.

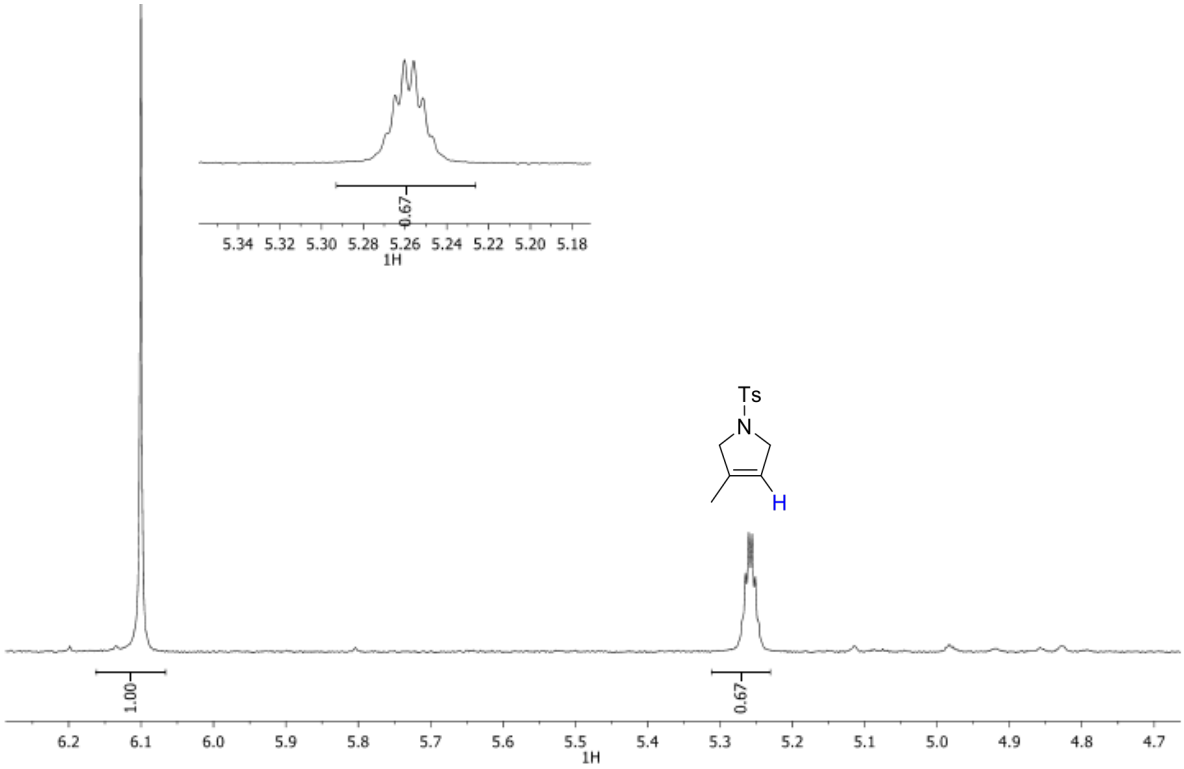
^{1}H-NMR spectra with Ru-**1d** at T0 :

Internal Standard

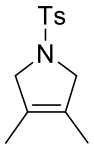


^{1}H-NMR spectra with Ru-**1d** at 99% conversion and 92% NMR yield [(0.67/0.73) x 100) = 92%] after 10 min of reaction:

Internal Standard



3,4-dimethyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (P10)



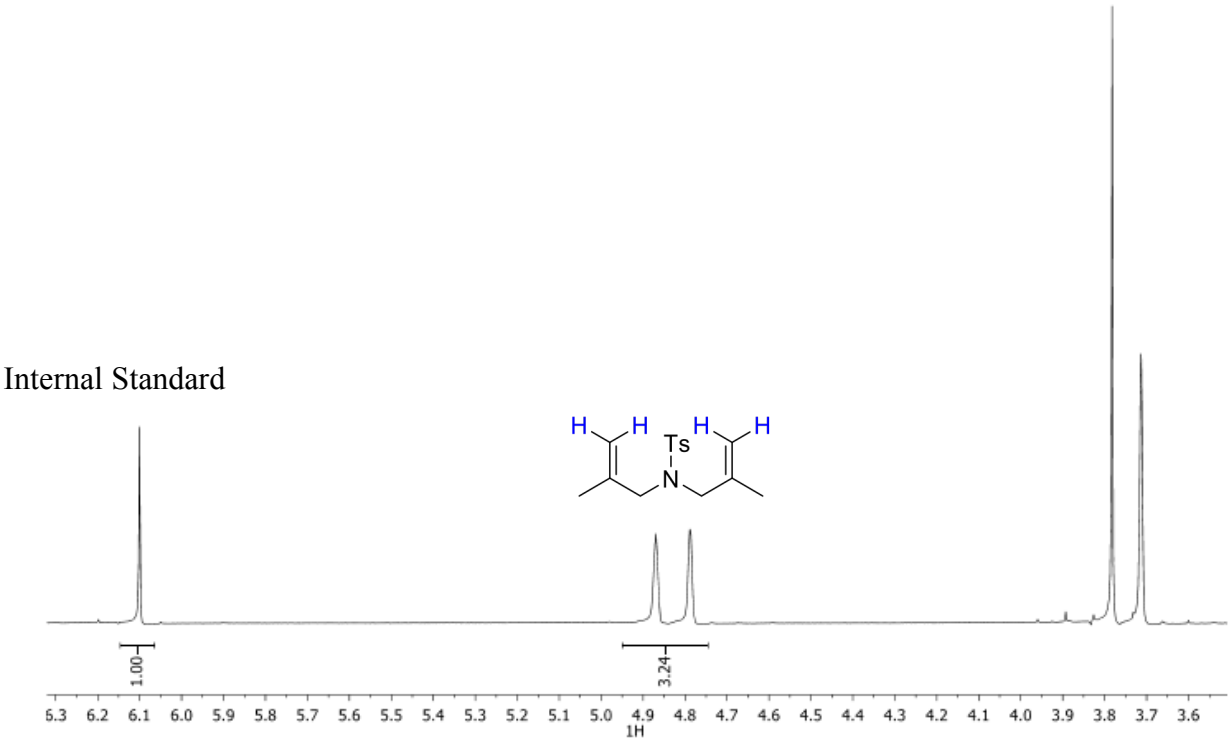
$C_{13}H_{17}NO_2S$
251.34 g.mol^{-1}

With Ru-**1c** - Freshly made solutions in toluene were prepared:

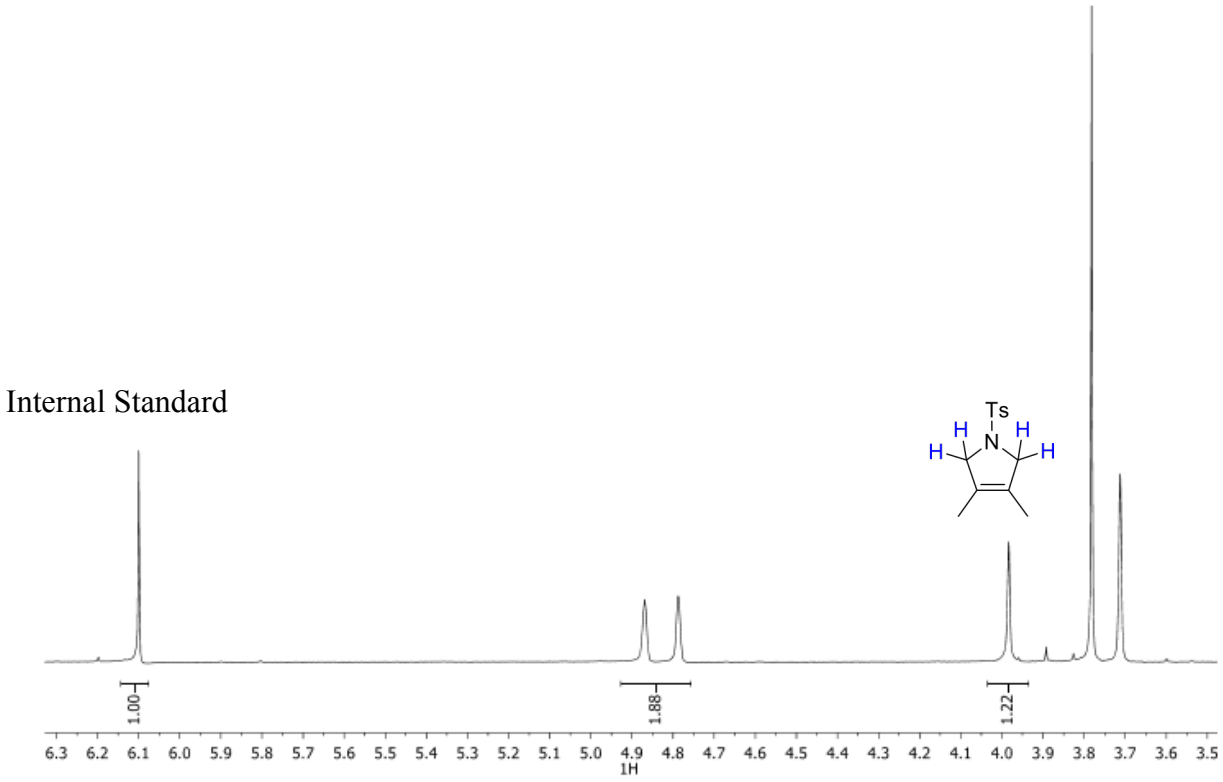
- 78.5 mg of 4-methyl-N,N-bis(2-methylallyl)benzenesulfonamide in 0.14 mL of toluene.
- 20.7 mg of 1,3,5-trimethoxybenzene in 0.19 mL of toluene.
- 5.5 mg of CuCl in 0.55 mL of toluene.
- 3.3 mg of Ru-**1c** in 0.17 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR. 42% conversion and 38% yield with Ru-**1c** after 30 min of reaction.

^{1}H-NMR spectra with Ru-**1c** at T0 :



^{1}H-NMR spectra with Ru-**1c** at 42% conversion [100 - (1.88/3.24) x 100) = 42%] and 38% NMR yield [(1.22/3.24) x 100) = 38%] after 30 min of reaction:

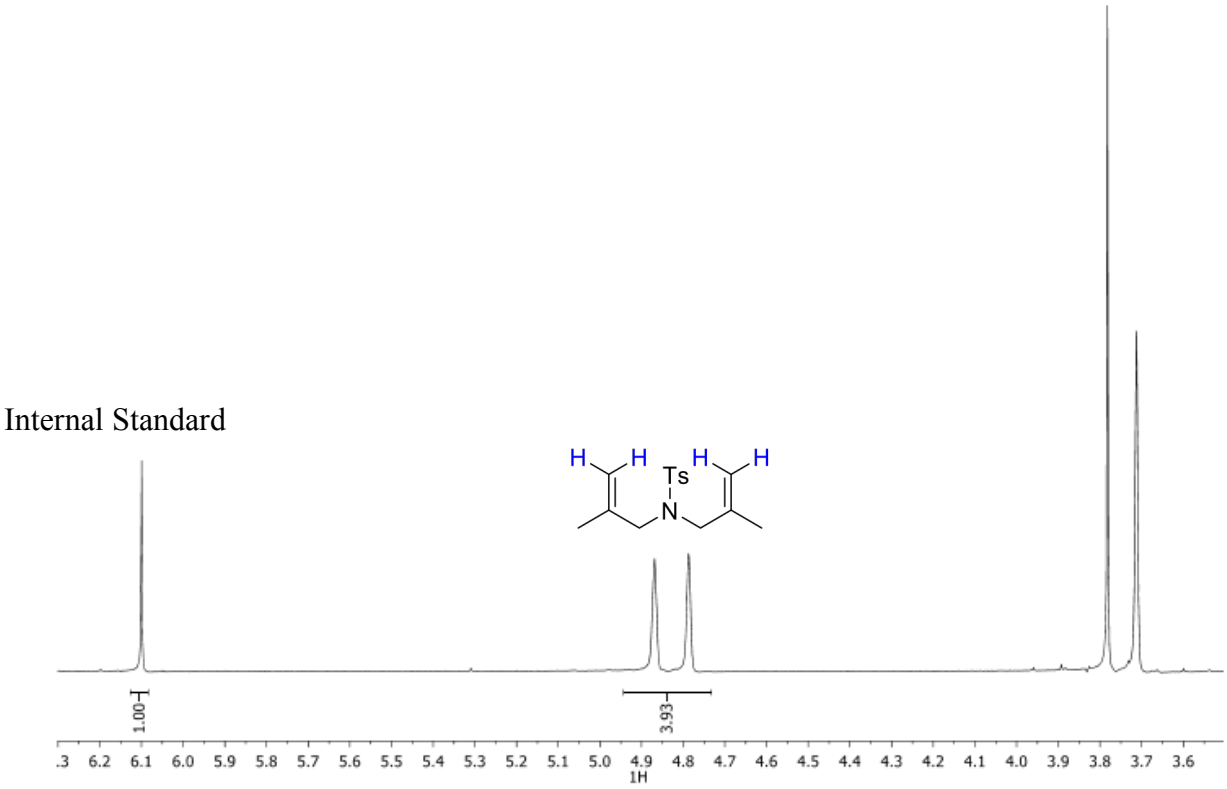


With Ru-**1d** - Freshly made solutions in toluene were prepared:

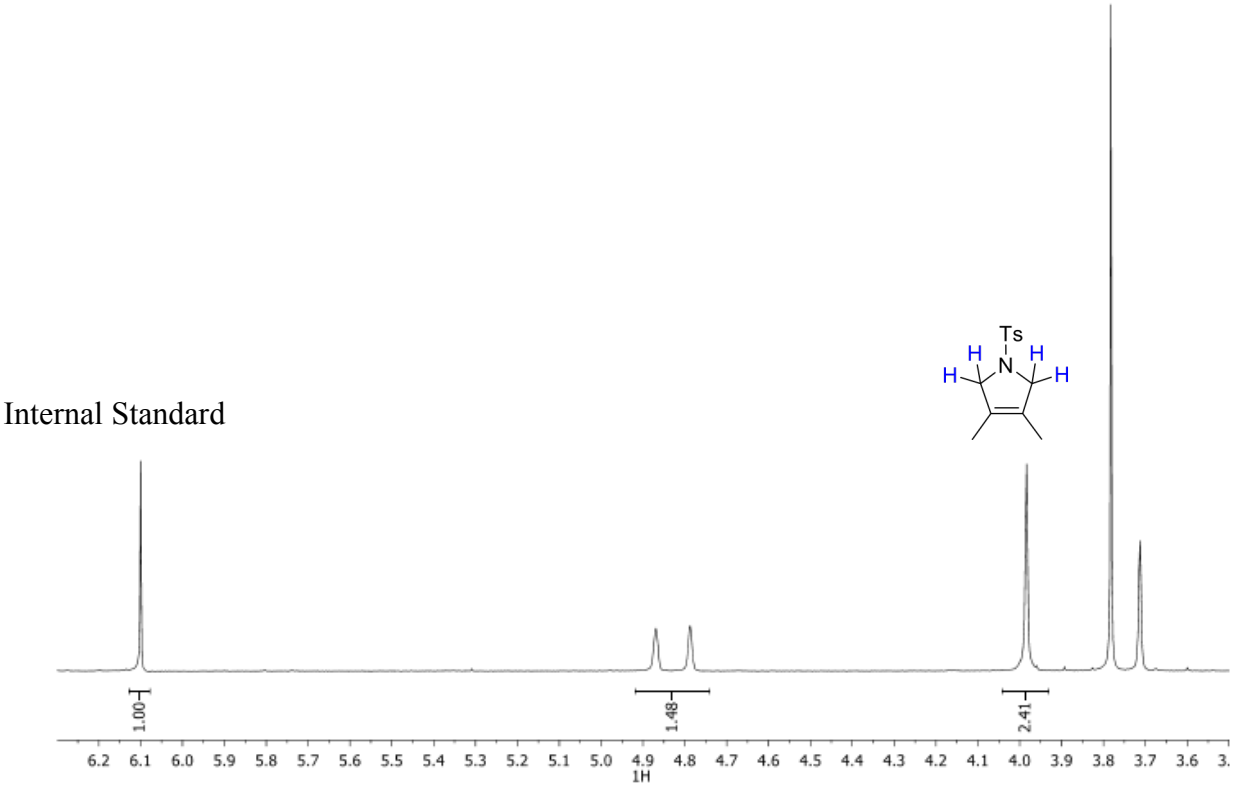
- 66.4 mg of 4-methyl-N,N-bis(2-methylallyl)benzenesulfonamide in 0.12 mL of toluene.
- 9.6 mg of CuCl in 0.96 mL of toluene.
- 4.4 mg of **Ru-1d** in 0.18 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.077 mmol, 12.9 mg) in Toluene (1.7 mL), conversion was determined by ^{1}H-NMR. 62% conversion and 61% yield with **Ru-1d** after 30 min of reaction.

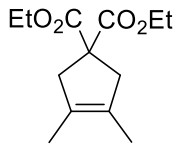
^{1}H-NMR spectra with Ru-**1d** at T0 :



^{1}H-NMR spectra with Ru-**1d** at 62% conversion [100 - (1.48/3.93) x 100) = 62%] and 61% NMR yield [(2.41/3.93) x 100) = 61%] after 30 min of reaction:



Diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate (P11)



$C_{13}H_{20}O_4$
240.30 g.mol^{-1}

With Ru-**1c** - Freshly made solutions in toluene were prepared:

- 127.1 mg of diethyl 2,2-bis(2-methylallyl)malonate in 0.24 mL of toluene.
- 33.3 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 7.3 mg of CuCl in 0.73 mL of toluene.
- 4.1 mg of Ru-**1c** in 0.21 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2,2-bis(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR.
0% conversion and 0% yield with **Ru-1c** after 30 min of reaction.

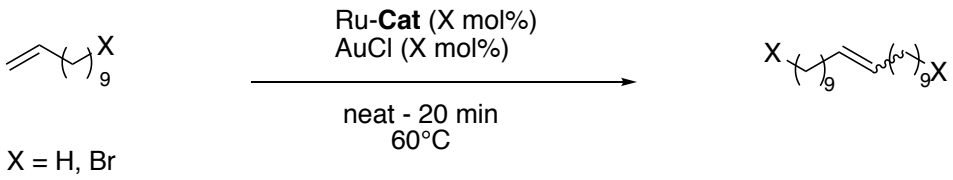
With Ru-**1d** - Freshly made solutions in toluene were prepared:

- 127.1 mg of diethyl 2,2-bis(2-methylallyl)malonate in 0.24 mL of toluene.
- 33.3 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 7.3 mg of CuCl in 0.73 mL of toluene.
- 3.8 mg of Ru-**1d** in 0.16 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2,2-bis(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by ^{1}H-NMR.
0% conversion and 0% yield with Ru-**1d** after 30 min of reaction.

6.2. Self-Metathesis (SM)

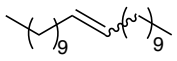
General procedure for Self-Metathesis



Alcene (1.0 equiv.) was added under Ar to a dry schlenk containing solid complex (0.001 equiv.) and internal standard (0.00002 equiv.). The reaction was initiating upon addition of activator (0.001 equiv.). The resulting mixture was allowed to stir at 60°C for 20 minutes. Aliquots of reactions (approximately 45 mg) were taken, filtered through syringe filter (0.2 μm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.

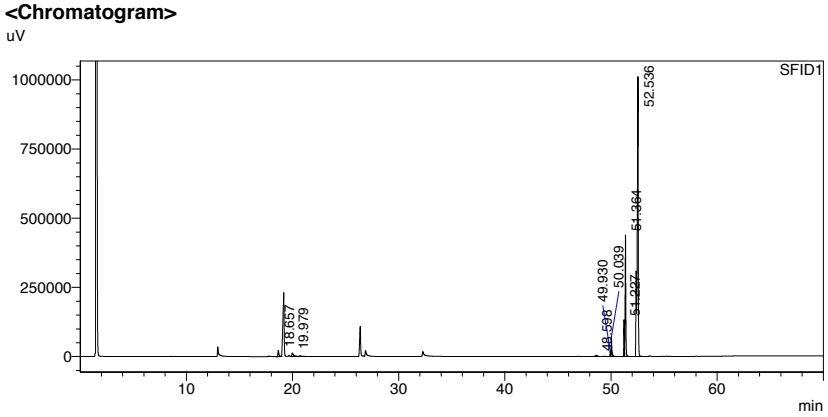
Self Metathesis of 1-dodecene with Ru-1c

1-dodecene (2 mL, 9.0 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-**1c** (22.5 mg, 0.023 mmol, 0.0025 equiv.) and internal standard tetradecane (25 μL, 0.0002 mmol, 0.028 equiv.). The reaction was initiating upon addition of CuCl (2.8 mg, 0.009 mmol, 0.003 equiv.). Aliquots of reactions (43.4 mg) were taken, filtered through syringe filter (0.2 μm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.



P12
$C_{22}H_{44}$
308,34 g.mol^{-1}

GC trace of **P12** with Ru-**1c**



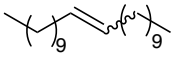
<Peak Table>

SFID1

Peak#	Name	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1		18.66	134352	21567	1.3	1.3	--
2		19.98	191837	12701	1.9	0.7	6.85
3		48.60	57537	4878	0.6	0.3	121.70
4		49.93	76182	20439	0.7	1.2	7.79
5		50.04	340464	71687	3.3	4.2	1.06
6		51.23	446944	131303	4.3	7.7	12.37
7		51.36	1951491	437769	18.9	25.6	1.38
8		52.54	7121600	1008666	69.0	59.0	9.01
Total			10320407	1709009	100.0	100.0	

Figure S15: *GC Chromatogram of* ***P12*** *with Ru-**1c** and CuCl: Selectivity 69%*

Self Metathesis of 1-dodecene with Ru-1d



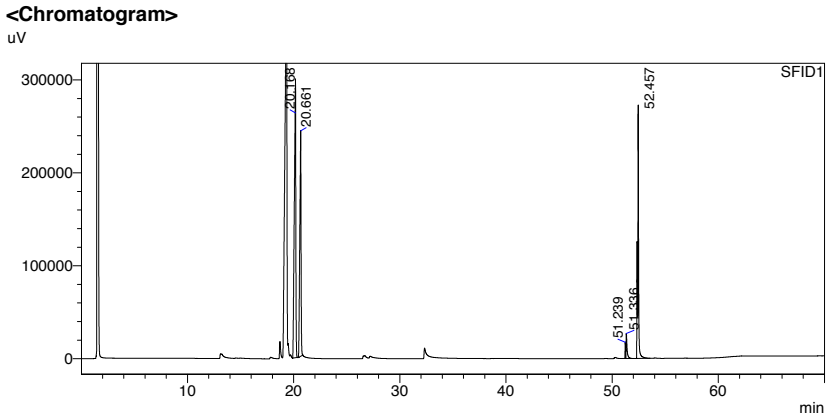
P12

$C_{22}H_{44}$

308,34 g.mol^{-1}

1-dodecene (2 mL, 9.0 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-**1d** (11.4 mg, 0.009 mmol, 0.001 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00002 equiv.). The reaction was initiating upon addition of CuCl (2.3 mg, 0.023 mmol, 0.0025 equiv.). Aliquots of reactions (42.5 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.

GC trace **P12** Ru-**1d**



<Peak Table>

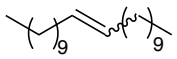
SFID1

Peak#	Name	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1		20.17	2886012	299539	42.9	34.9	--
2		20.66	1970260	242076	29.3	28.2	2.05
3		51.24	61199	17473	0.9	2.0	190.05
4		51.34	186838	26959	2.8	3.1	0.74
5		52.46	1625956	271931	24.2	31.7	8.76
Total			6730266	857978	100.0	100.0	

Figure S16: *GC Chromatogram of* ***P12*** *with Ru-**1d** and CuCl: Selectivity 24%*

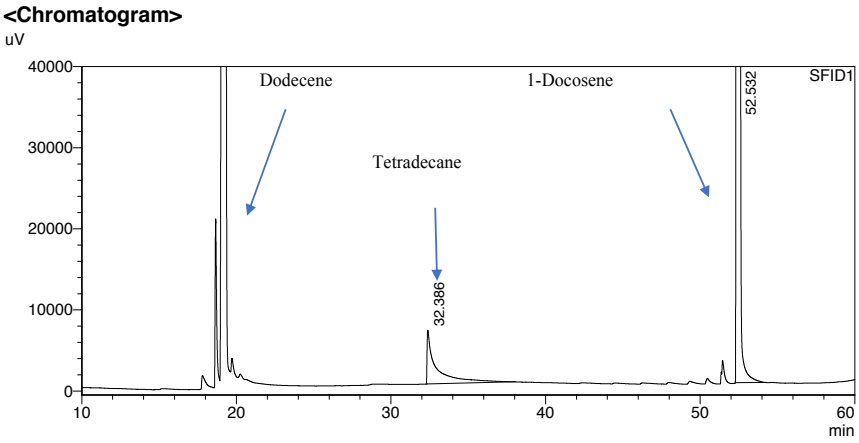
Self Metathesis of 1-dodecene with Ru-1c

1-dodecene (2 mL, 9.0 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-**1c** (9.2 mg, 0.009 mmol, 0.001 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00002 equiv.). The reaction was initiating upon addition of AuCl (2.3 mg, 0.009 mmol, 0.001 equiv.). Aliquots of reactions (46.4 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.



