Electronic Supplementary Material (ESI) for Dalton Transactions.

Cyclic (amino)(barrelene)carbene Ru-complexes: synthesis and reactivity in olefin metathesis

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Table of contents

1 Experimental

1.1 General information

All commercial reagents were used as purchased and without further purification, unless otherwise mentioned. Diethyl diallylmalonate (DEDAM) was passed through alumina and distilled and degassed prior to use. Cyclic (amino) (barrelene) carbenes (CABC) were prepared accordingly to the previous report.[1] For the synthesis of CABC salts, all reactions were performed under an atmosphere of argon using standard Schlenk techniques or glovebox when mentioned. Toluene, tetrahydrofuran, dichloromethane and diethyl ether used for complex synthesis and catalysis, were purified using MBraun Solvent Purification Systems; all other used solvents were dried and degassed using standard procedures. Catalysis reactions were performed under Argon atmosphere using standard Schlenk techniques or in a glove box when mentioned. Reactions at elevated temperature were maintained by thermostatically controlled oil-baths. A temperature of 0 °C was obtained with an ice slush bath and −50 °C or −78 °C were obtained with a mixture of acetone and liquid nitrogen bath. Reactions were monitored by thin-layer chromatography (TLC) carried out on aluminum backed silica gel 60 (F254) plates from MERCK (grain-size distribution 60/20 μm); visualized using 254 nm UV light and $KMnO_4$ in water for staining. Purifications were performed by column chromatography with silica gel (spherical, particle size 40 μm, neutral) purchased from Sigma-Aldrich. The eluents employed are reported as volume (volume ratios). The required amounts of [Ru] were taken prior each reaction from freshly prepared stock solutions. All the reactions were quenched with ethylvinyl ether (EVE). Multinuclear NMR spectra were recorded on a Bruker (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz) spectrometer with complete proton decoupling for nucleus other than ^{1}H. Chemical shifts are reported in parts per million (ppm), coupling constants (*J*) are reported in Hertz (Hz). 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, C_6D_6 ^{1}H: δ 7.16 ppm, ^{13}C: δ 128.06 ppm). Multiplicities in ^{1}H NMR are reported using following abbreviations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. GC-MS spectra have been performed on SH-Rxi-5ms column (30.0 m x 0.25 mm ID; 0.25 μm thickness) (Shimadzu) using two different methods. For Ru complexes and catalysis products, HRMS were recorded on a Waters QTof-I spectrometer using ESI at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. X-Ray crystallography: Intensity data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON

100 detector using MoKα radiation (0.71073 Å) at T = 150 K. Data reduction was performed using the SHELXT program. The structures were resolved using the software SHELXS-97 by the direct methods and refined using SHELXL-2013-4. The CIF files of complexes Ru-4a-d have been deposited with CCDC numbers:

Ru-4a CCDC 2260084

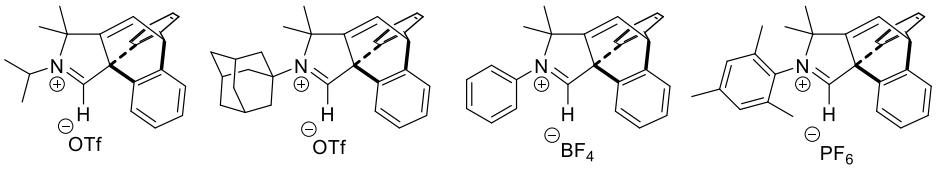
Ru-4b CCDC 2253659

Ru-4c CCDC 2253660

Ru-4d CCDC 2253658

Ru-4f CCDC 2256504

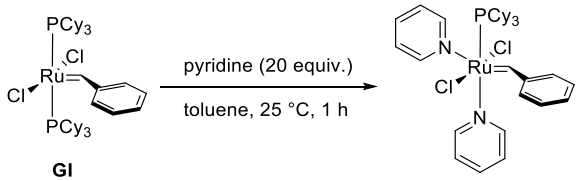
1.2 Synthesis of CABC salts



CABC(a).OTf **CABC(b).OTf** **CABC(c).BF_4** **CABC(d).PF_6**

The salts **CABC(a-c).X** were prepared according to the previously published procedure,[1] involving subsequent [4+2] intramolecular cycloaddition, alkylation/arylation and anion exchange. For **CABC(d).X**, an alternative approach described in the same publication was used. The obtained salts were pre-treated at 100 °C for 16 hours under high *vacuum* and then introduced to Ar-filled glovebox.