P12
$C_{22}H_{44}$
308,34 g.mol^{-1}

GC trace of **P12** with Ru-**1c**



<Peak Table>

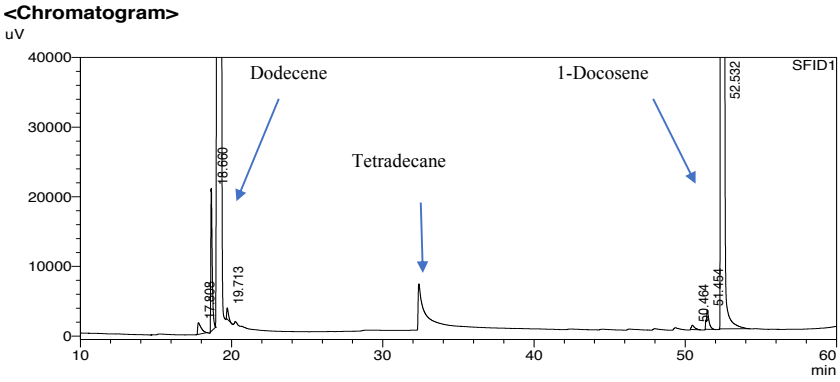
SFID1

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	32.39	280611	6638	3.5	0.7	--
2	52.53	7758212	1008804	96.5	99.3	60.71
Total		8038823	1015442	100.0	100.0	

Figure S17: *GC Chromatogram of* ***P12*** *with Ru-**1c***

Calculation detail:

Yield of **1-Docosene** = [[(0.7499*(7758212/280611)-0.6522) * ((46.4*19)/1565.6) * (1516/46.4)/308.6] / [(758/168.32)/2]]* 100 = 67 %



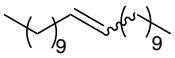
<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	17.81	26557	1658	0.3	0.2	--
2	18.66	136374	20508	1.7	2.0	2.96
3	19.71	13032	1625	0.2	0.2	5.55
4	50.46	8826	613	0.1	0.1	109.18
5	51.45	33412	2802	0.4	0.3	3.30
6	52.53	7758212	1008804	97.3	97.4	5.34
Total		7976414	1036009	100.0	100.0	

Figure S18: *GC Chromatogram of* ***P12*** *with Ru-**1c**: Selectivity >97%*

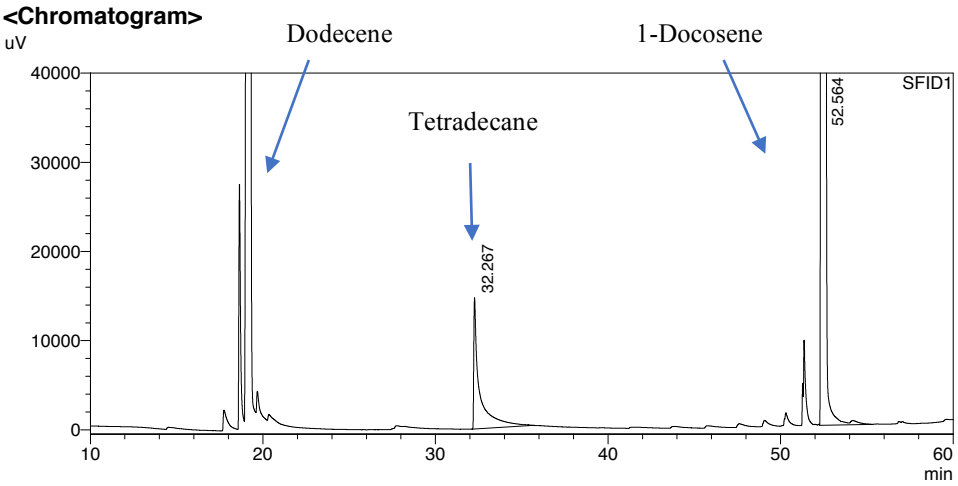
Self Metathesis of 1-dodecene with Ru-1d



P12
$C_{22}H_{44}$
308,34 g.mol^{-1}

1-dodecene (2 mL, 9.0 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-**1d** (11.3 mg, 0.009 mmol, 0.001 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00002 equiv.). The reaction was initiating upon addition of AuCl (2.4 mg, 0.009 mmol, 0.001 equiv.). Aliquots of reactions (47.7 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.

GC trace of **P12** Ru-**1d**



<Peak Table>

SFID1

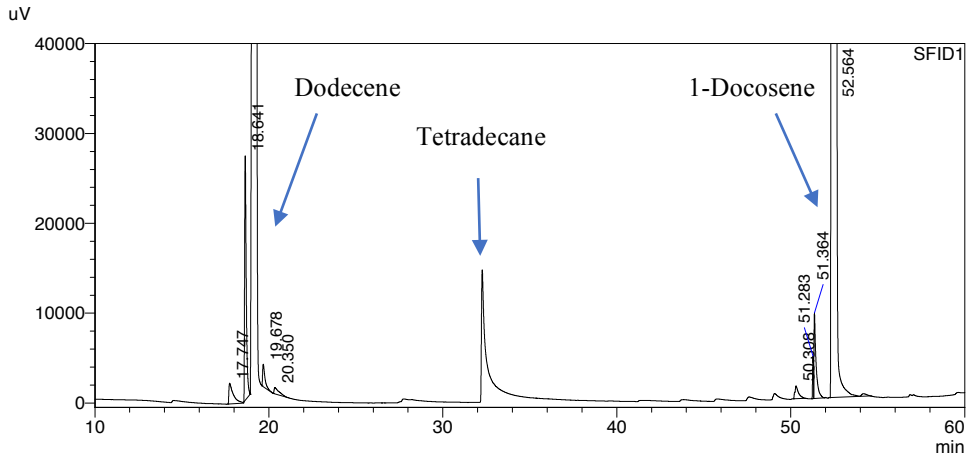
Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	32.27	342470	14714	2.9	1.1	--
2	52.56	11454487	1353758	97.1	98.9	83.44
Total		11796956	1368472	100.0	100.0	

Figure S19: *GC Chromatogram of* ***P12*** *with Ru-**1d***

Calculation detail:

Yield of **1-Docosene** = [[(0.7499*(11454487/322470)-0.6522) * ((47.7*19)/1570.3) * (1516/47.7)/308.6] / [(758/168.32)/2]]* 100 = 69 %

<Chromatogram>



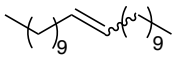
<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	17.75	40586	2304	0.3	0.2	--
2	18.64	175813	27186	1.5	1.9	3.18
3	19.68	23601	2517	0.2	0.2	5.50
4	20.35	14558	714	0.1	0.1	1.78
5	50.31	20136	1415	0.2	0.1	70.05
6	51.28	17342	4724	0.1	0.3	--
7	51.36	79164	9530	0.7	0.7	--
8	52.56	11439654	1353649	96.9	96.5	6.63
Total		11810857	1402040	100.0	100.0	

Figure S20: *GC Chromatogram of* ***P12*** *with Ru-**1d**: Selectivity >97%*

Self Metathesis of 1-dodecene with Ru-1b



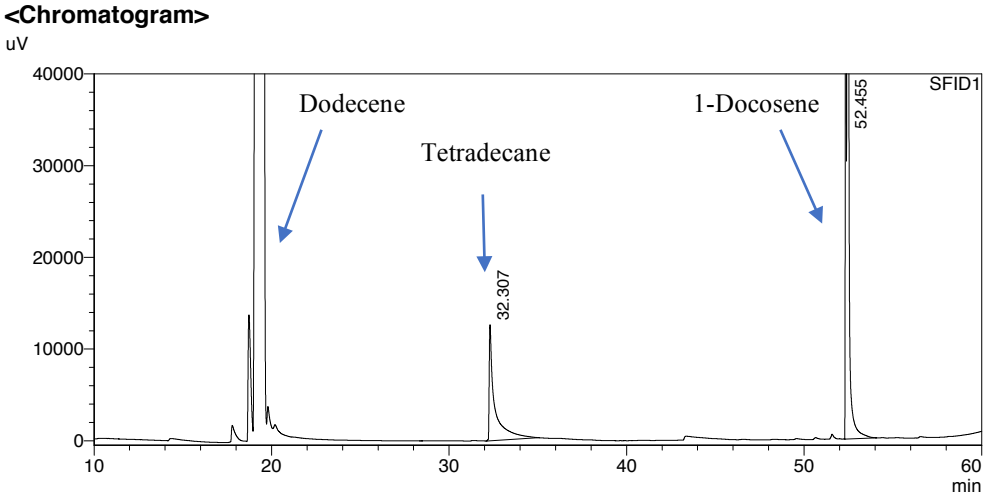
P12

$C_{22}H_{44}$

308,34 g.mol^{-1}

1-dodecene (1 mL, 4.50 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-**1b** (21.8 mg, 0.022 mmol, 0.005 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00004 equiv.). The reaction was initiating upon addition of AuCl (27.7 mg, 0.119 mmol, 0.026 equiv.). Aliquots of reactions (49.5 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.

GC trace of **P12** with Ru-**1b**



<Peak Table>

SFID1

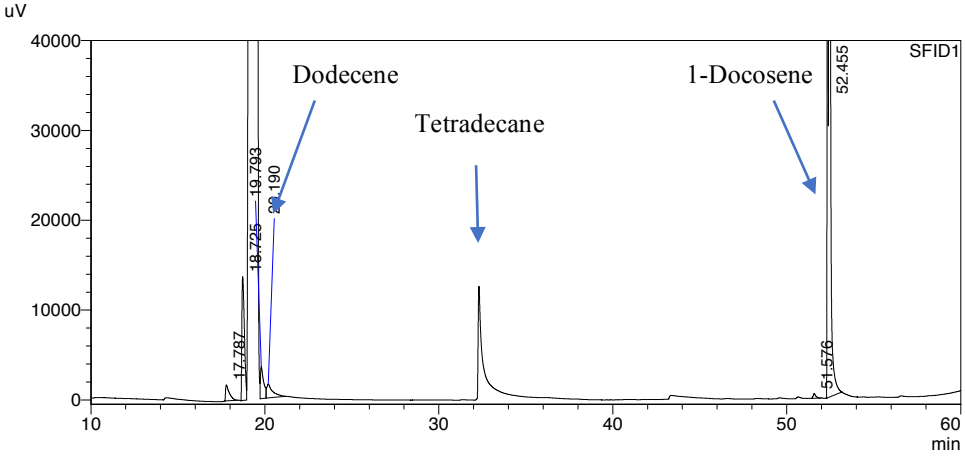
Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	32.31	271217	12634	14.1	4.0	--
2	52.46	1655045	306181	85.9	96.0	99.47
Total		1926262	318814	100.0	100.0	

Figure S21: *GC Chromatogram of* ***P12*** *with Ru-****1b***

Calculation detail:

Yield of **1-Docosene** = [[(0.7499*(1655045/271217)-0.6522) * ((49.5*19)/826.5) * (758/49.5)/308.6] / [(758/168.32)/2]]* 100 = 10 %

<Chromatogram>



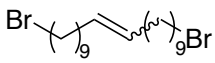
<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	17.79	26266	1767	1.4	0.5	--
2	18.73	140837	13794	7.5	4.2	2.90
3	19.79	45417	3552	2.4	1.1	3.37
4	20.19	37006	1524	2.0	0.5	--
5	51.58	5431	530	0.3	0.2	--
6	52.46	1626740	306056	86.5	93.5	5.27
Total		1881697	327223	100.0	100.0	

Figure S22: *GC Chromatogram of* ***P12*** *with Ru-**1b**: Selectivity 87%*

Self Metathesis of 11-bromoundecene with Ru-1c



P13

$C_{20}H_{38}Br_2$

436,13 g.mol^{-1}

A stock solution of Ru-**1c** complex (5 mg) in toluene (300 µL) was prepared under argon. A stock solution of AuCl (2.7 mg) in toluene (500 µL) was prepared in toluene.

11-bromoundecene (94.7 mg, 0.41 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing internal standard 1,2,3-trimethoxybenzene (23.1 mg, 0.137 mmol, 0.33 equiv.). 24 µL of the freshly stock solution of complex Ru-**1c** was added. The reaction was initiating upon addition of 17 µL of the freshly stock solution of AuCl). First aliquot of reactions was taken and filtered through syringe filter (0.2 µm, 25 mm), rinsed with $CDCl_3$ (0,5mL) and then analyzed by ^{1}H NMR. After evaporation of solvent, the aliquot was diluted with Et_2O (1.5 mL) and analyzed by GC.

^{1}H-NMR spectra with Ru-**1c** at T0 :

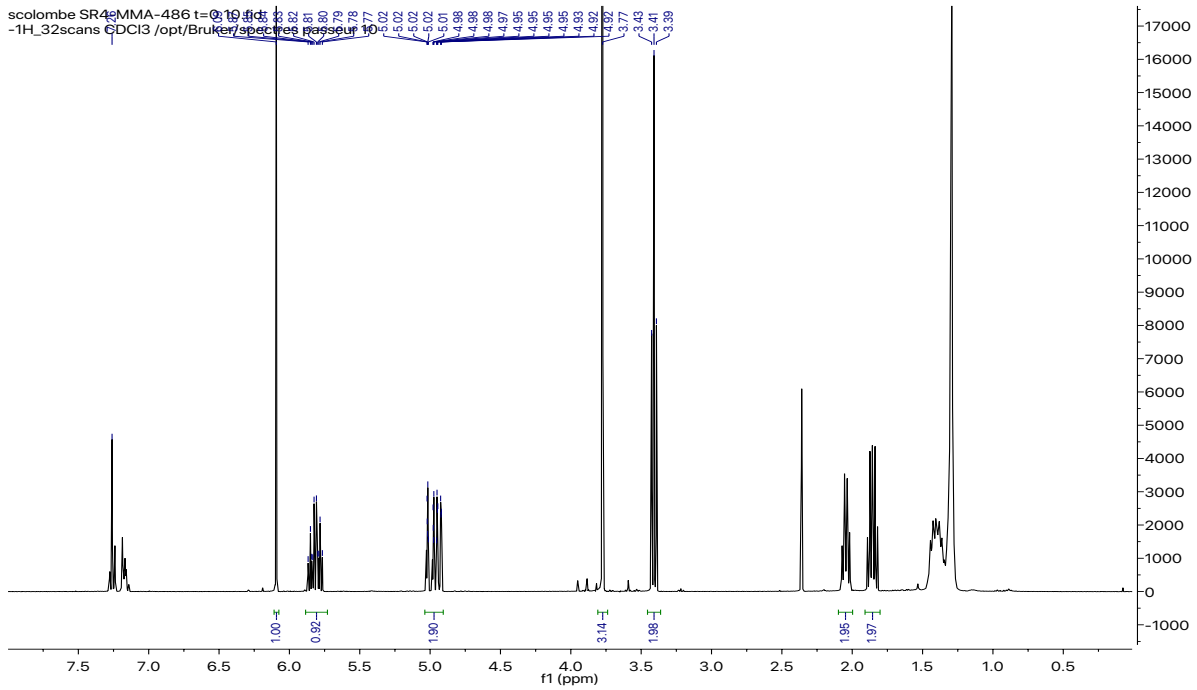


Figure S23: *^{1}H-NMR of **P13**: T0*

^{1}H-NMR spectra with Ru-**1c** at T20min :

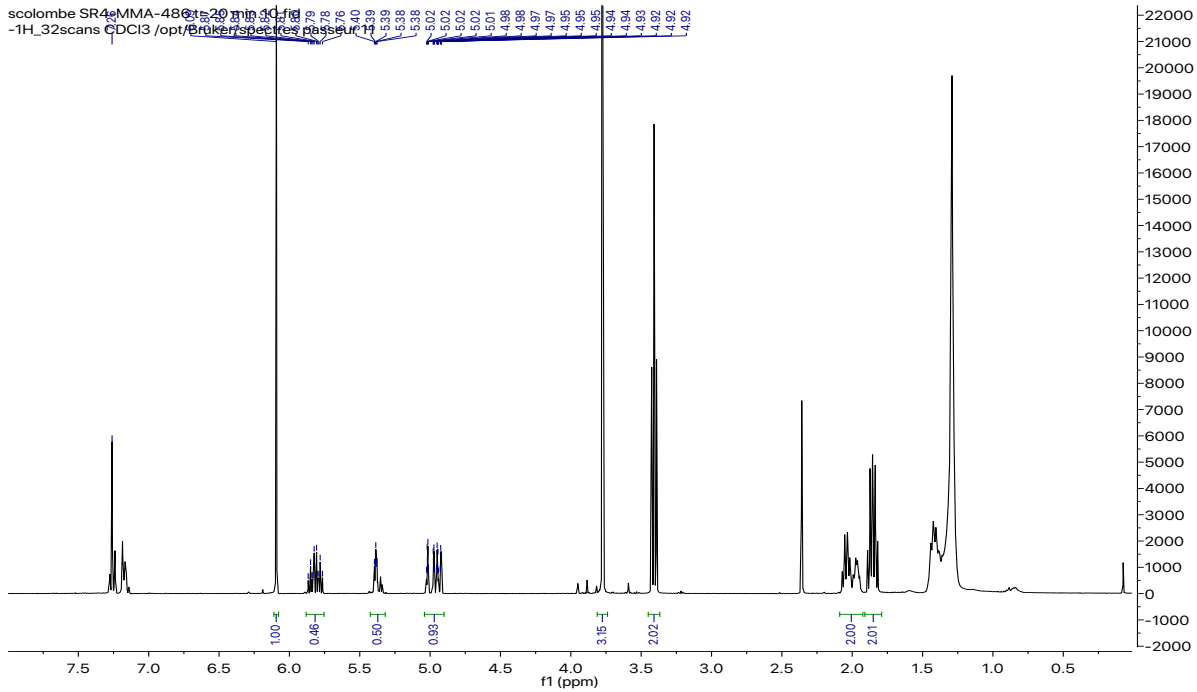
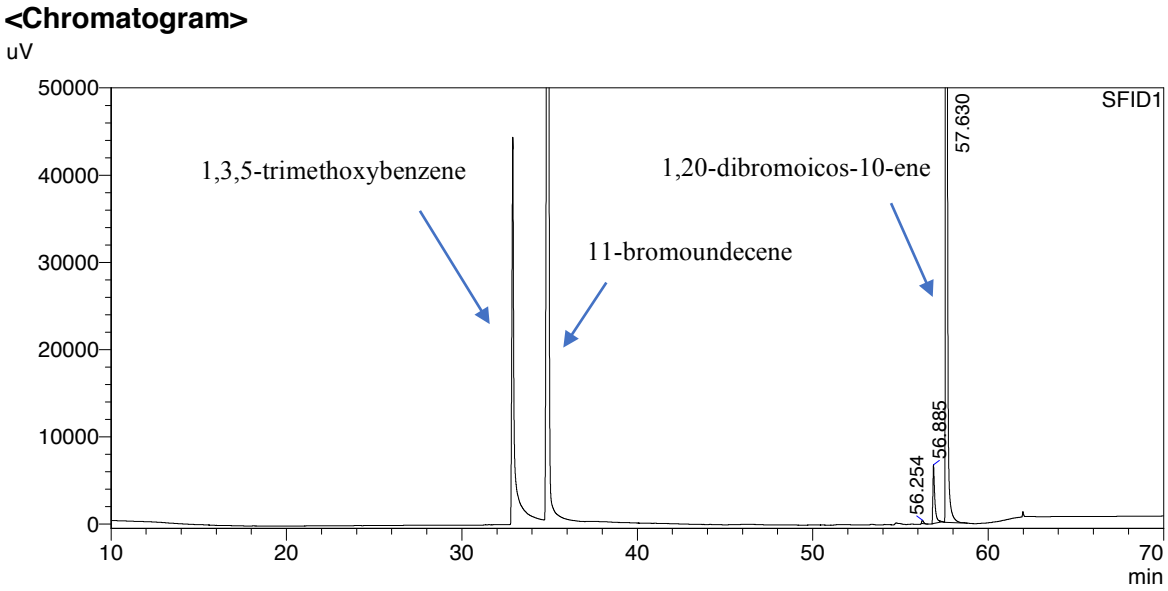


Figure S24: *^{1}H-NMR of **P13** with Ru-**1c** at T20min*

Yield of **1,20-dibromoicos-10-ene** = (0.50/0.92) X 100= 54%

GC trace of **P13** with Ru-**1c**



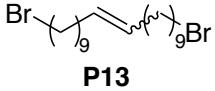
<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	56.25	2777	386	0.3	0.2	--
2	56.89	51247	6729	4.6	3.1	3.52
3	57.63	1050817	211837	95.1	96.8	5.50
Total		1104841	218952	100.0	100.0	

Figure S25: *GC Chromatogram of* ***P13*** *with Ru-**1c**: Selectivity >95%*

Self Metathesis of 11-bromoundecene with Ru-1d



P13

$C_{20}H_{38}Br_2$

436,13 g.mol^{-1}

A stock solution of Ru-**1c** complex (5 mg) in toluene (300 µL) was prepared under argon. A stock solution of AuCl (2.7 mg) in toluene (500 µL) was prepared in toluene.

11-bromoundecene (95.9 mg, 0.41 mmol,1.0 equiv.) was added under Ar to a dry schlenk containing internal standard 1,2,3-trimethoxybenzene (22 mg, 0.131 mmol, 0.33 equiv.). 31 µL

of the freshly stock solution of complex Ru-**1d** was added .The reaction was initiating upon addition of 17 µL of the freshly stock solution of AuCl. First aliquot of reactions was taken and filtered through syringe filter (0.2 µm, 25 mm), rinsed with $CDCl_3$ (0,5mL) and then analyzed by ^1H NMR. After evaporation of solvent, the aliquot was diluted with Et_2O (1.5 mL) and analyzed by GC.