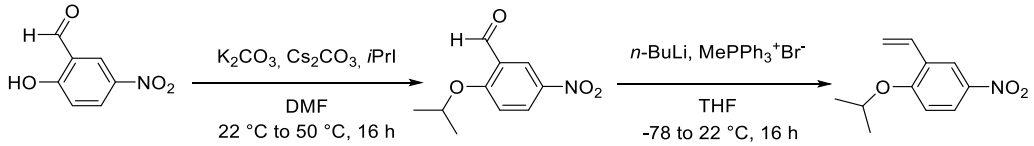
1.3 Synthesis of Pyr-GI



GI **Pyr-GI**

Pyr-GI phosphine complex was prepared according to the previously published procedure by ligand exchange starting from the **GI** (>90% yield).[2]

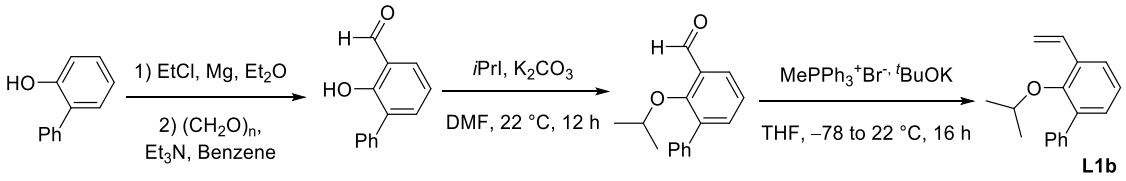
1.4 Synthesis of styrene derivative L1a



L1a

Styrene derivative **L1a** was synthetized following a previously published two step procedure starting from 2-hydroxy-5-nitrobenzaldehyde by subsequent O-alkylation and Wittig olefination.[3]