^{1}H-NMR spectra with Ru-**1d** at T0 :

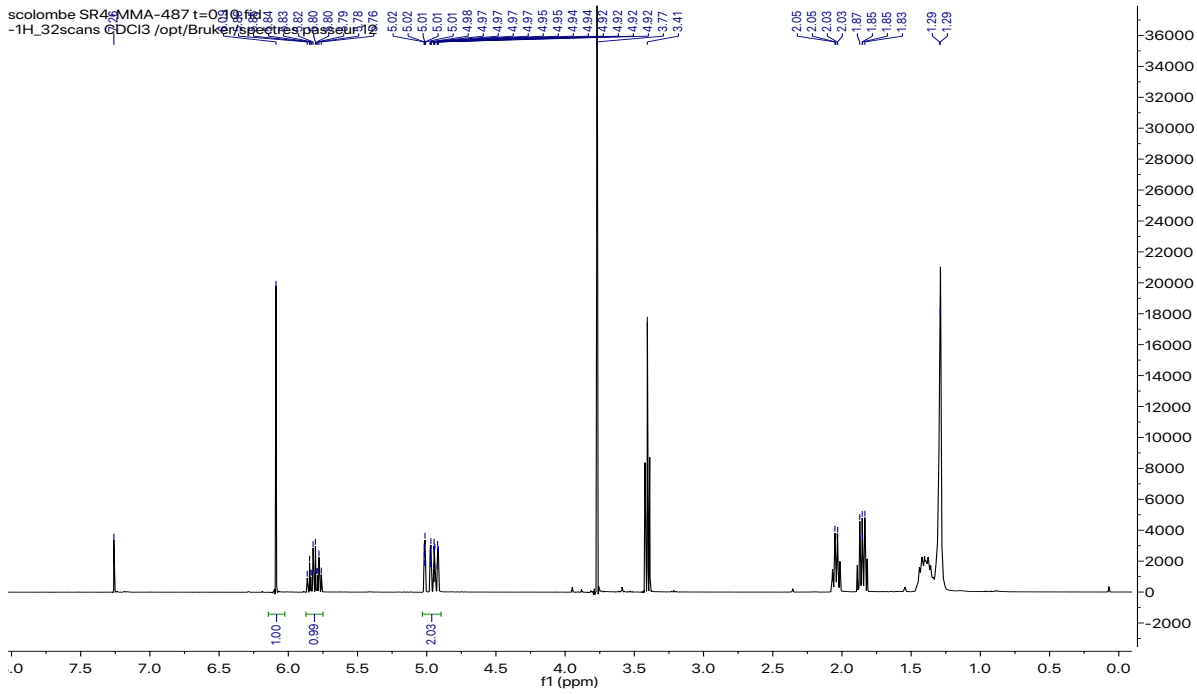


Figure S26: *^{1}H-NMR of **P13**: T0*

^{1}H-NMR spectra with Ru-**1c** at T20min :

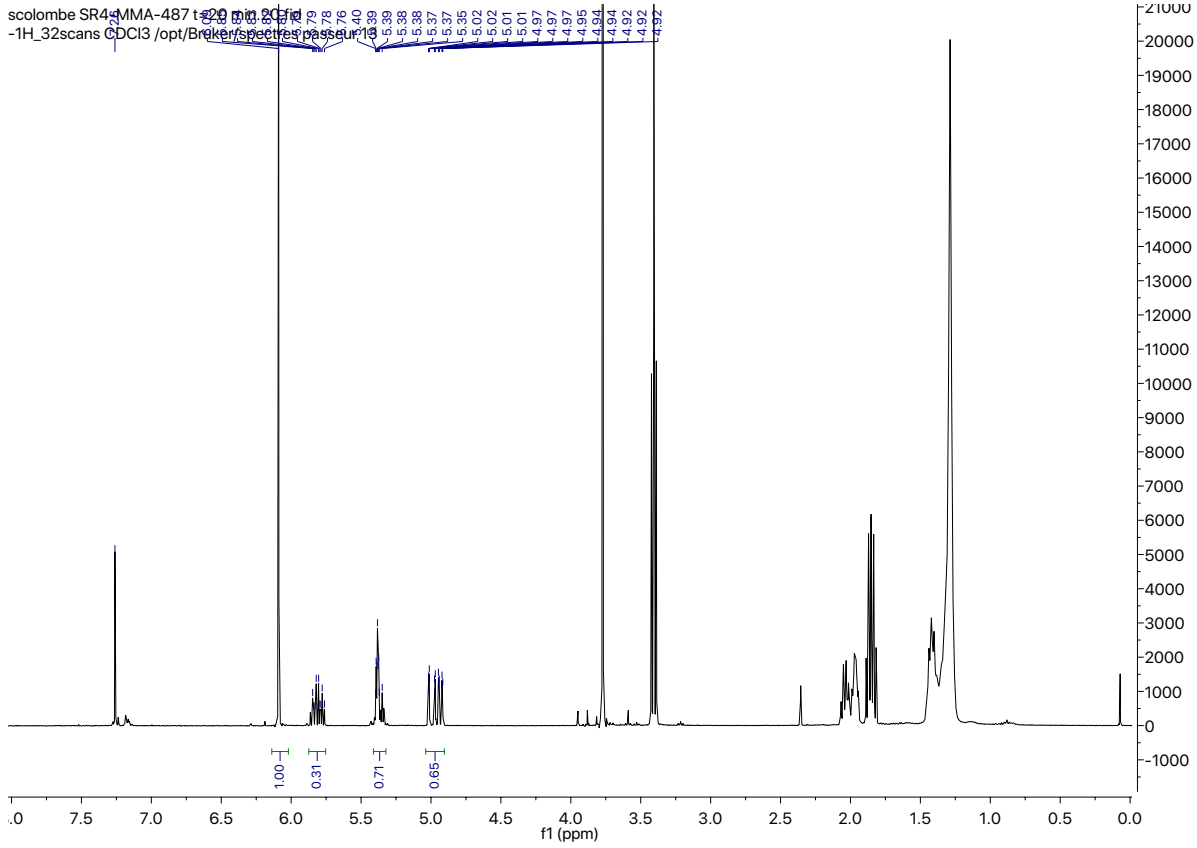
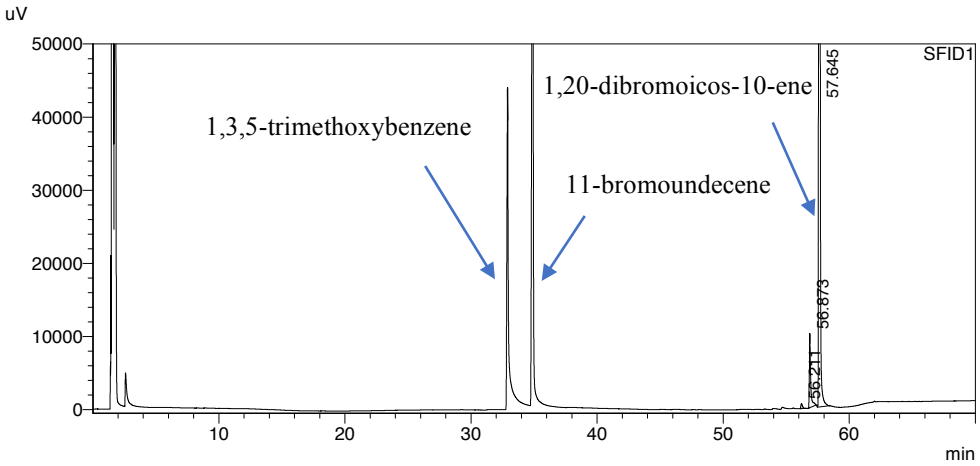


Figure S27: *^{1}H-NMR of **P13** with Ru-**1d** at T20min*

Yield of **1,20-dibromoicos-10-ene** = (0.71/0.99) X 100= 72%

GC trace of **P13** with Ru-**1d**

<Chromatogram>



<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Area%	Height%	Resolution(JP)
1	56.21	5718	690	0.3	0.2	--
2	56.87	72190	10141	4.3	3.1	3.72
3	57.64	1592116	317473	95.3	96.7	6.16
Total		1670024	328304	100.0	100.0	

Figure S28: *GC Chromatogram of* ***P13*** *with Ru-****1d****: Selectivity >95%*