1.5 **Synthesis of styrene derivative L1b**

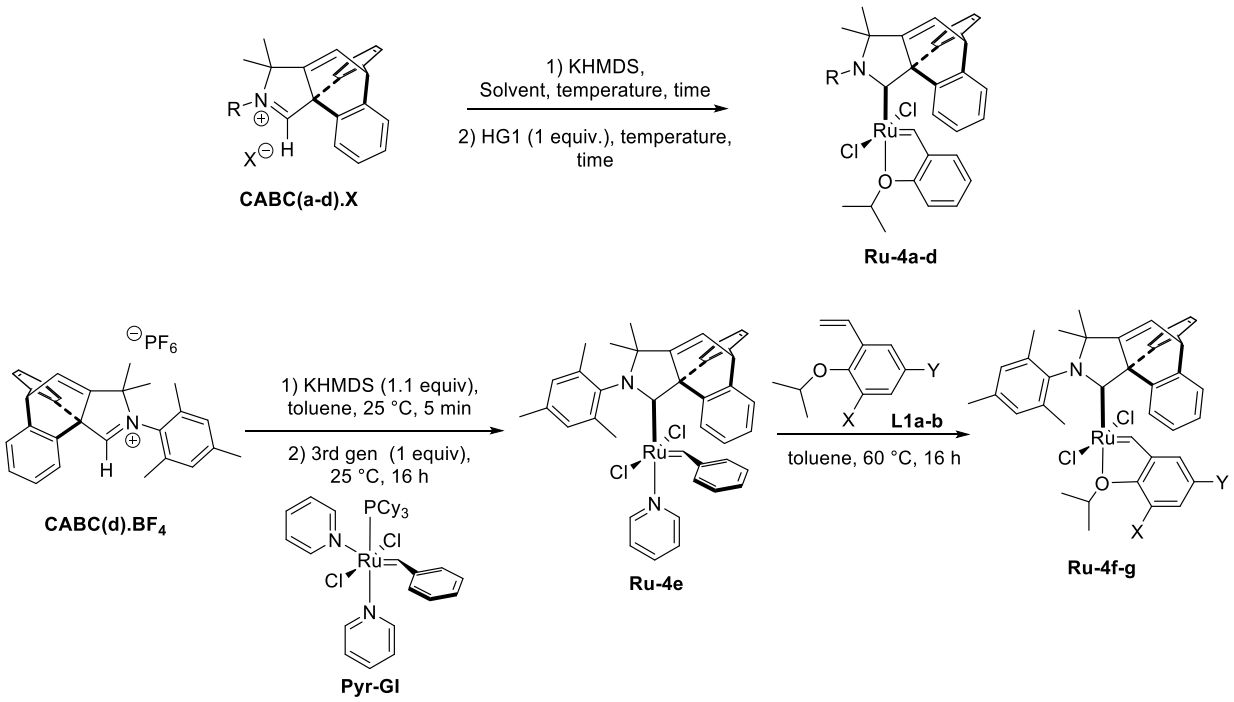


L1b

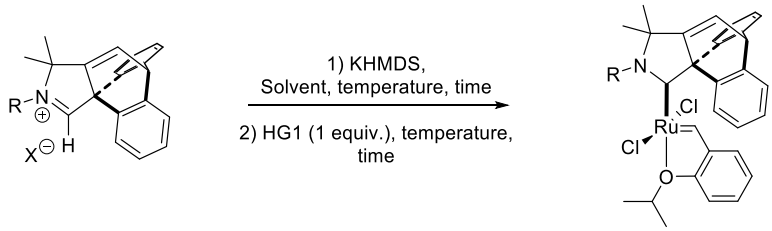
Styrene derivative **L1b** was synthetized following a previously published three step procedure starting from [1,1'-biphenyl]-2-ol by subsequent formylation, O-alkylation and Wittig olefination.[4]

2 Complexes synthesis

2.1.1 General scheme of synthesis



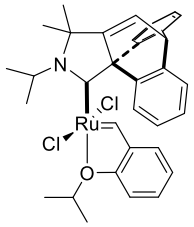
2.1.2 General procedure for CABC Hoveyda type complexes



Procedure A: In an Ar-filled glove box, CABC salt (1.5 equiv.) was dissolved in solvent of choice. KHMDS (1.6 equiv.) was added. The mixture was allowed to stir for the indicated time at 25 °C. To this mixture, Hoveyda-Grubbs 1st generation complex (HG1) (1 equiv.) was added and the mixture was stirred the indicated time at 25 °C. The solvent was removed under *vacuum* and the product was purified by column chromatography (eluent: toluene). The solid was further diluted in dichloromethane and precipitated in hexane.

Procedure B: In an Ar-filled glove box, CABC salt (1.5 equiv.), KHMDS (1.6 equiv.) and HG1 (1 equiv.) were charged in an oven-dried Schlenk tube which was further cooled to −78 °C outside the glovebox. The appropriate amount of THF, previously cooled to −78 °C was cannulated to the Schlenk tube. The mixture was stirred for 16 hours and allowed to warm up to 25 °C. The solvent was removed under *vacuum* and the product was purified by column chromatography (eluent: toluene). The solid was further diluted in dichloromethane and precipitated in hexane.

2.1.2.1 *N*-isopropyl CABC Hoveyda type Ru complex (Ru-4a)



Chemical Formula: $C_{33}H_{35}Cl_2NORu$
Exact Mass: 633,11

Ru-4a was prepared according to the procedure **B**, with **CABC(a).OTf** (102.3 mg, 0.244 mmol, 1.5 equiv.), THF (1.5 mL), KHMDS (56.0 mg, 0.281 mmol, 1.6 equiv.), and HG-1 complex (102.5 mg, 0.171 mmol, 1.0 equiv.). The desired product was obtained after purification (eluent: pentane/acetone 9:1) as a brown solid (27.7 mg, 26 % yield).