7. NMR Spectra

7.1. NHC Precursors

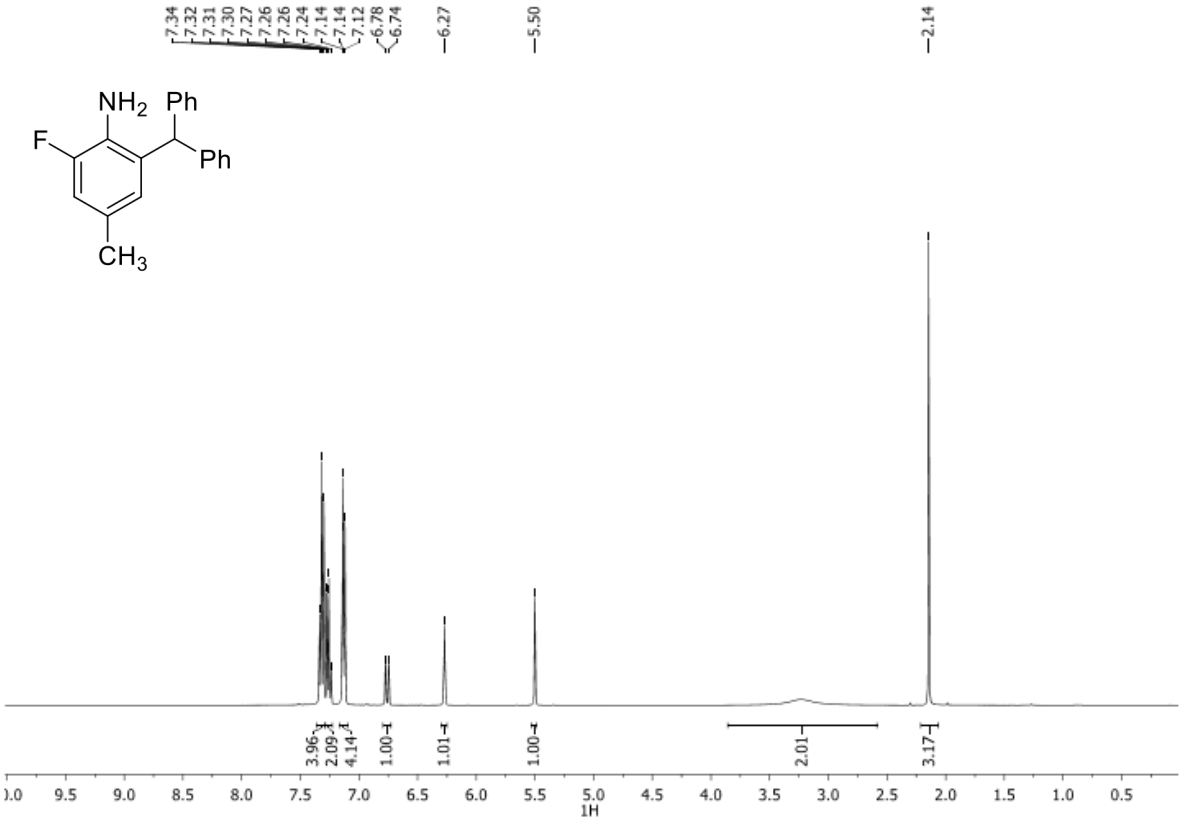


Figure S29**: [1]H NMR (400 MHz, $CDCl_3$) of **3a

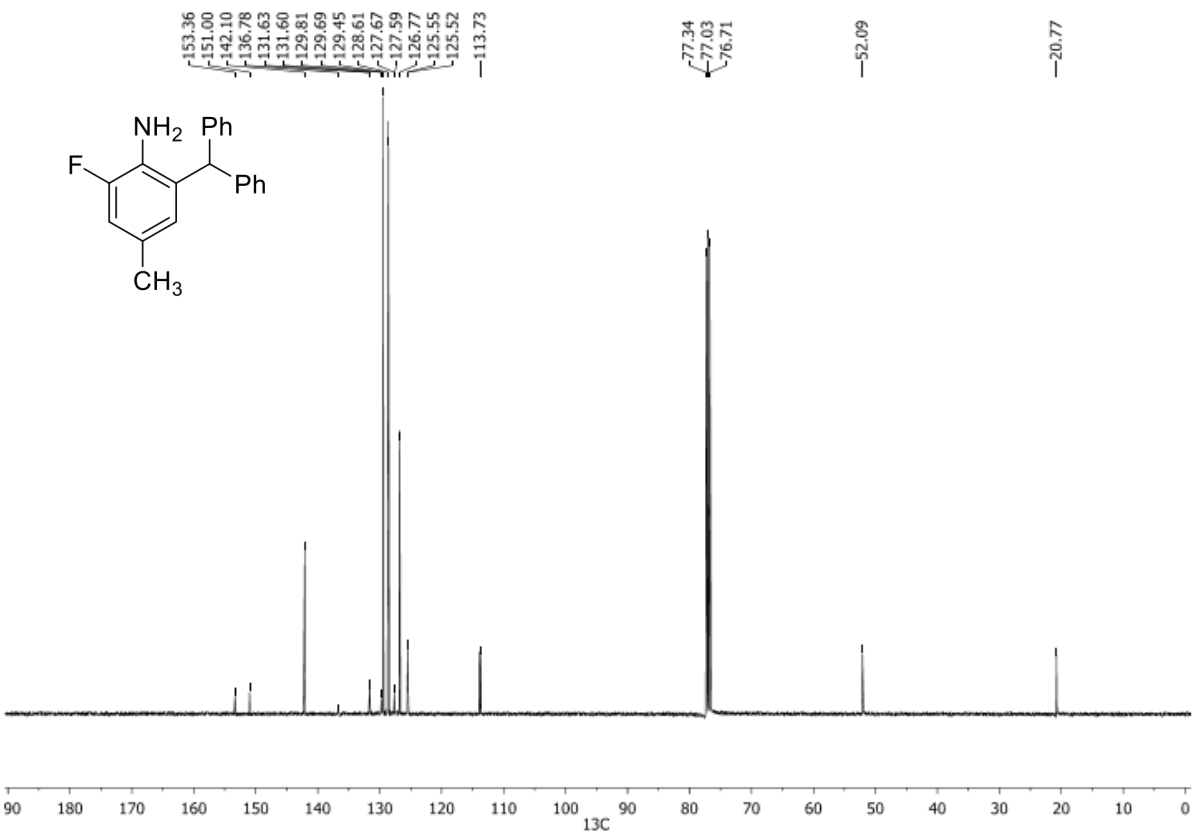


Figure S30: *^{13}C NMR (101 MHz, $CDCl_3$) of* ***3a***

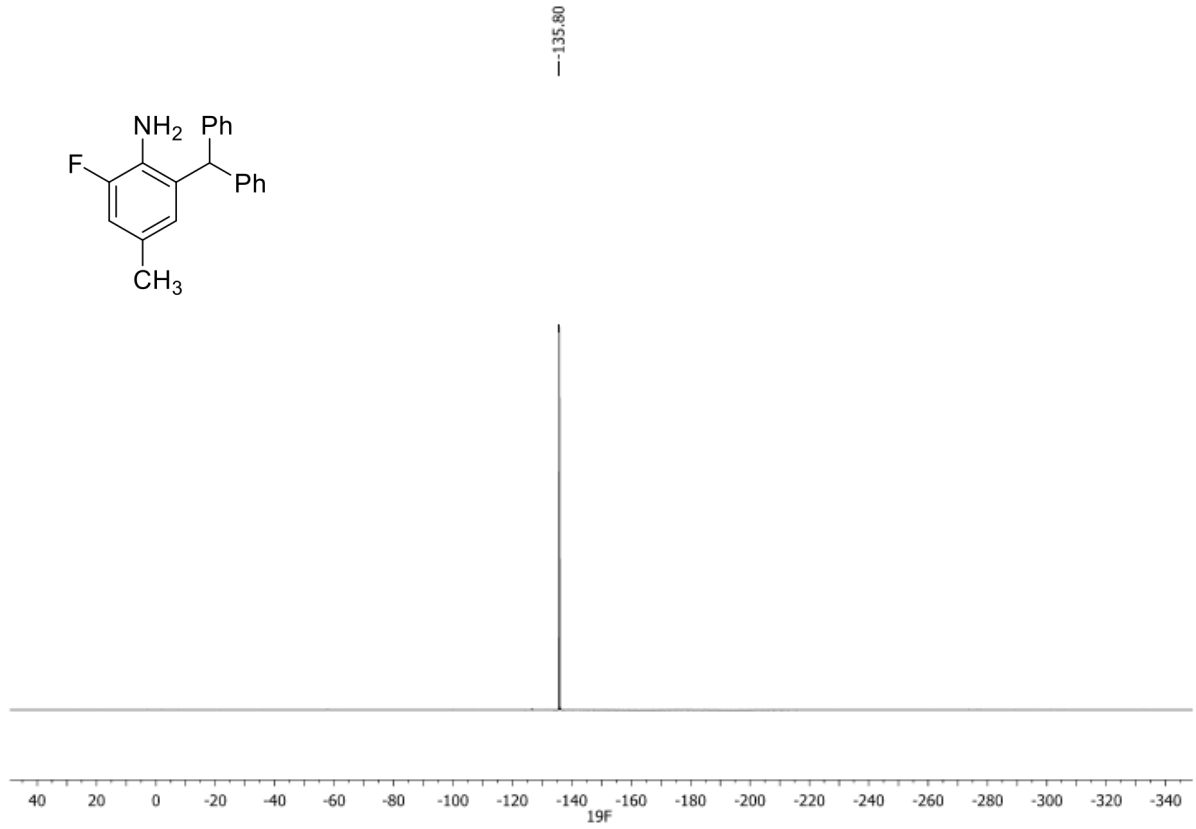


Figure S31: *^{19}F NMR (376 MHz, $CDCl_3$) of* ***3a***

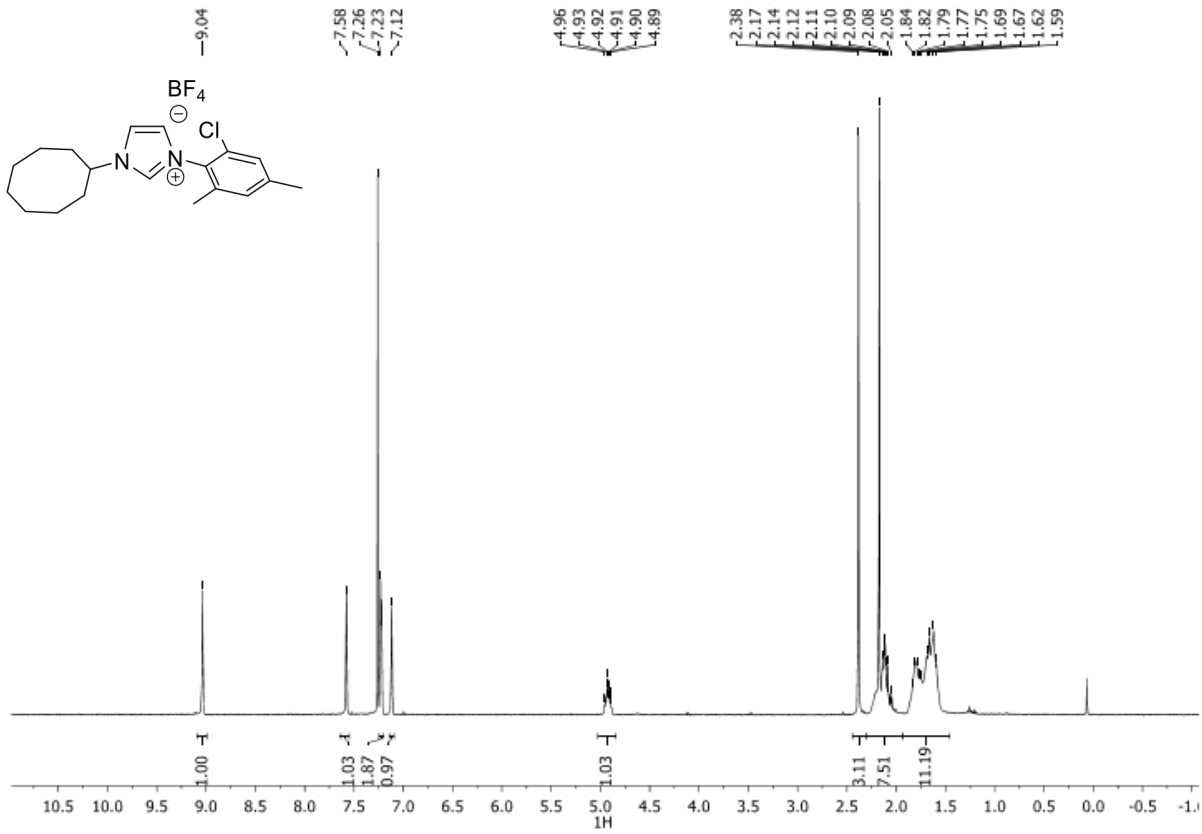


Figure S32: *^{1}H NMR (400 MHz, $CDCl_3$) of* ***4a***

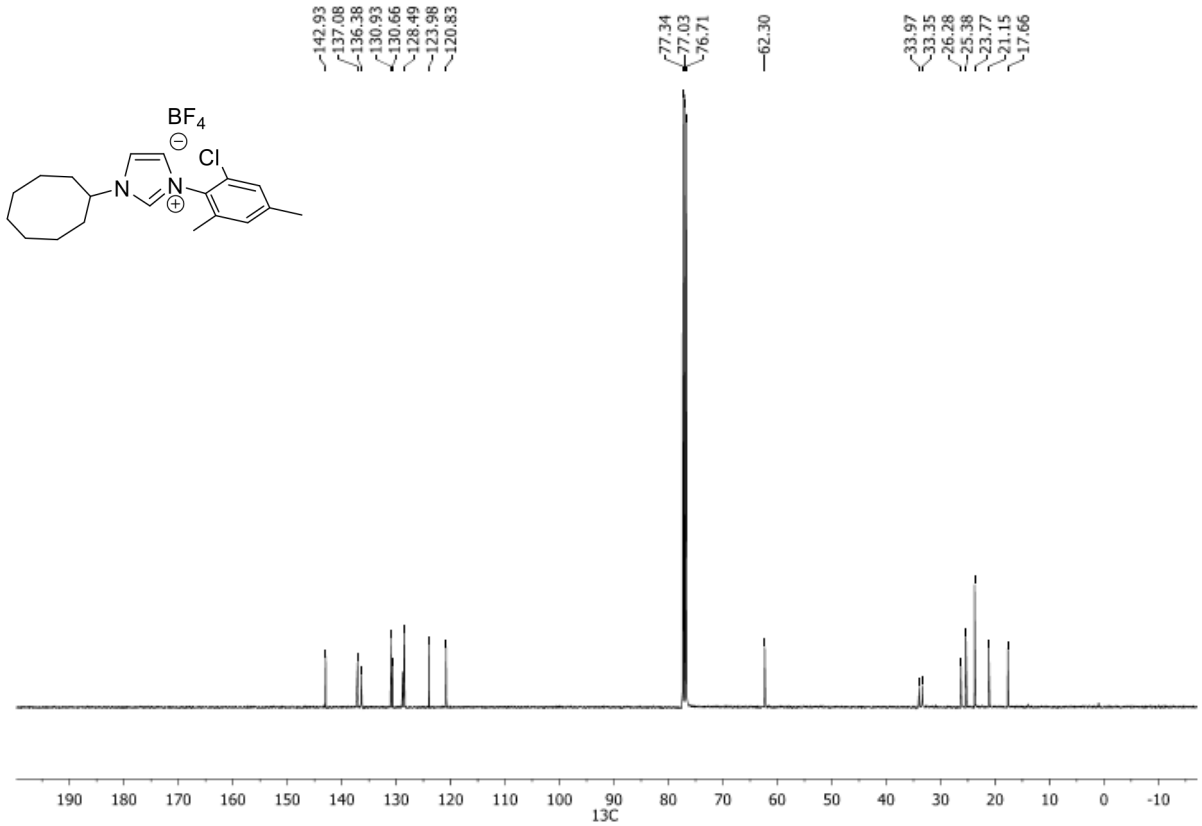


Figure S33: *^{13}C NMR (101 MHz, $CDCl_3$) of* ***4a***

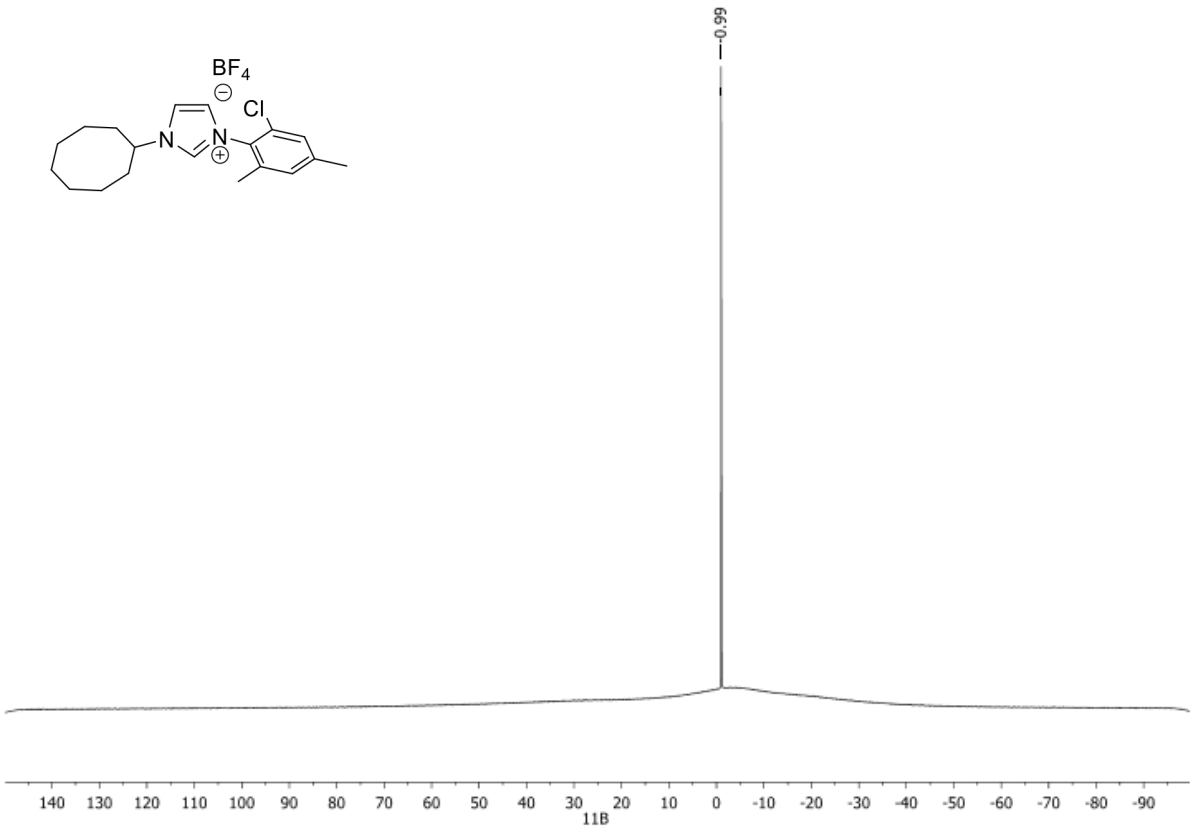


Figure S34**: [11]B NMR (128 MHz, $CDCl_3$) of **4a

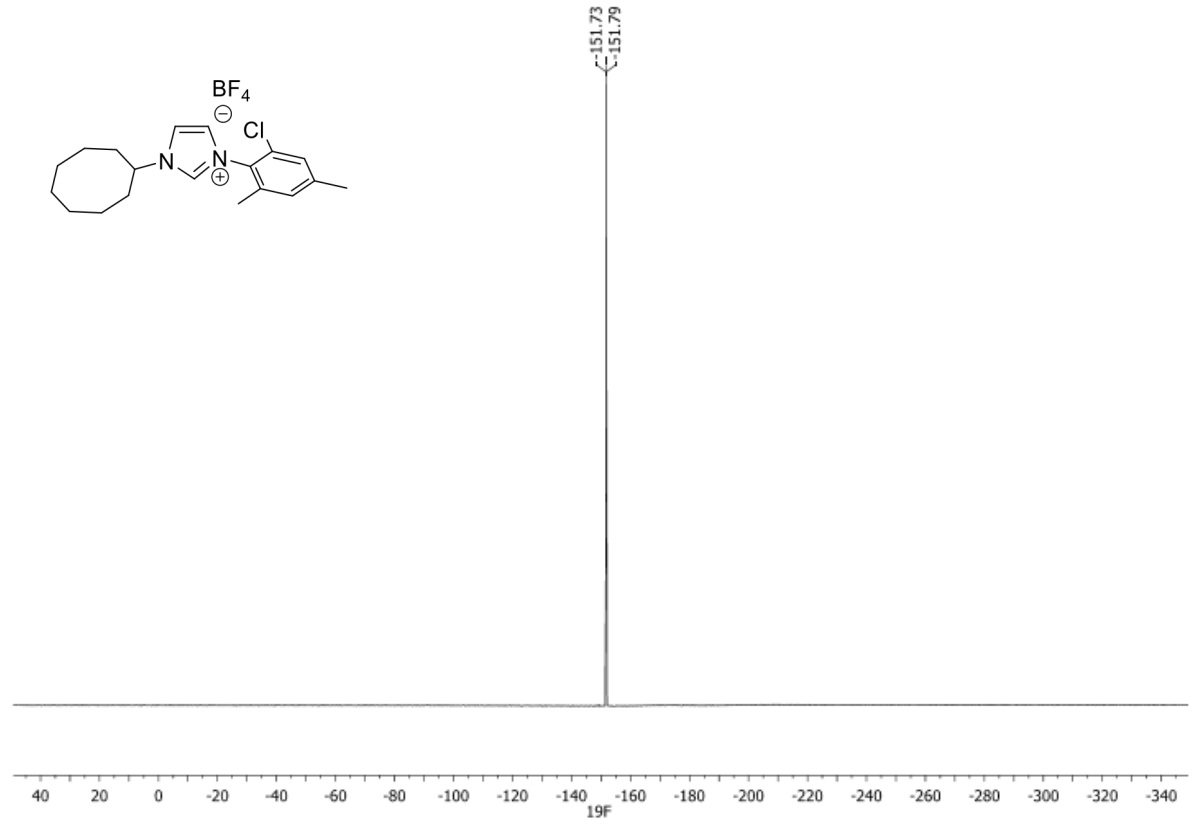


Figure S35**: [19]F NMR (376 MHz, $CDCl_3$) of **4a

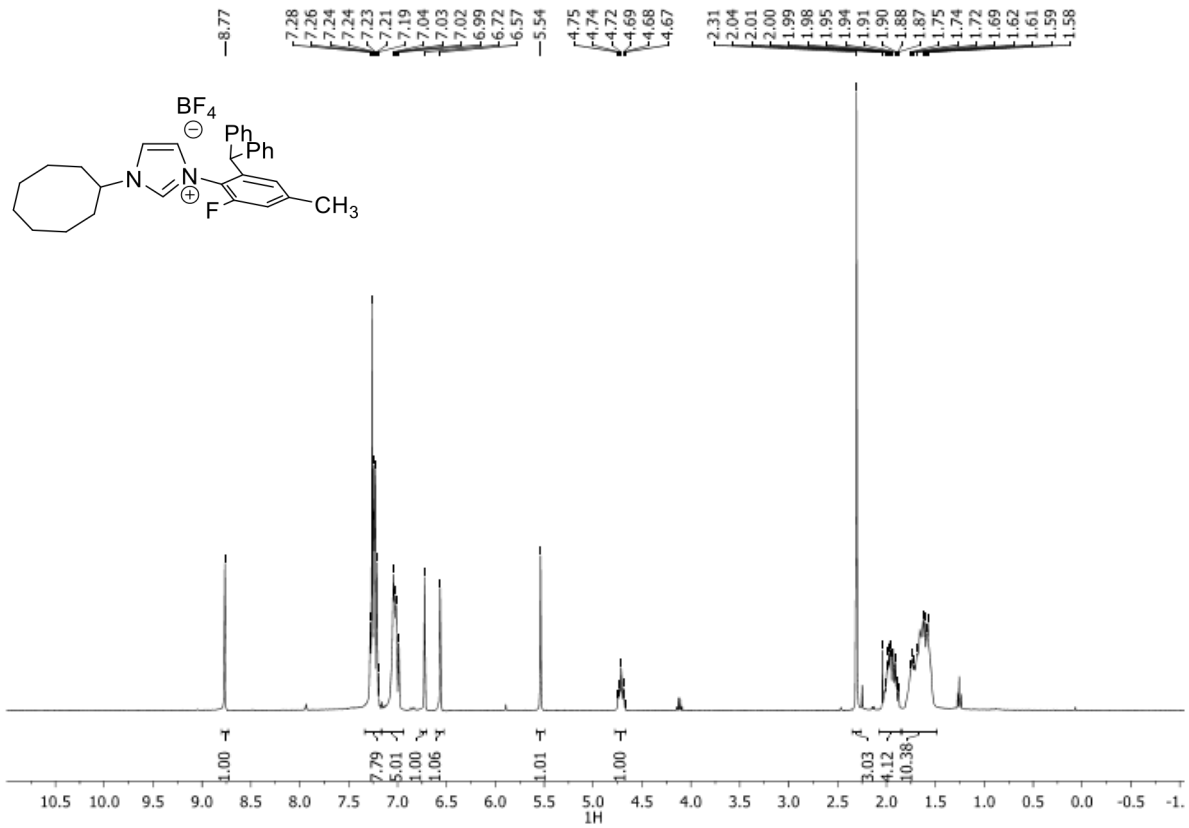


Figure S36**: [1]H NMR (400 MHz, $CDCl_3$) of **4b

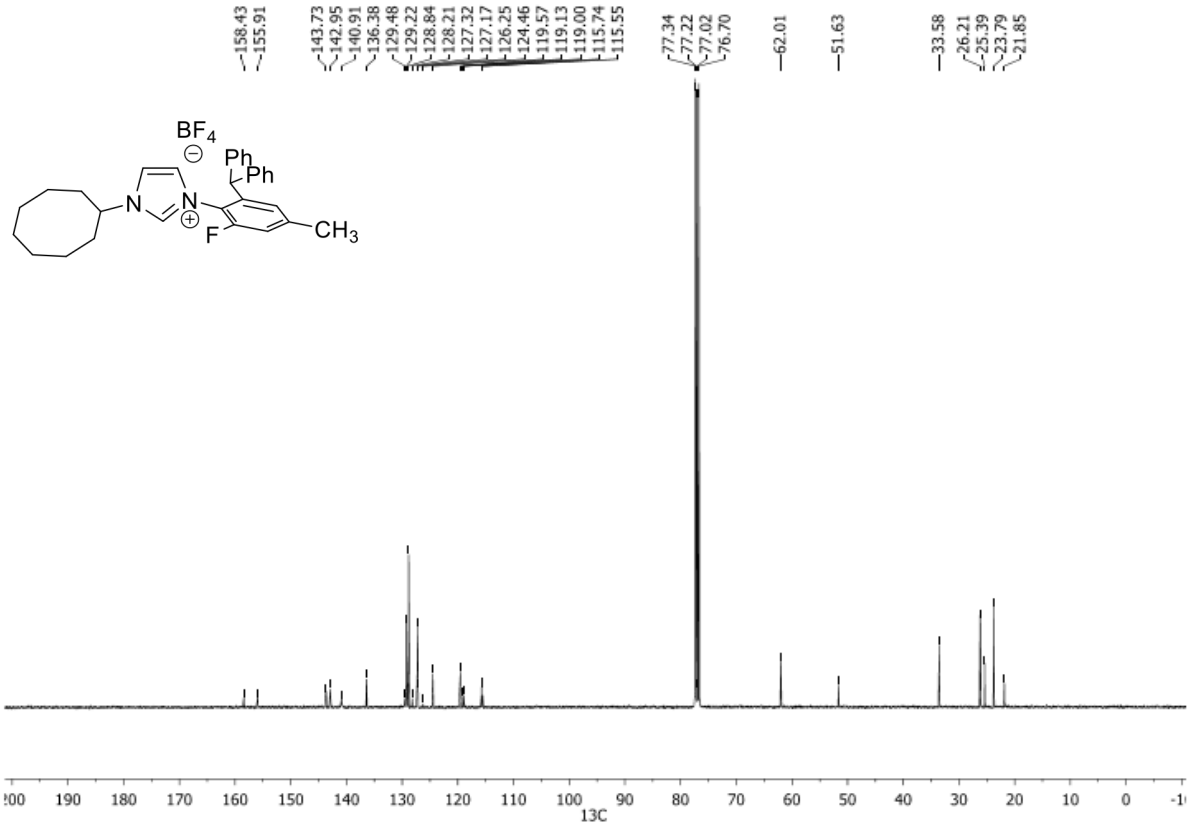


Figure S37**: [13]C NMR (101 MHz, $CDCl_3$) of **4b

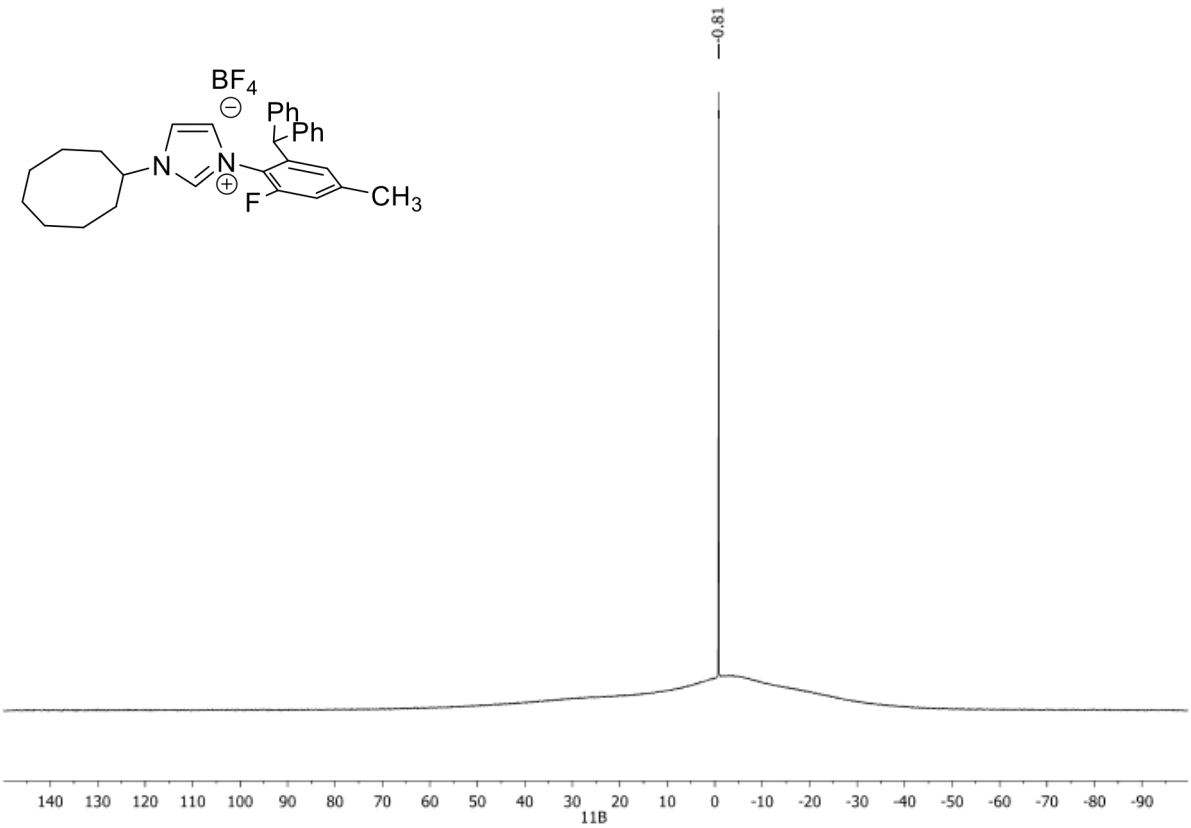


Figure S38: *^{11}B NMR (128 MHz, $CDCl_3$) of* ***4b***

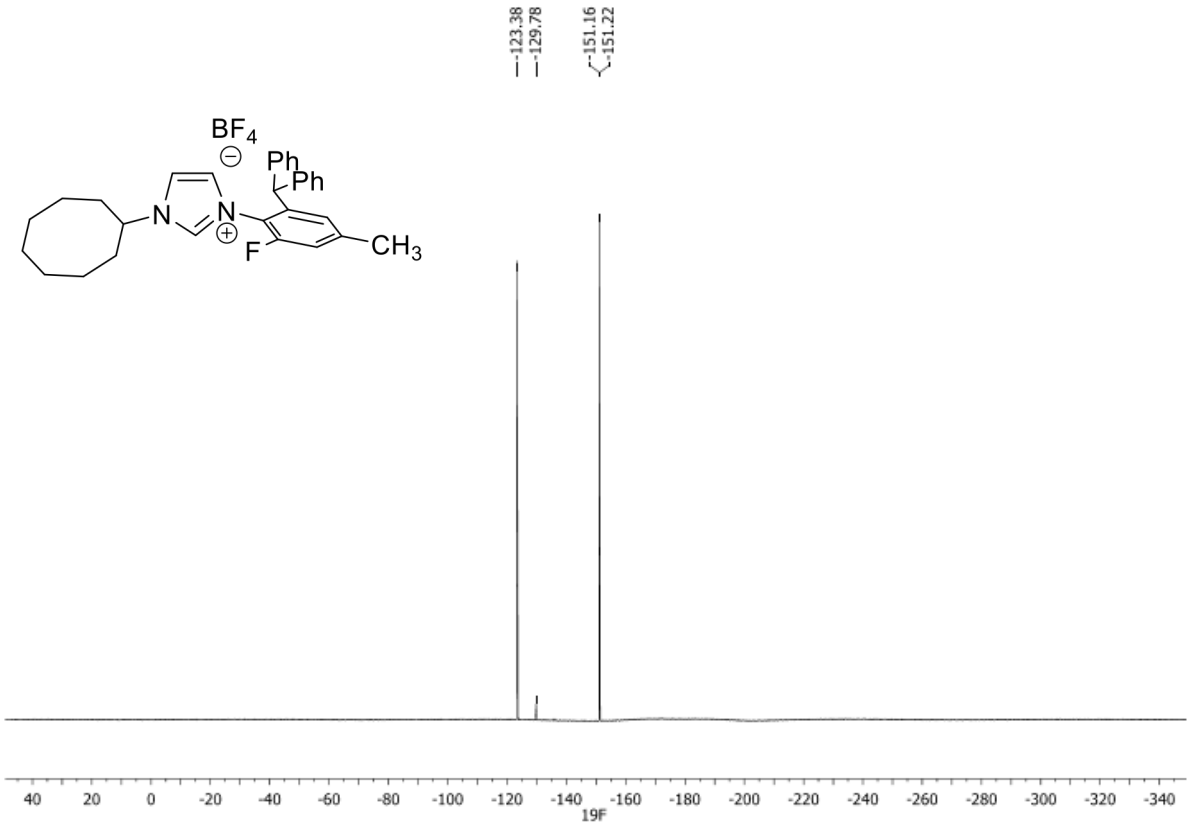


Figure S39: *^{19}F NMR (376 MHz, $CDCl_3$) of* ***4b***

7.2. *Ruthenium Complexes*

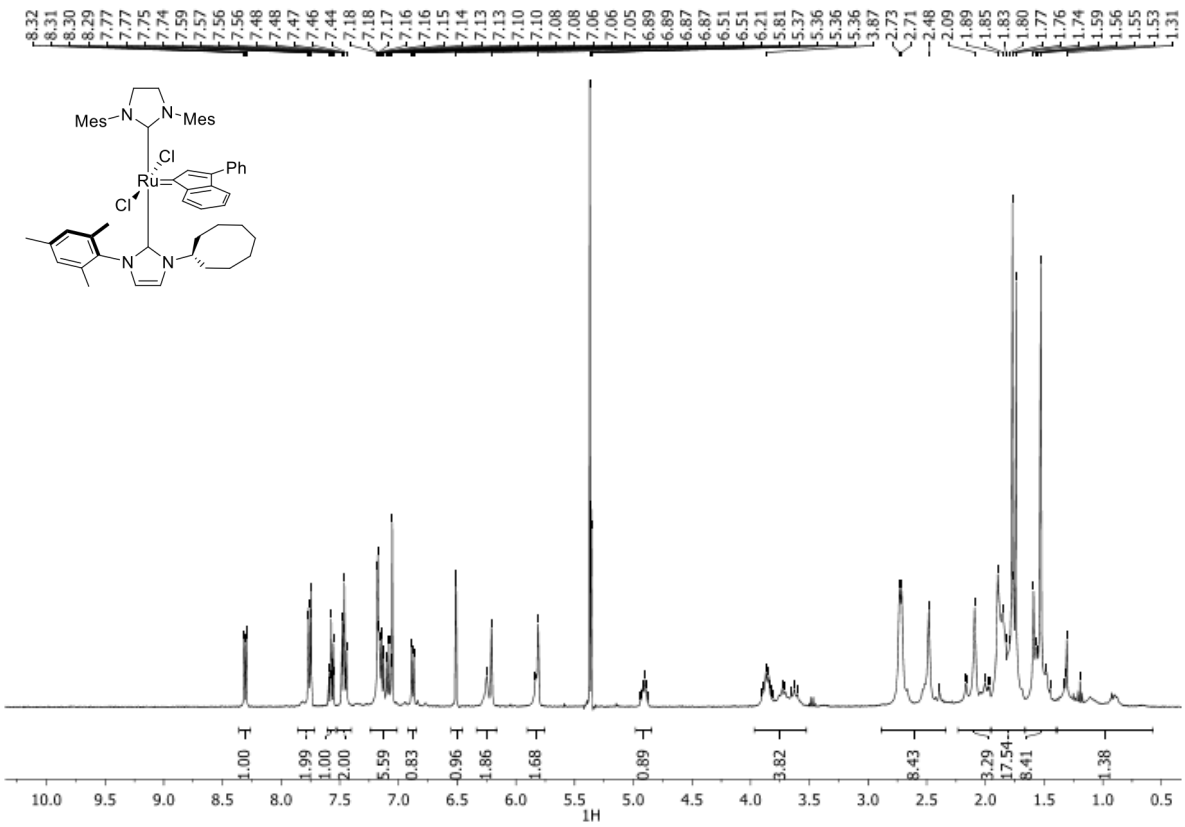


Figure S40**: ^{1}H NMR (400 MHz, CD_2Cl_2) of Ru-**1b

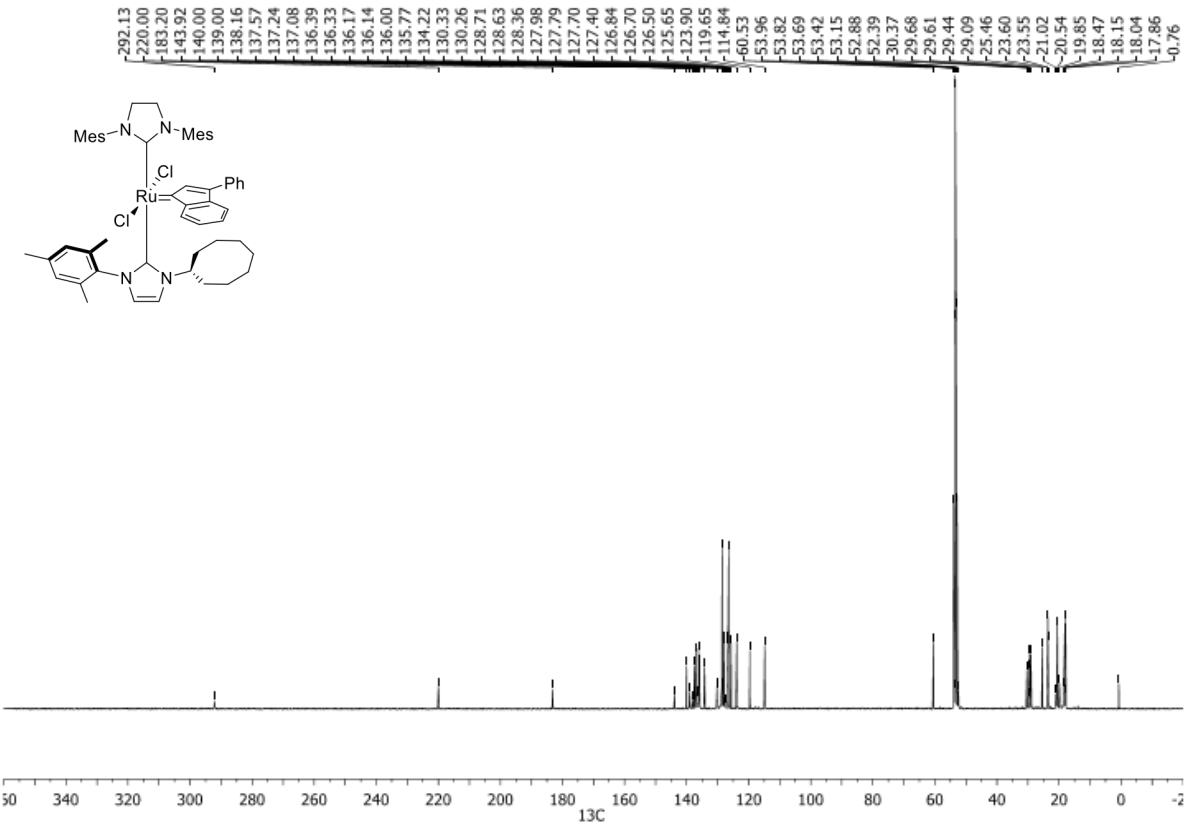


Figure S41**: ^{13}C NMR (101 MHz, CD_2Cl_2) of Ru-**1b

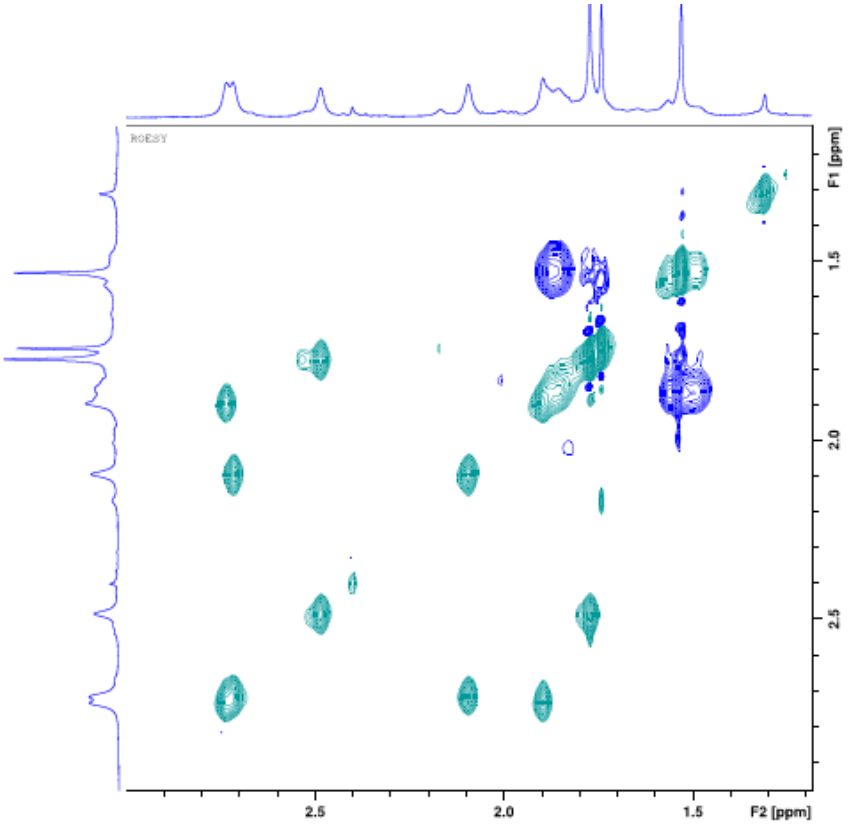


Figure S42**: ROESY NMR of Ru-**1b

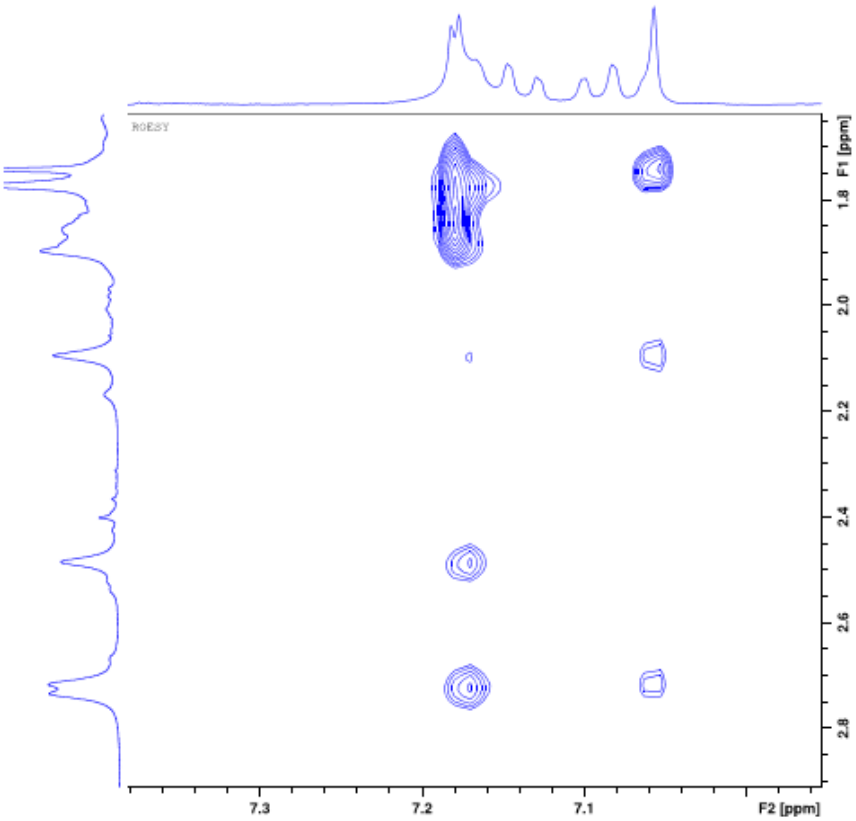


Figure S43**: ROESY NMR of Ru-**1b

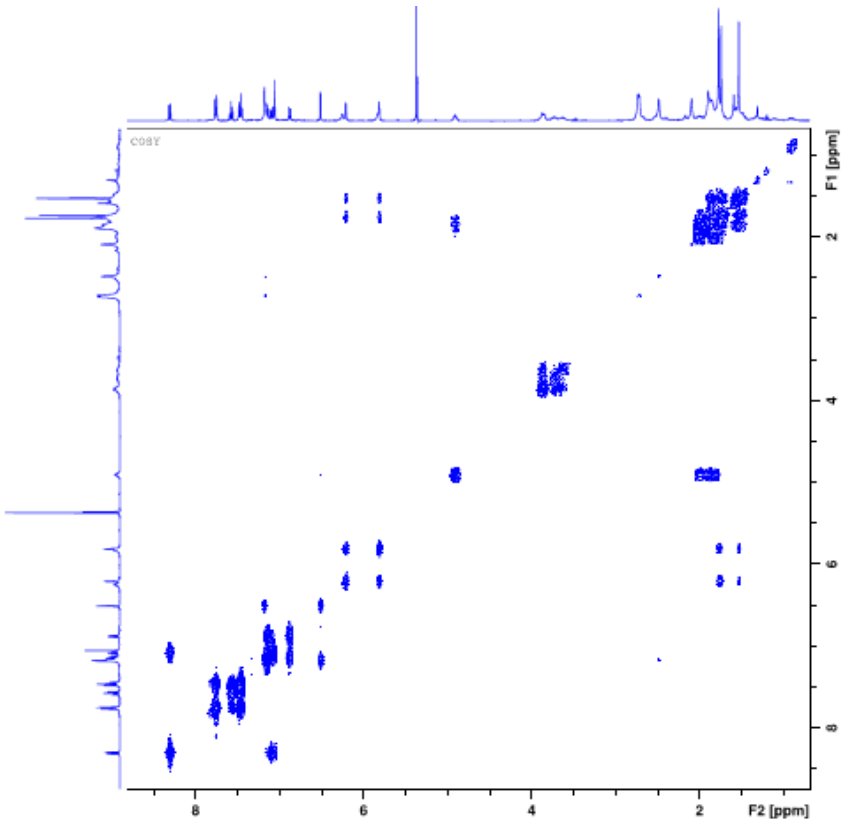


Figure S44**: COSY NMR of Ru-**1b

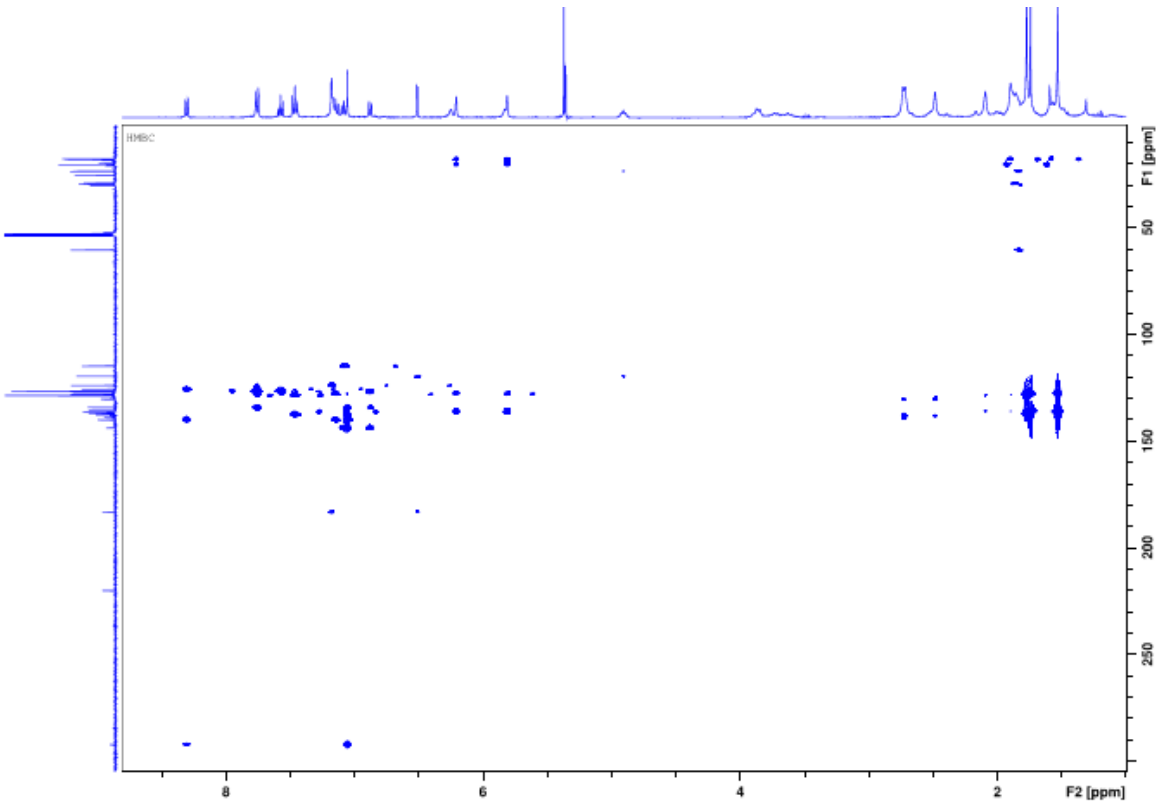


Figure S45**: HMBC NMR of Ru-**1b

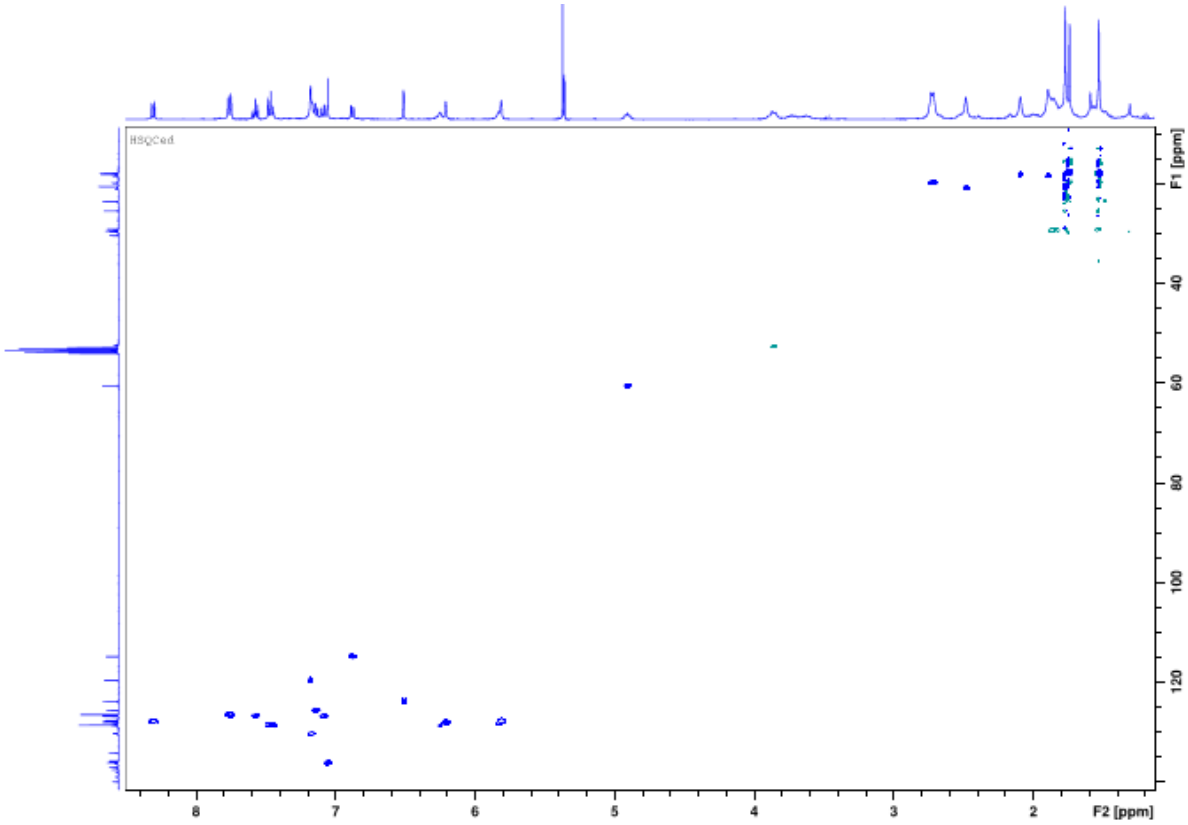


Figure S46**: HSQCed NMR of Ru-**1b

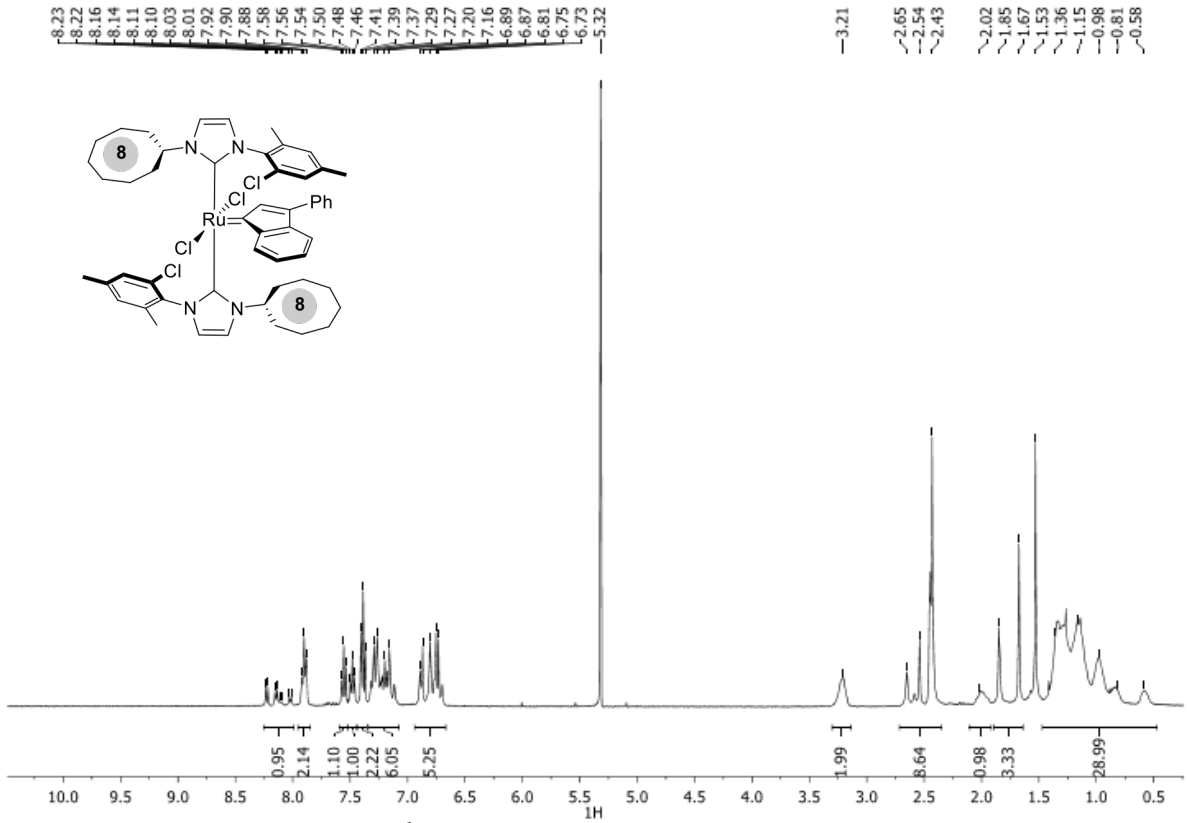


Figure S47**: ^{1}H NMR (500 MHz, CD_2Cl_2, 250 K) of Ru-**1c

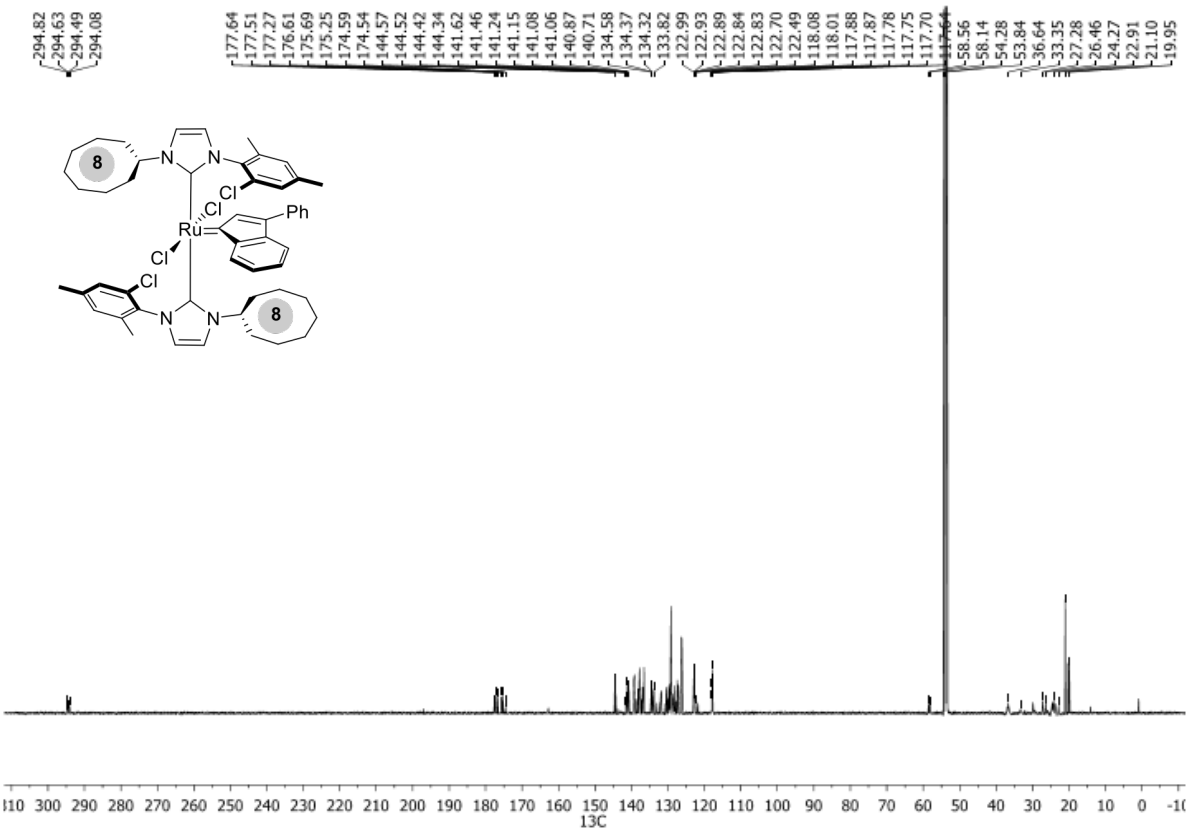