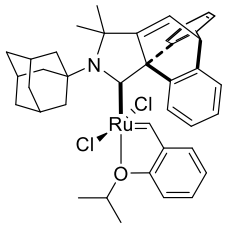
^{1}H NMR (400 MHz, $CDCl_3$) δ 18.02 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.60 (m, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.96 (td, *J* = 7.4, 1.1 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.78 (td, *J* = 7.6, 1.3 Hz, 2H), 6.65 (d, *J* = 6.0 Hz, 1H), 5.98 (sept, *J* = 6.7 Hz, 1H), 5.38 (sept, *J* = 6.2 Hz, 1H), 5.22 (d, *J* = 6.0 Hz, 1H), 2.05 – 1.94 (m, 12H), 1.49 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 295.2 - 294.8, 258.3, 161.2, 154.8, 146.6, 145.4, 142.9, 142.8, 131.2, 126.8, 124.7, 124.6, 124.2, 123.6, 122.7, 122.3, 113.4, 75.3, 73.9, 73.4, 62.5, 51.9, 31.9, 25.0, 22.4.

HRMS/ESI for **(**C_{36} H_{33} N O $^{35}Cl_2$ ^{102}Ru**)** (M+.): calc.: 633.11337, found: 633.1135.

X-ray diffraction: CCDC 2260084

2.1.2.2 *N*-Adamantyl CABC Hoveyda type Ru complex (Ru-4b)



Chemical Formula: $C_{40}H_{43}Cl_2NORu$
Exact Mass: 725,18

Ru-4b was prepared according to the procedure **A** for the room temperature stable carbenes complexes synthesis with **CABC(b).OTf** (198 mg, 0.356 mmol, 1.05 equiv.), toluene (3 mL), KHMDS (108 mg, 0.541 mmol, 1.6 equiv.), and HG-1 complex (200 mg, 0.333 mmol, 1.0 equiv.). The salt was deprotonated during 30 minutes at 25 °C, followed by 2 hours of stirring with HG1 at 25°C. The desired product was obtained after purification (eluent: toluene) as a green solid (179.7 mg, 74 % yield).

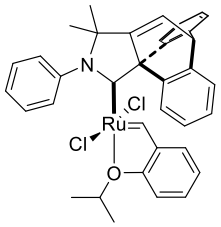
^{1}H NMR (400 MHz, $CDCl_3$) δ 18.49 (s, 1H), 8.21 – 8.14 (m, 2H), 7.66 – 7.57 (m, 1H), 7.35 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.02 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.95 (td, *J* = 7.4, 1.1 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.76 (td, *J* = 7.6, 1.4 Hz, 2H), 6.63 (d, *J* = 6.0 Hz, 1H), 5.28 (hept, *J* = 6.2 Hz, 1H), 5.19 (d, *J* = 6.0 Hz, 1H), 3.28 – 3.24 (m, 6H), 2.51 (s, 3H), 2.08 (m, 3H), 1.88 (m, 8H), 1.83 (m, 1H), 1.58 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 313.0 – 312.8, 259.6, 161.3, 155.6, 147.9, 145.3, 143.7, 132.6, 127.2, 125.4, 124.8, 124.6, 124.4, 122.3, 122.2, 113.7, 75.8, 75.1, 74.6, 66.7, 52.0, 35.8, 33.6, 31.1, 22.8.

HRMS/ESI for (C_{40} H_{43} N O $^{35}Cl_2$ ^{102}Ru) (M+.): calc.: 725.1759, found : 725.1758.

X-ray diffraction: CCDC 2253659

2.1.2.3 *N*-Phenyl CABC Hoveyda type Ru complex (Ru-4c)



Chemical Formula: $C_{36}H_{33}Cl_2NORu$
Exact Mass: 667,10

Ru-4c was prepared according to procedure **B** with **CABC(c).BF$_4$** (217.4 mg, 0.500 mmol, 1.5 equiv.), THF (3 mL), KHMDS (106.3 mg, 0.533 mmol, 1.6 equiv.), and HG1 complex (200.0 mg, 0.333 mmol, 1.0 equiv.). The reaction time was modified: after the addition of THF in the mixture, it was stirred for one hour during which time the temperature increased from -78°C to approximately -50°C, before removal from the acetone bath. The mixture was stirred for one more hour at 25°C. The desired product was obtained after purification (eluent: toluene) as a brown solid (127.6 mg, 62 % yield).