Figure S48: *^{13}C NMR (126 MHz, CD_2Cl_2, 250 K) of Ru-**1c***

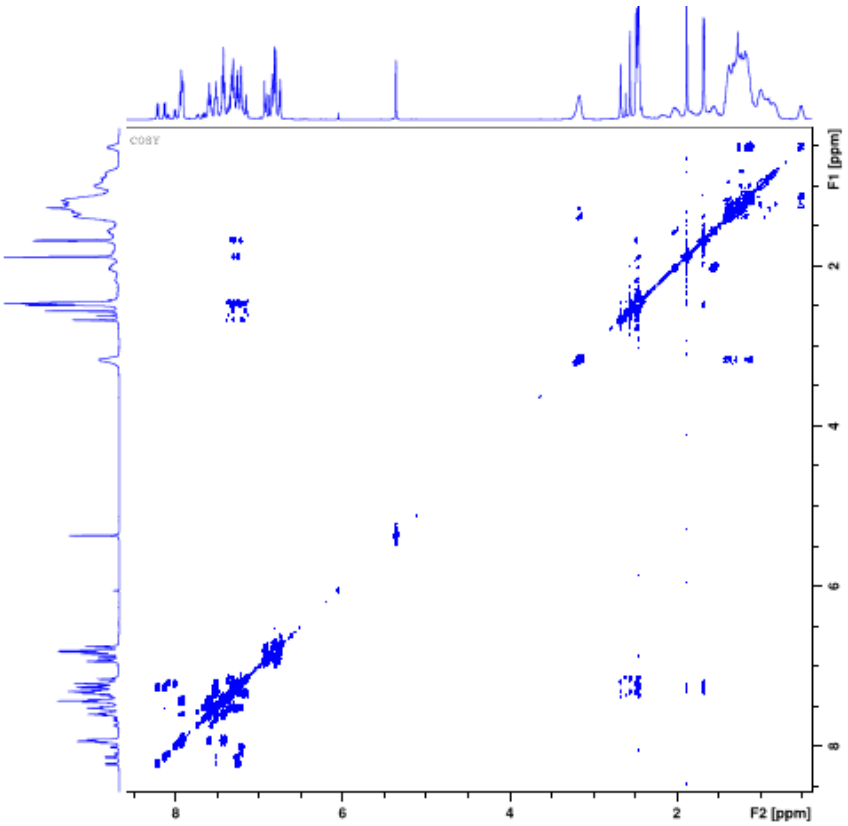


Figure S49: *COSY NMR of Ru-**1c***

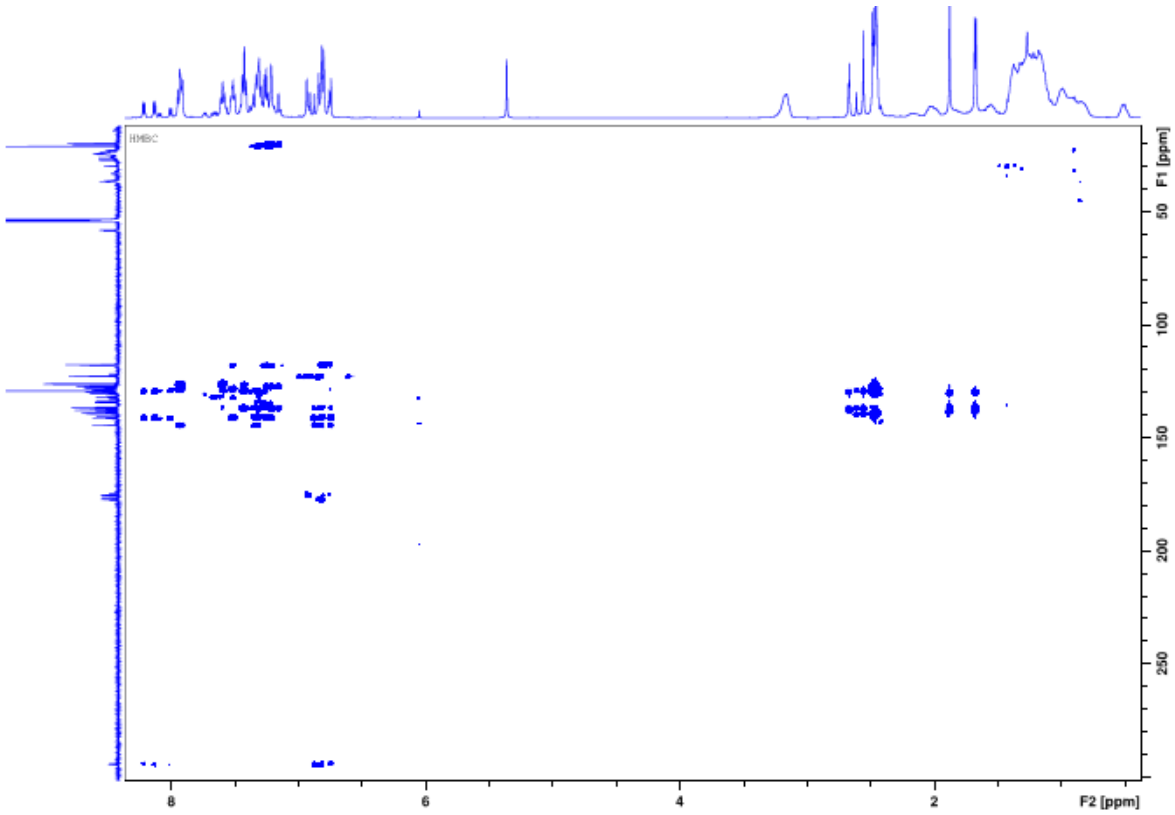


Figure S50**: HMBC NMR of Ru-**1c

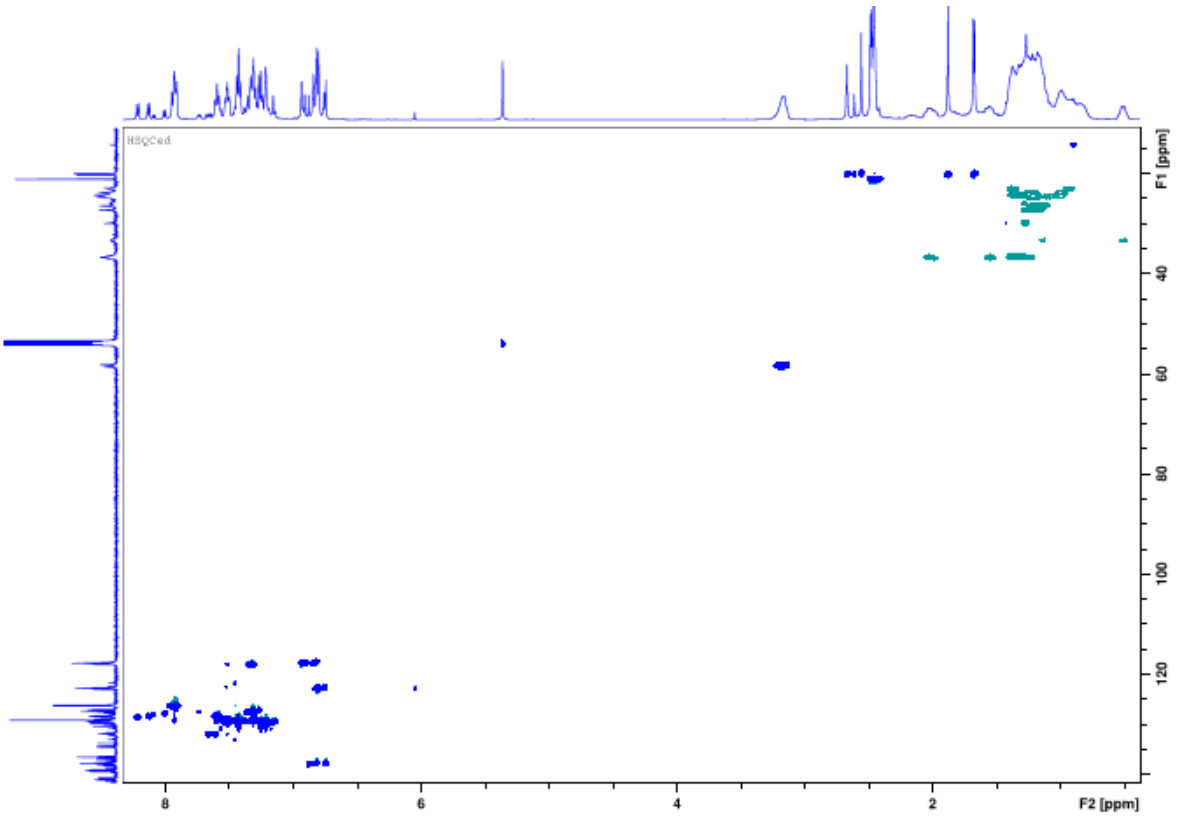


Figure S51**: HSQCed NMR of Ru-**1c

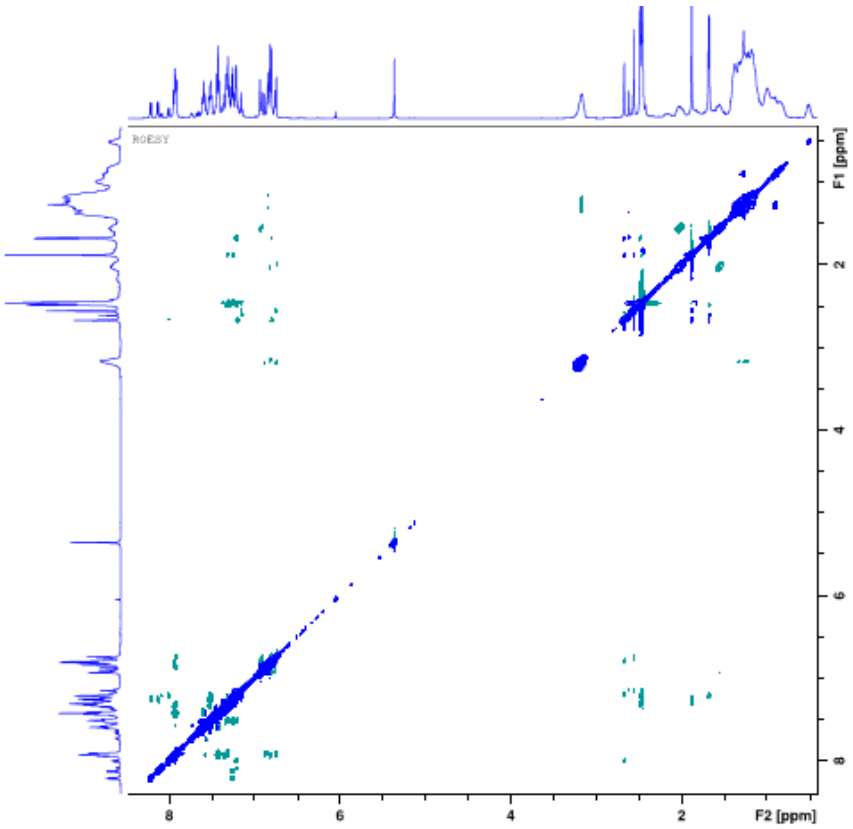


Figure S52**: ROESY NMR of Ru-**1c

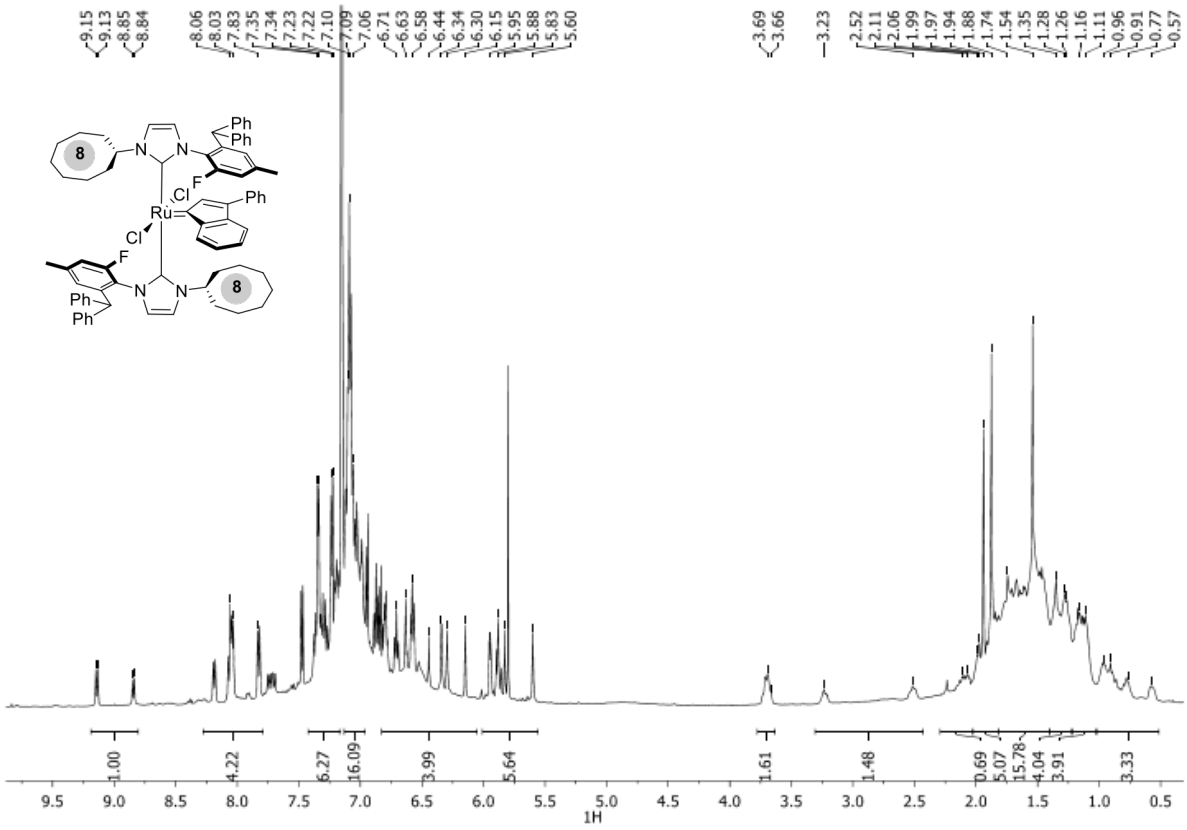


Figure S53**: ^{1}H NMR (500 MHz, C_6D_6, 300 K) of Ru-**1d

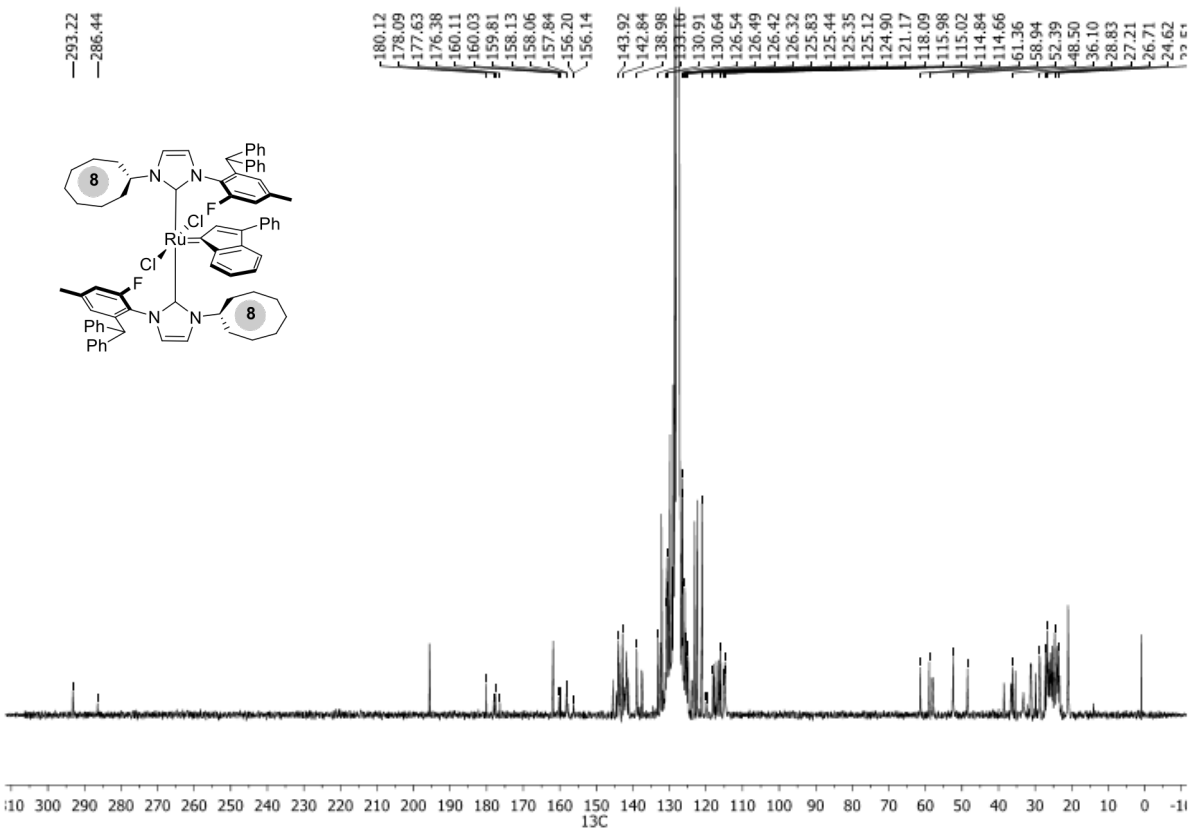


Figure S54**: [13]C NMR (500 MHz, C_6D_6, 300 K) of Ru-**1d

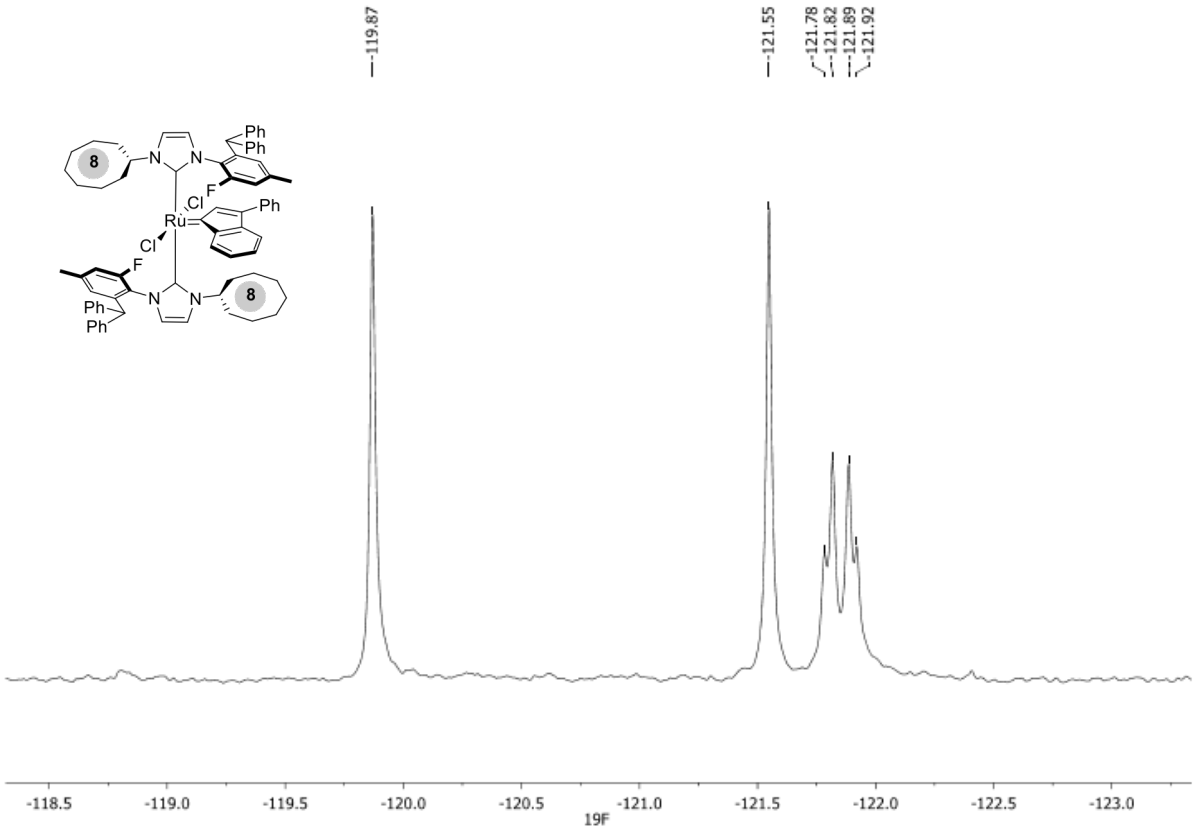


Figure S55**: [19]F NMR (471 MHz, C_6D_6, 300 K) of Ru-**1d

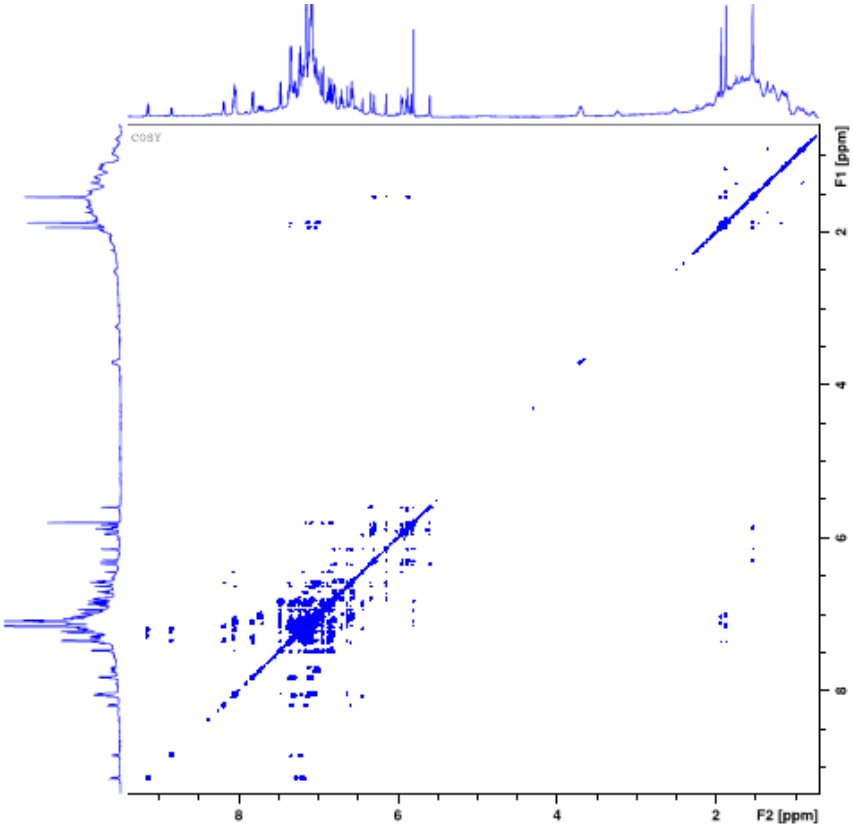


Figure S56**: COSY NMR of Ru-**1d

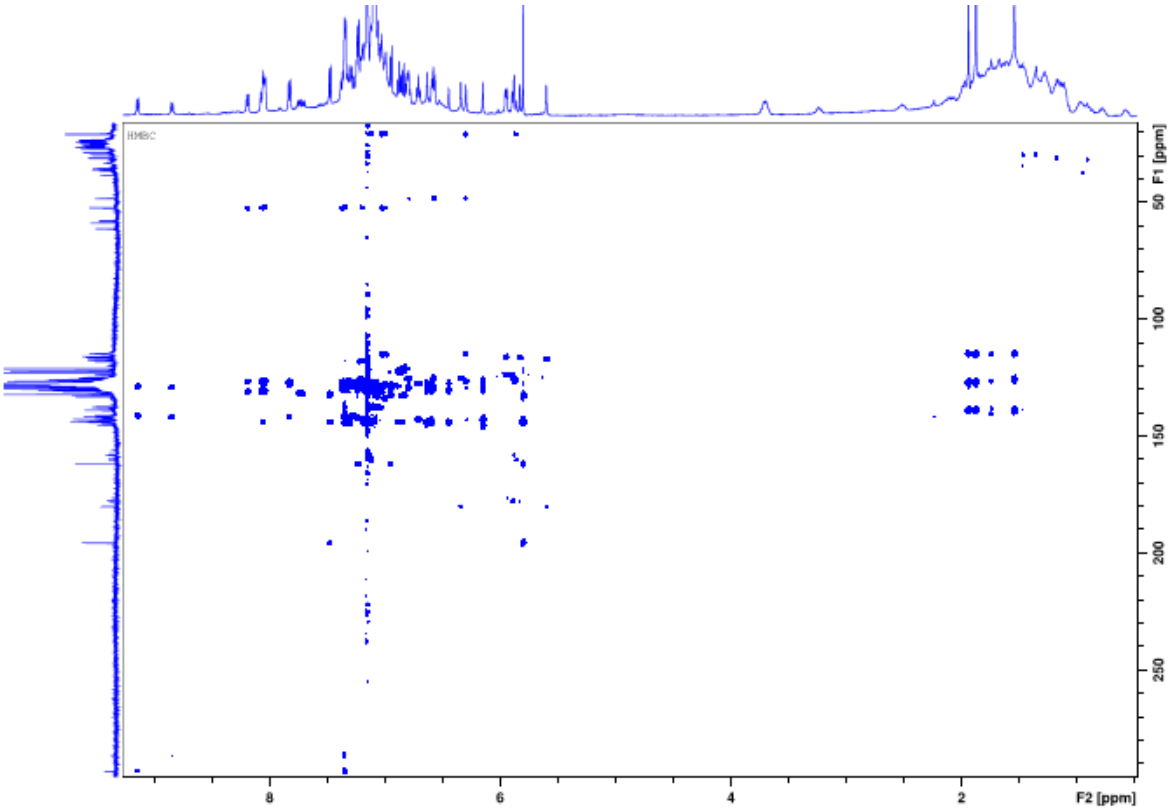


Figure S57**: HMBC NMR of Ru-**1d

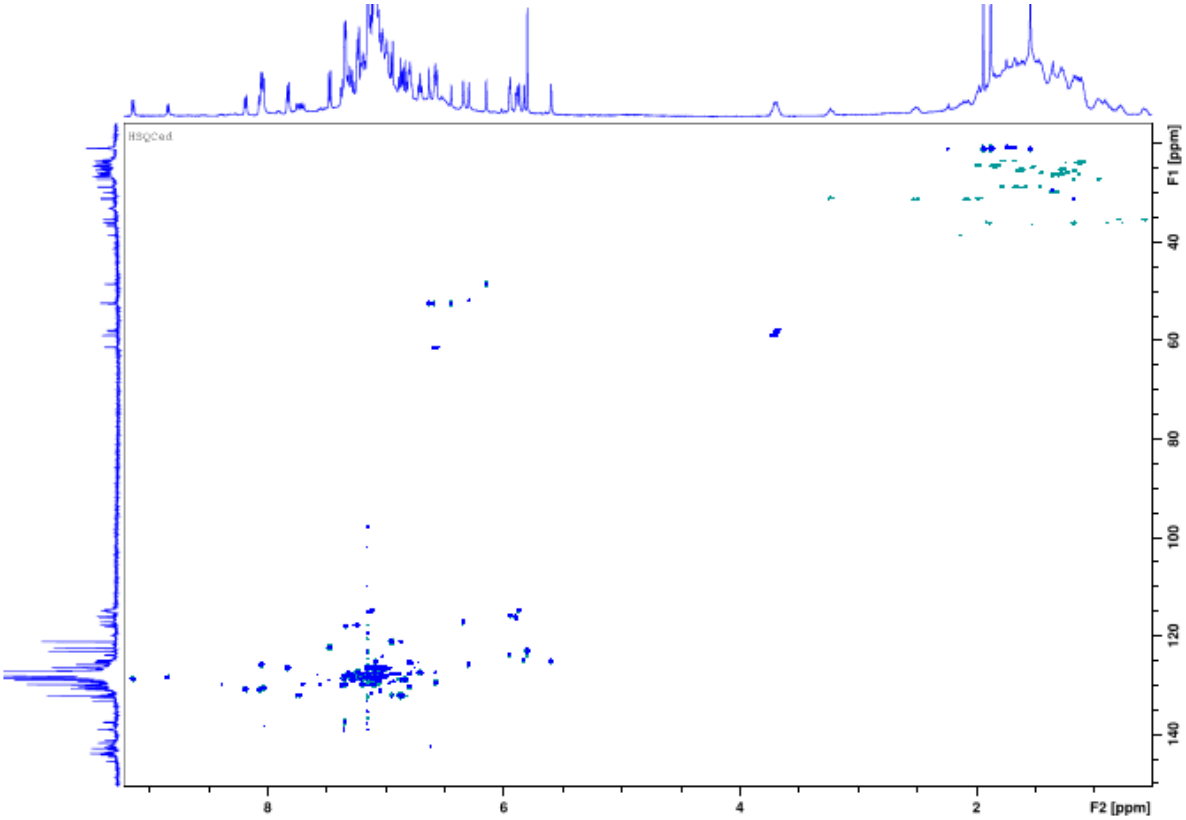


Figure S58**: HSQCed NMR of Ru-**1d

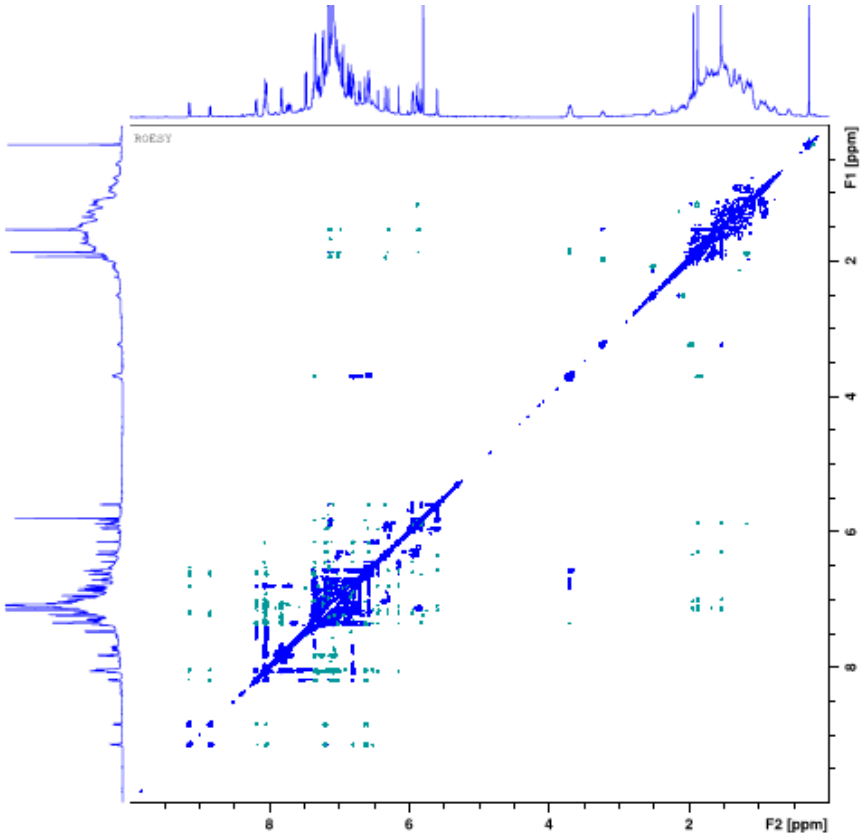


Figure S59**: ROESY NMR of Ru-**1d

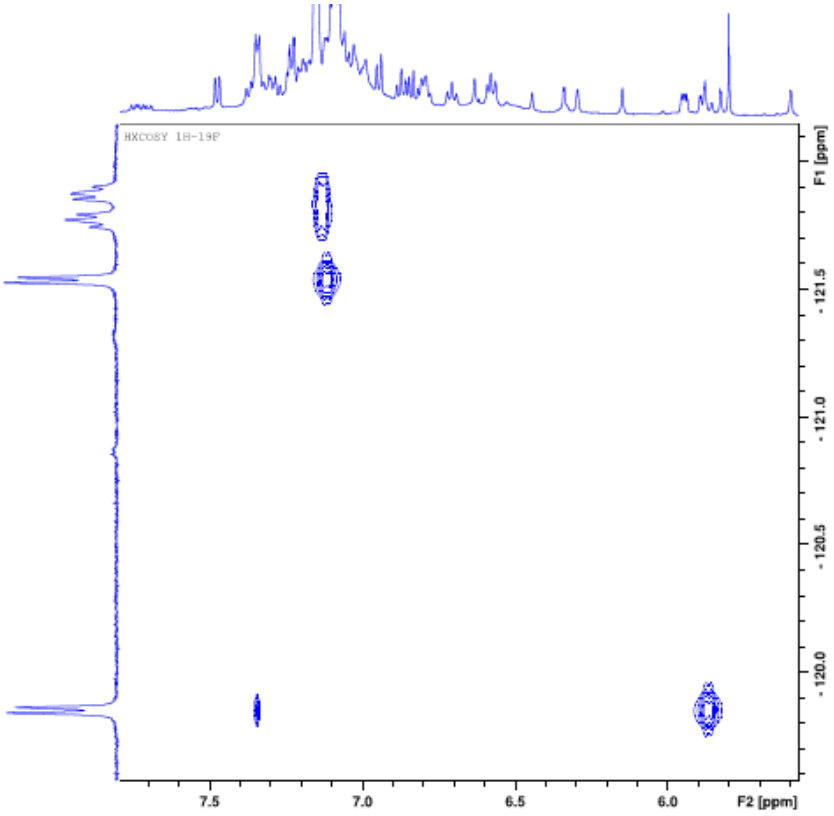


Figure S60: *COSY* ^{1}H-^{19}F *NMR of Ru-**1d***

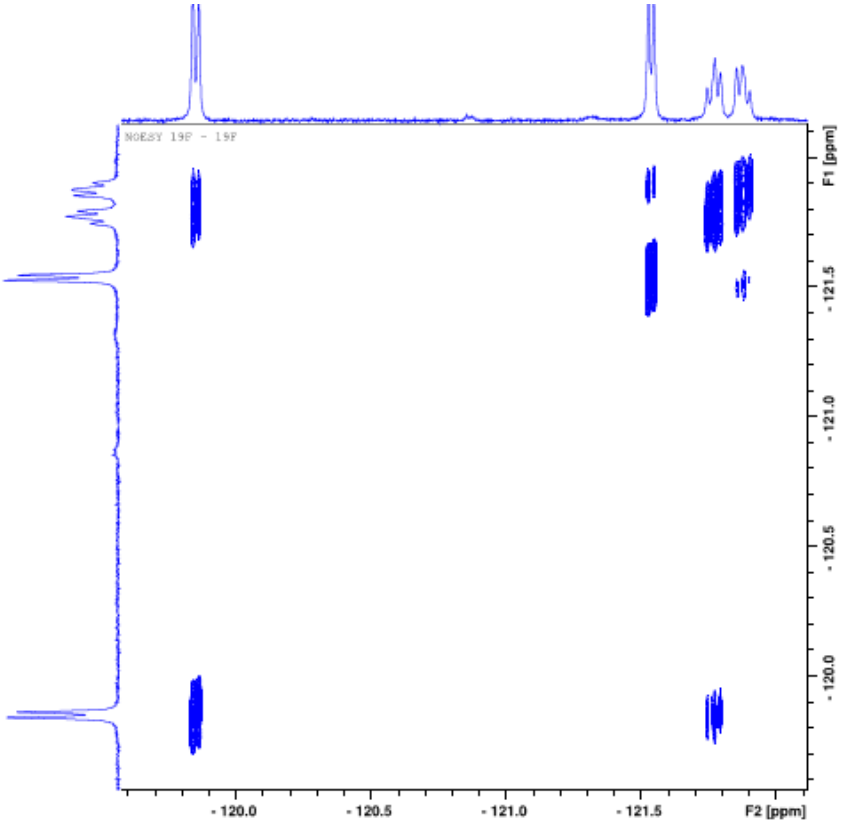


Figure S61: *NOESY* ^{19}F-^{19}F *NMR of Ru-**1d***

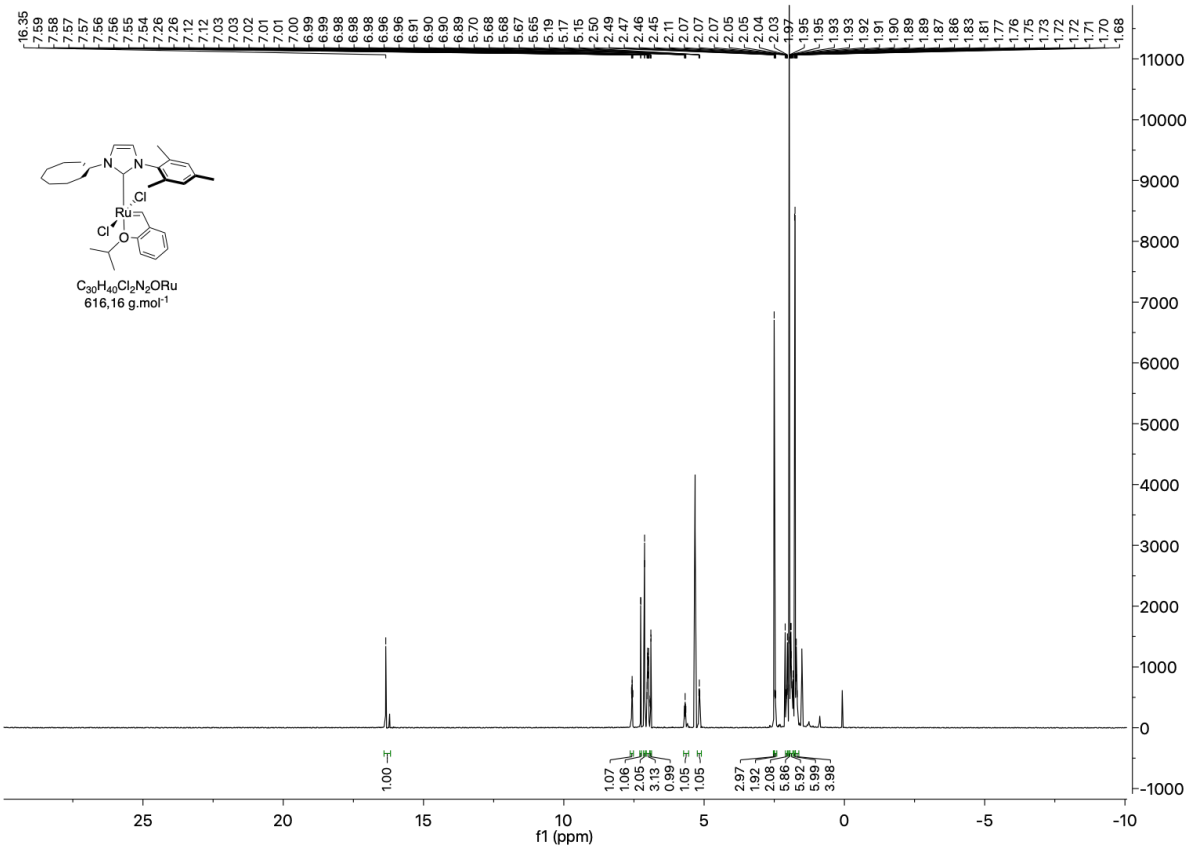


Figure S62**: ^{1}H NMR (400 MHz, CD_2Cl_2) of Ru-**2a

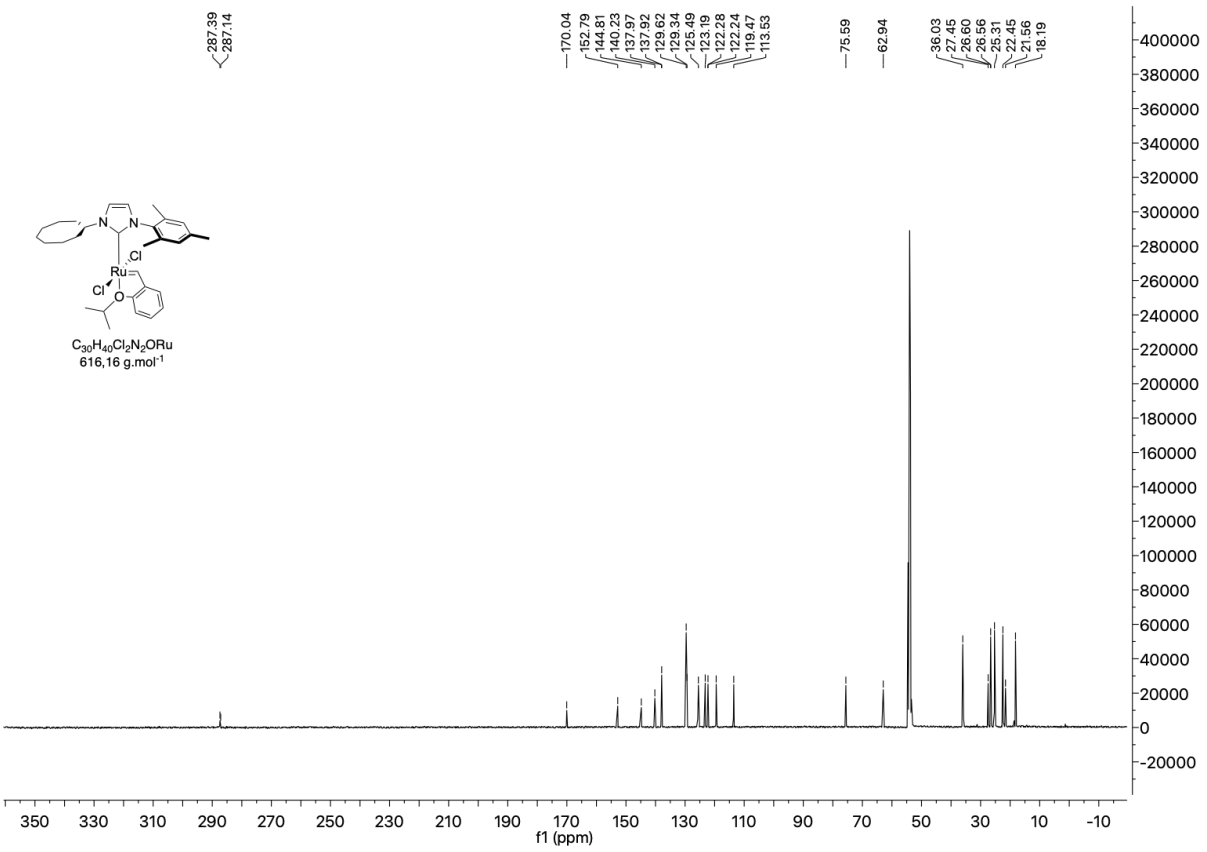


Figure S63**: ^{13}C NMR (101 MHz, CD_2Cl_2) of Ru-**2a

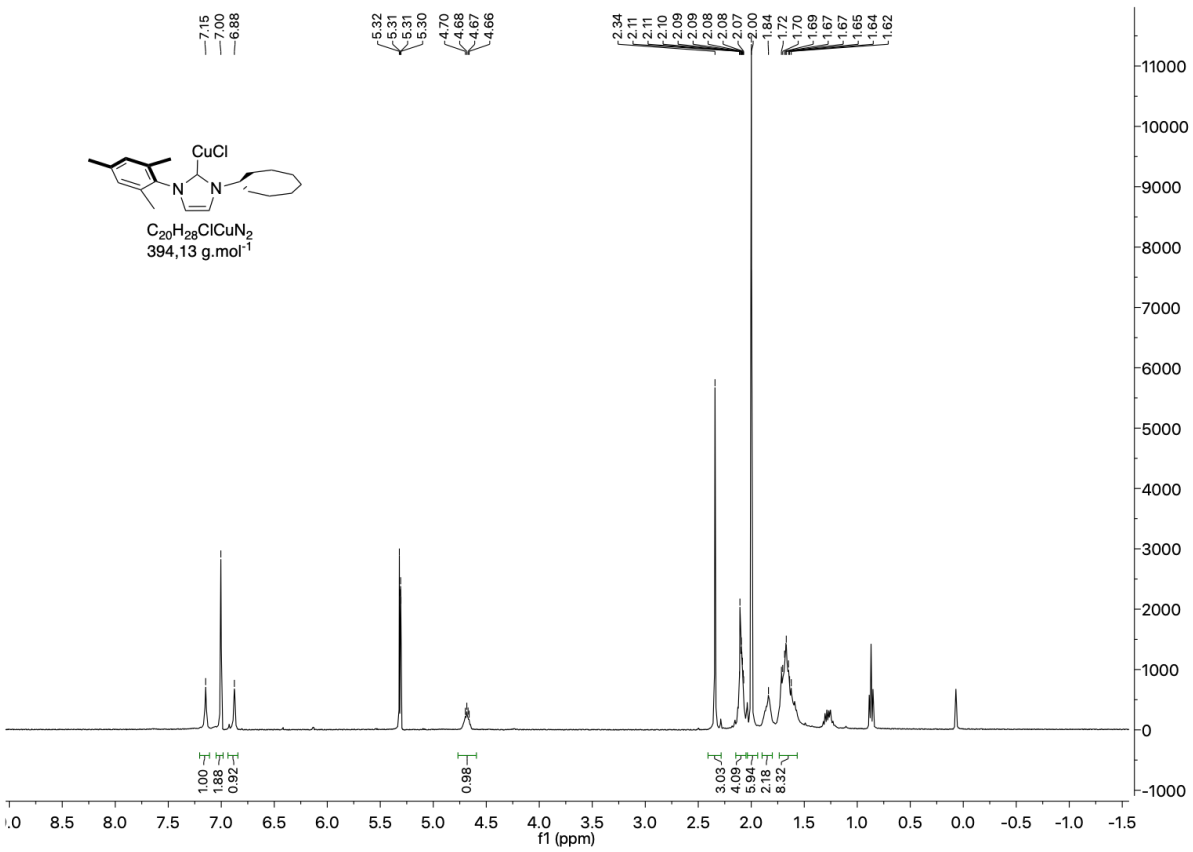


Figure S64**: [1]H NMR (400 MHz, CD_2Cl_2) of Cu-**1a

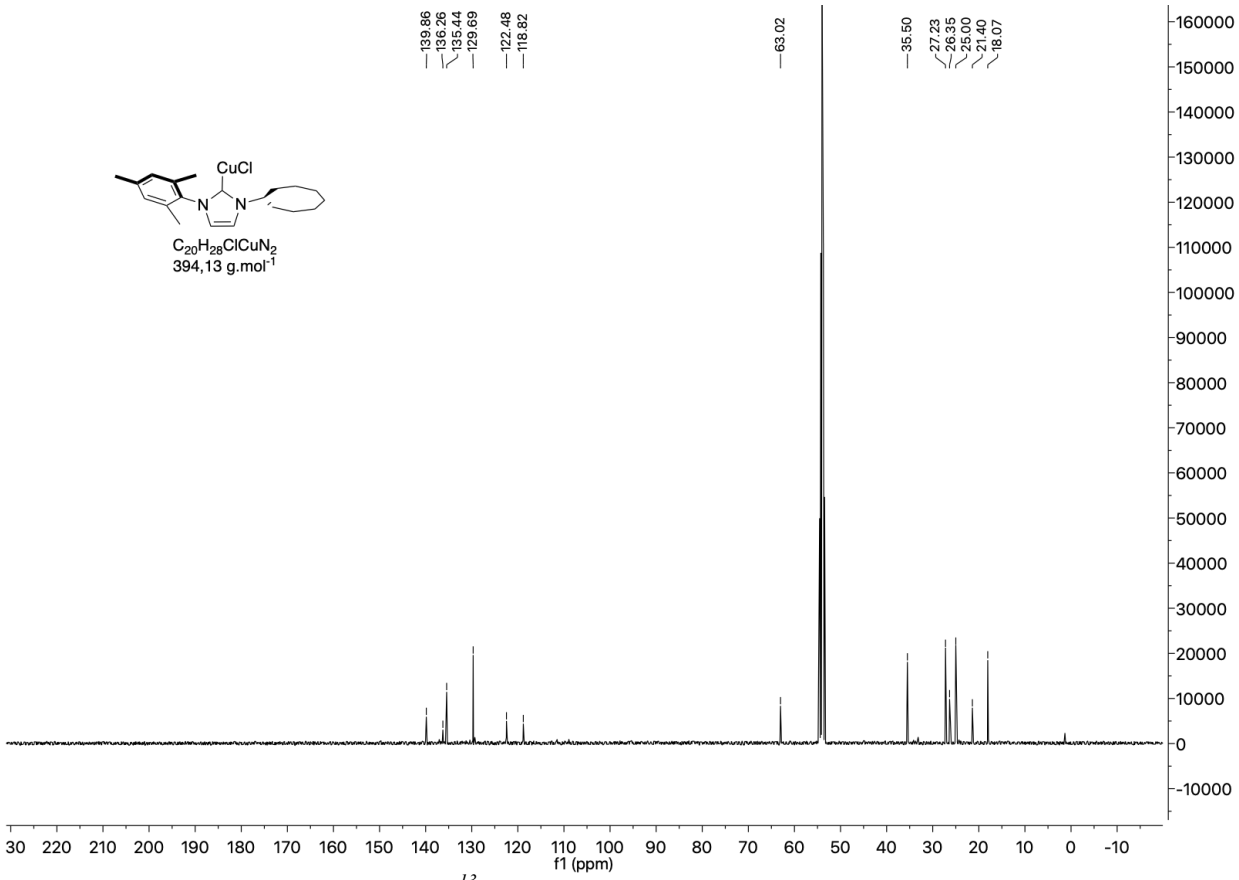


Figure S65**: [13]C NMR (101 MHz, CD_2Cl_2) of Cu-**1a

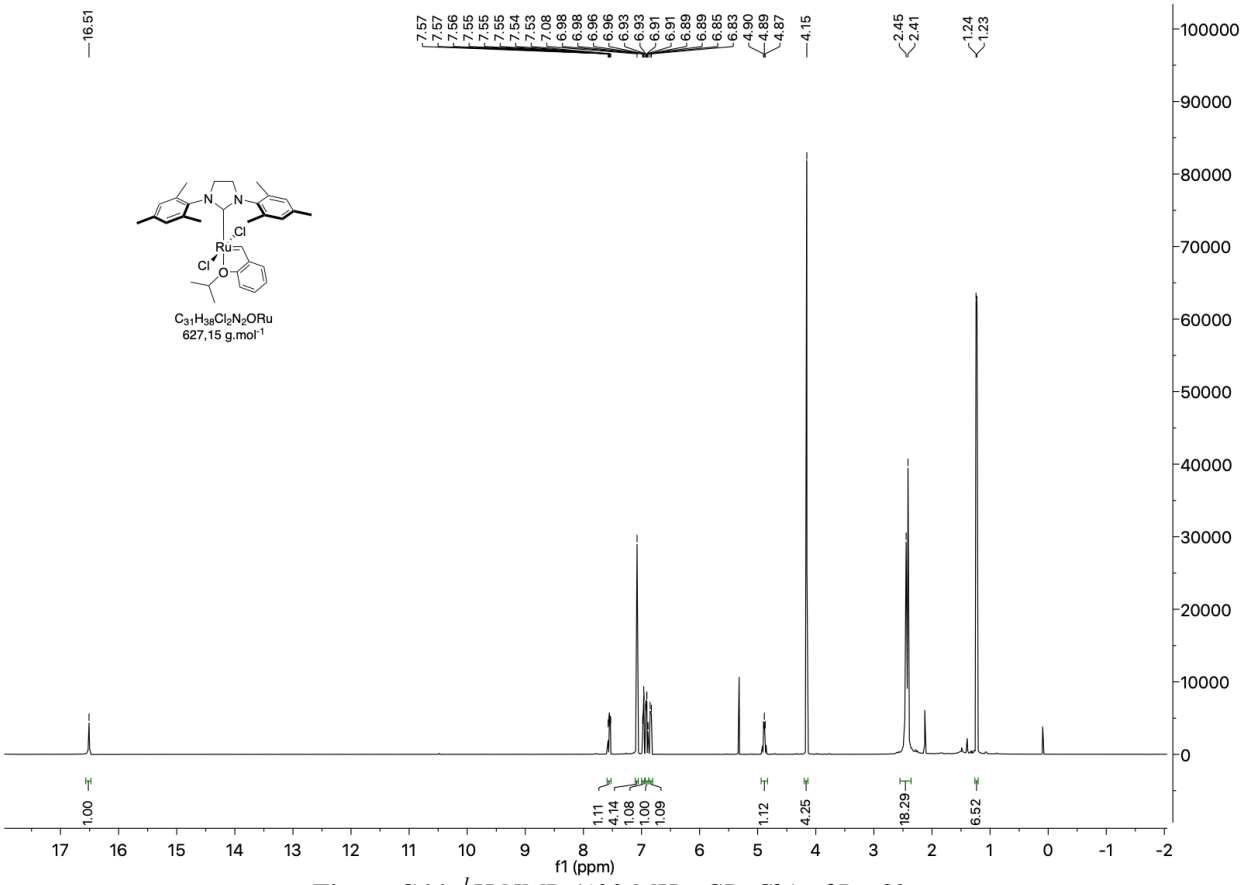


Figure S66**: [1]H NMR (400 MHz, CD_2Cl_2) of Ru-**2b

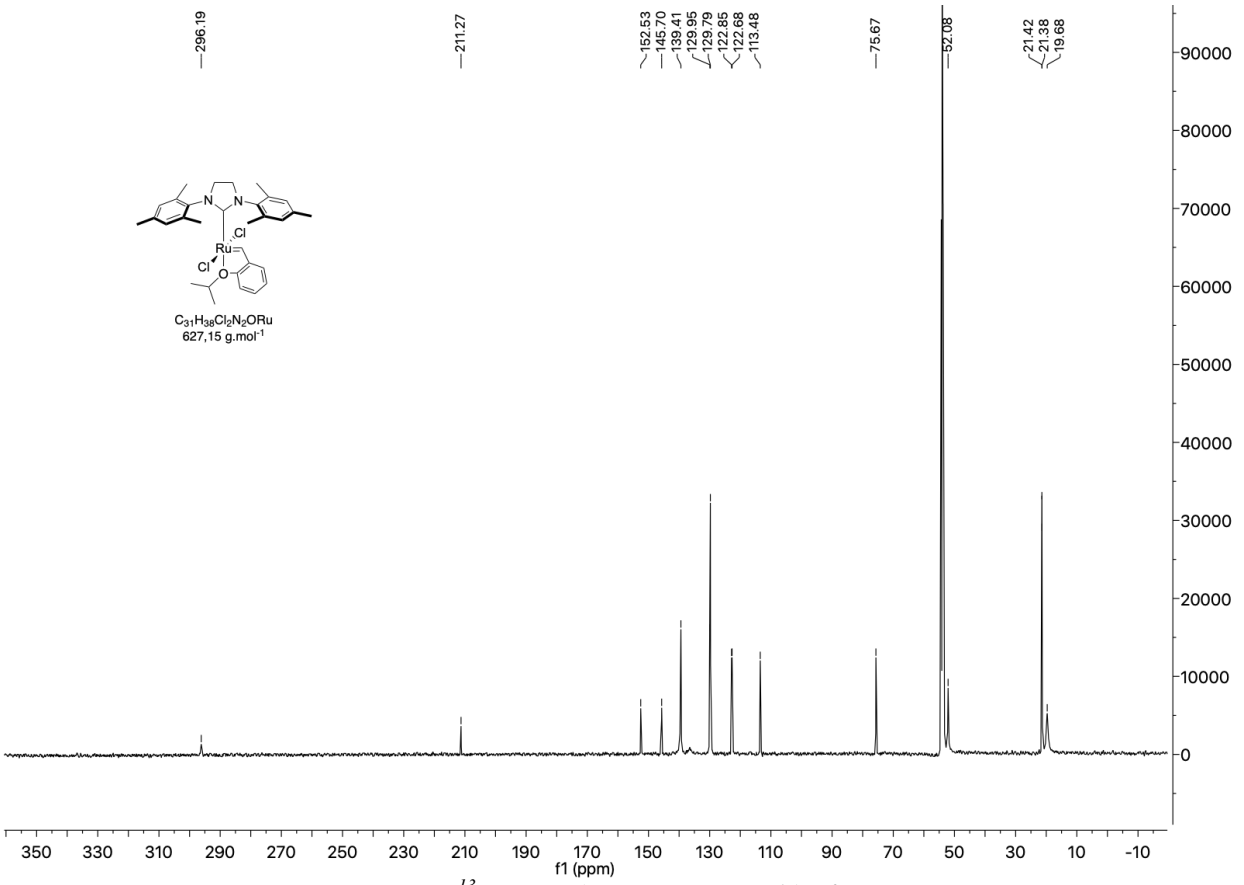


Figure S67**: [13]C NMR (101 MHz, CD_2Cl_2) of Ru-**2b

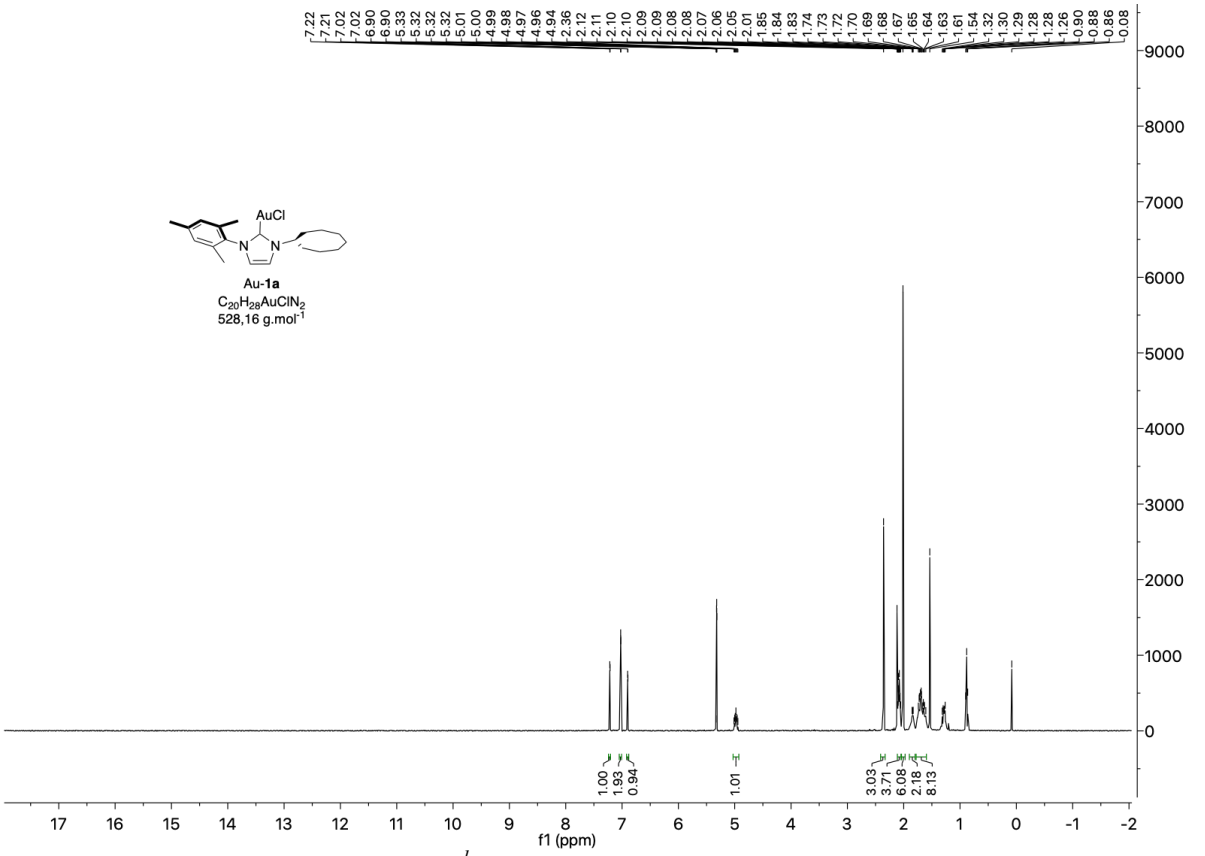


Figure S68**: ^{1}H NMR (400 MHz, CD_2Cl_2) of Au-**1a

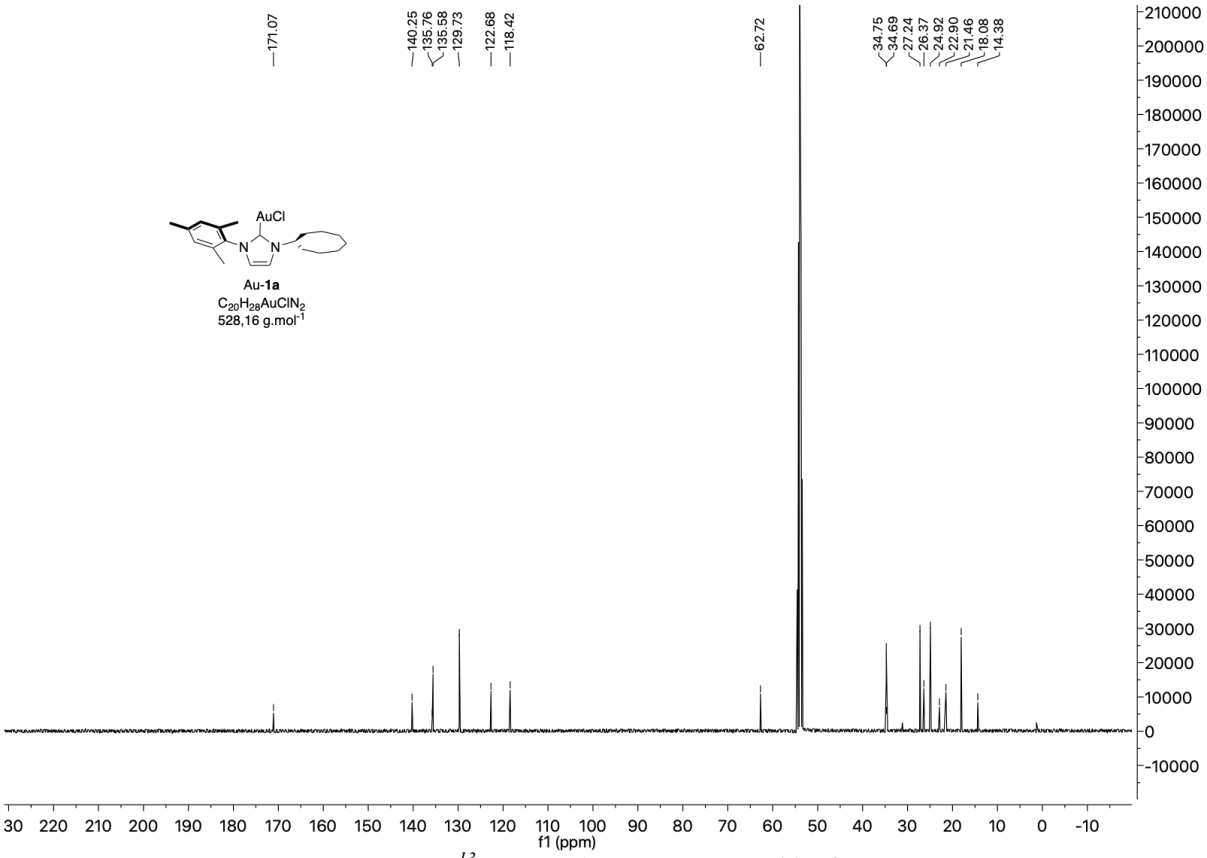
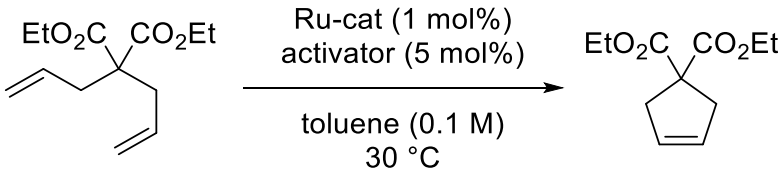
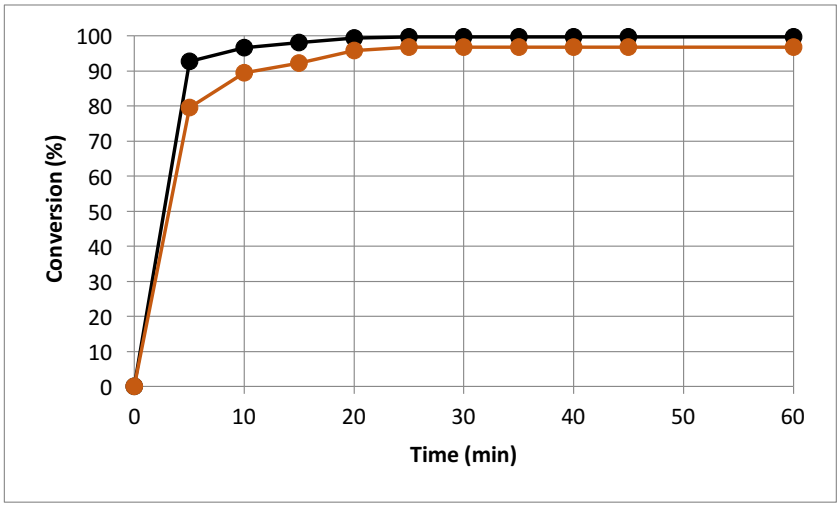
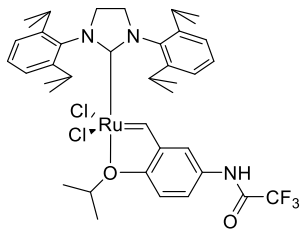


Figure S69**: ^{13}C NMR (101 MHz, CD_2Cl_2) of Au-**1a

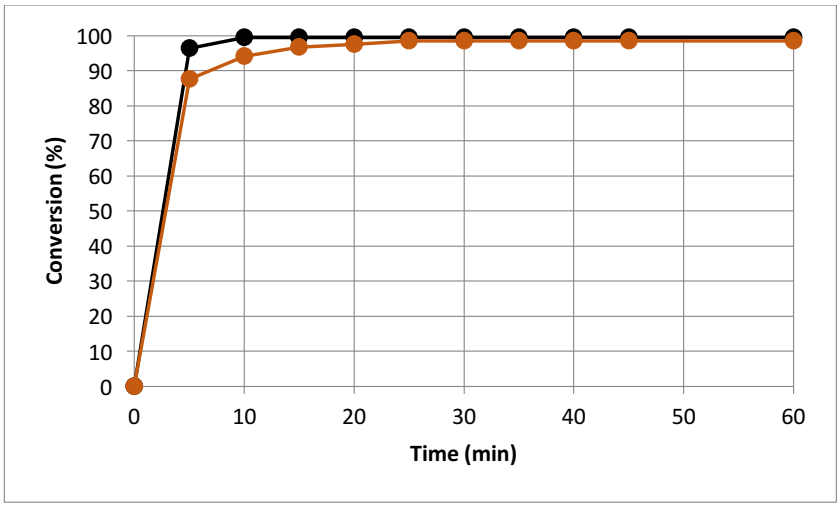


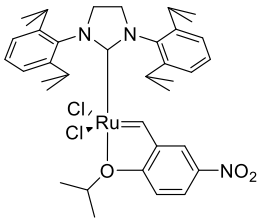




M71 SIPr

Figure S70: *Catalytic activity profiles of complex* ***M71 SIPr*** *(1 mol%) for RCM of DEDAM* ***S1*** *at 30 °C. Conversions were monitored by* ^{1}*H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard.* ***CuCl*** *5 mol% (orange) ;* ***without activator*** *(black).*





Grela SIPr

Figure S71: *Catalytic activity profiles of complex* ***Grela SIPr*** *(1 mol%) for RCM of DEDAM* ***S1*** *at 30 °C. Conversions were monitored by* ^{1}*H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard.* ***CuCl*** *5 mol% (orange) ;* ***without activator*** *(black).*

8. X-Ray crystallographic data

X-Ray structure of 4b

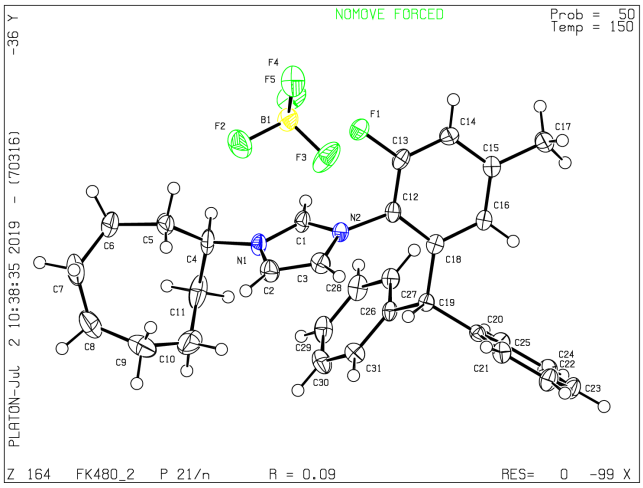


Table S1**: Crystal data and structure refinement for **4b

Empirical formula		$C_{31}H_{34}BF_5N_2$
	Formula weight	540.41 g/mol
	Temperature	150 *K*
	Wavelength	0.71073 Å
	Crystal system, space group	monoclinic, *P* $2_1/n$
	Unit cell dimensions	a = 9.3875(17) Å
		b = 19.402(3) Å
		c = 15.257(4) Å
		α = 90 °
		β = 98.302(10) °
		γ = 90 °
	Volume	2749.7(10) $Å^3$
	Z, Calculated density	4, 1.305 $g.cm^{-3}$
	Absorption coefficient	0.099 mm^{-1}
	F(000)	1136
	Crystal size	0.670 x 0.160 x 0.120 mm
	Crystal color	colourless
	Theta range for data collection	2.431 to 27.553 °
	h_min, h_max	-12, 12
	k_min, k_max	-24, 25
	l_min, l_max	-19, 19
	Reflections collected / unique	21188 / 6168 [R(int)[a] =0.0909]
	Reflections [I>2σ]	4164
	Completeness to theta_max	0.972
	Absorption correction type	multi-scan
	Max. and min. transmission	0.988, 0.506
	Refinement method	Full-matrix least-squares on F^2
	Data / restraints / parameters	6168 / 0 / 353
	[b]S (Goodness-of-fit)	1.025
	Final *R* indices [I>2σ]	*R*1[c] = 0.0893, *wR*2[d] = 0.2275
	R indices (all data)	*R*1[c] = 0.1244, *wR*2[d] = 0.2646
	Largest diff. peak and hole	0.739 and -0.743 $e^-.Å^{-3}$

X-Ray structure of Ru-1b

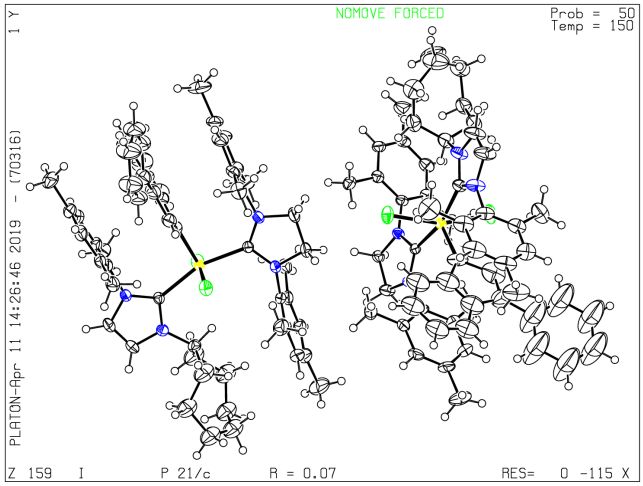


Table S2**: Crystal data and structure refinement for Ru-**1b

Empirical formula		*$C_{56}H_{64}Cl_2N_4Ru$*
	Formula weight	*965.08 g/mol*
	Temperature	*150 K*
	Wavelength	*0.71073 Å*
	Crystal system, space group	*monoclinic, P $2_1/c$*
	Unit cell dimensions	*a = 19.709(2) Å*
		b = 35.361(4) Å
		c = 16.4229(17) Å
		α = 90 °
		β = 104.021(4) °
		γ = 90 °
	Volume	*11105(2) $Å^3$*
	Z, Calculated density	*8, 1.155 $g.cm^{-3}$*
	Absorption coefficient	*0.415 mm^{-1}*
	F(000)	*4048*
	Crystal size	*0.320 x 0.210 x 0.160 mm*
	Crystal color	*red*
	Theta range for data collection	*2.149 to 27.510 °*
	h_min, h_max	*-25, 25*
	k_min, k_max	*-45, 45*
	l_min, l_max	*-21, 21*
	Reflections collected / unique	*97591 / 25363 [R(int)[a]=0.0372]*
	Reflections [I>2σ]	*21968*
	Completeness to theta_max	*0.993*
	Absorption correction type	*multi-scan*
	Max. and min. transmission	*0.936, 0.791*
	Refinement method	*Full-matrix least-squares on F^2*
	Data / restraints / parameters	*25363 / 2 / 1016*
	[b]S (Goodness-of-fit)	*1.036*
	Final R indices [I>2σ]	*R1[c] = 0.0745, wR2[d] = 0.1900*
	R indices (all data)	*R1[c] = 0.0843, wR2[d] = 0.1981*
	Largest diff. peak and hole	*2.850 and -1.597 $e^-.Å^{-3}$*

X-Ray structure of complexe Ru-2a

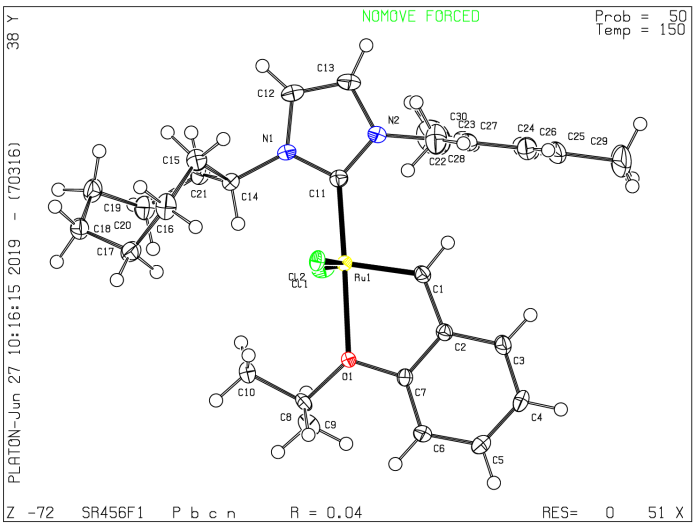


Table S3: Crystal data and structure refinement for Ru-2a

Empirical formula	$C_{30}H_{40}Cl_2N_2ORu$
Formula weight	616.61 g/mol
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *P b c n*
Unit cell dimensions	a = 11.8611(19) Å
	b = 14.803(2) Å
	c = 33.715(4) Å
	α = 90 °
	β = 90 °
	γ = 90 °
Volume	5919.6(14) $Å^3$
Z, Calculated density	8, 1.384 $g.cm^{-3}$
Absorption coefficient	0.735 mm^{-1}
F(000)	2560
Crystal size	0.460 x 0.260 x 0.090 mm
Crystal color	black
Theta range for data collection	2.965 to 27.481 °
h_min, h_max	-15, 13
k_min, k_max	-19, 18
l_min, l_max,	-41, 43
Reflections collected / unique	51163 / 6766 [R(int)[a] = 0.0352]
Reflections [I>2σ]	6113
Completeness to theta_max	0.996
Absorption correction type	multi-scan
Max. and min. transmission	0.936, 0.773
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6766 / 0 / 330
[b]S (Goodness-of-fit)	1.143
Final *R* indices [I>2σ]	$R1^c$ = 0.0373, $wR2^d$ = 0.0879
R indices (all data)	$R1^c$ = 0.0429, $wR2^d$ = 0.0903
Largest diff. peak and hole	0.889 and -0.818 $e^-.Å^{-3}$

X-Ray structure of complexe Au-1a

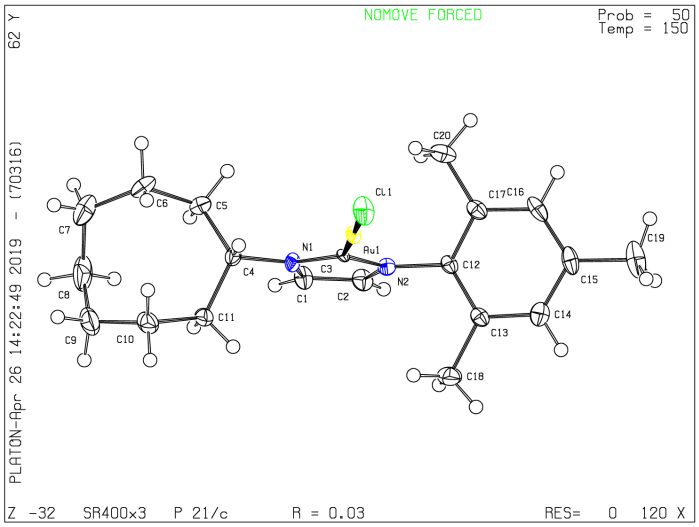


Table S4: Crystal data and structure refinement for Au-1a

Empirical formula	$C_{20}H_{28}AuClN_2$
Formula weight	528.86 g/mol
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *P* $2_1/c$
Unit cell dimensions	a = 9.5726(16) Å b = 10.5813(19) Å c = 20.181(3) Å α = 90 ° β = 97.631(6) ° γ = 90 °
Volume	2026.1(6) $Å^3$
Z, Calculated density	4, 1.734 $g.cm^{-3}$
Absorption coefficient	7.397 mm^{-1}
F(000)	1032
Crystal size	0.500 x 0.290 x 0.170 mm
Crystal color	grey
Theta range for data collection	2.962 to 27.485 °
h_min, h_max	-12, 12
k_min, k_max	-13, 12
l_min, l_max	-24, 26
Reflections collected / unique	16293 / 4623 [R(int)[a] = 0.0502]
Reflections [I>2σ]	4182
Completeness to theta_max	0.991
Absorption correction type	multi-scan
Max. and min. transmission	0.284, 0.108
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4623 / 0 / 220
[b]S (Goodness-of-fit)	1.130
Final *R* indices [I>2σ]	$R1^c$ = 0.0306, $wR2^d$ = 0.0677
R indices (all data)	$R1^c$ = 0.0358, $wR2^d$ = 0.0695
Largest diff. peak and hole	1.116 and -2.205 $e^-.Å^{-3}$