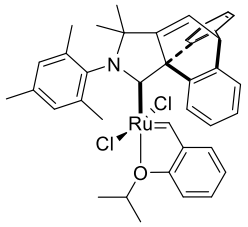
^{1}H NMR (400 MHz, $CDCl_3$) δ 18.19 (d, *J* = 0.8 Hz, 1H), 8.00 – 7.92 (m, 4H), 7.67 – 7.53 (m, 4H), 7.41 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.24 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.08 – 6.95 (m, 3H), 6.93 – 6.79 (m, 4H), 5.32 – 5.26 (m, 1H), 5.18 (sept, *J* = 6.1 Hz, 1H), 1.50 (d, *J* = 6.1 Hz, 6H), 1.31 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 298.6 – 298.4, 262.3, 158.6, 154.9, 146.8, 145.3, 143.2, 137.2, 134.2, 131.4, 129.9, 128.9, 128.5, 128.1, 124.9, 124.8, 124.1, 123.4, 122.9, 122.8, 122.2, 113.3, 75.6, 74.9, 73.5, 52.0, 43.6, 29.4, 21.7.

HRMS/ESI for **(**C_{36} H_{33} N O $^{35}Cl_2$ ^{102}Ru**)** (M+.): calc.: 667.09772, found: 667.0979.

X-ray diffraction: CCDC 2253660

2.1.2.4 *N*-Mesityl CABC Hoveyda type Ru complex (Ru-4d)



Chemical Formula: $C_{39}H_{39}Cl_2NORu$
Exact Mass: 709,15

Ru-4d was prepared according to the procedure **A**, using **CABC(d).PF$_6$** (106.7 mg, 0.2 mmol, 1.3 equiv.), THF (2 mL), KHMDS (39.7 mg, 0.2 mmol, 1.3 equiv.), and HG1 (95.7 mg, 0.16 mmol, 1.0 equiv.). The mixture was stirred for 2 hours at 25 °C. The desired product was obtained after purification (eluent: toluene) as a green solid (92 mg, 78 % yield).

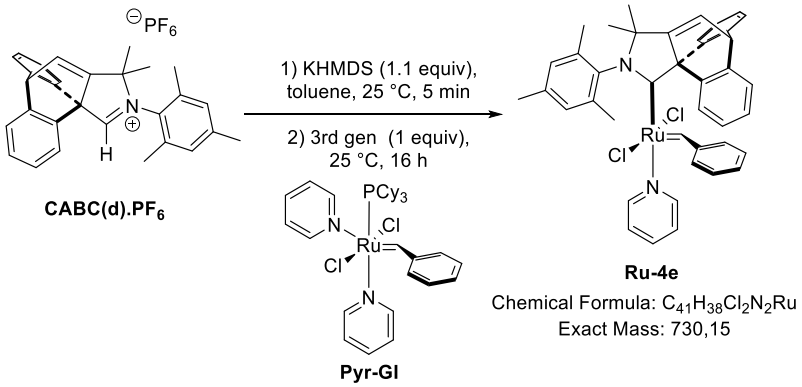
^{1}H NMR (400 MHz, $CDCl_3$) δ 18.17 (s, 1H), 8.03 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.41 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.25 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.16 (s, 2H), 7.08 – 6.97 (m, 3H), 6.94 – 6.79 (m, 3H), 6.81 (d, *J* = 6.0 Hz, 1H), 5.28 (d, *J* = 6.0 Hz, 1H), 5.13 (sept, *J* = 6.1 Hz, 1H), 2.44 (s, 6H), 2.41 (s, 3H), 1.53 (d, *J* = 6.1 Hz, 6H), 1.34 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 297.6 – 297.3, 266.9, 159.4, 154.9, 147.3, 145.4, 143.7, 139.4, 139.0, 135.9, 131.5, 130.6, 127.8, 124.8, 124.7, 124.2, 123.9, 122.8, 121.9, 113.4, 75.7, 75.5, 52.1, 31.7, 30.7, 25.1, 21.6, 21.1.

HRMS/ESI for **(**C_{39} H_{39} N O $^{35}Cl_2$ ^{102}Ru**)** (M+.): calc.: 709.1446, found: 709.1449.

X-ray diffraction: CCDC 2253658

2.1.3 Synthesis of *N*-Mesityl CABC CHPh Pyridine Ru complex (Ru-4e)

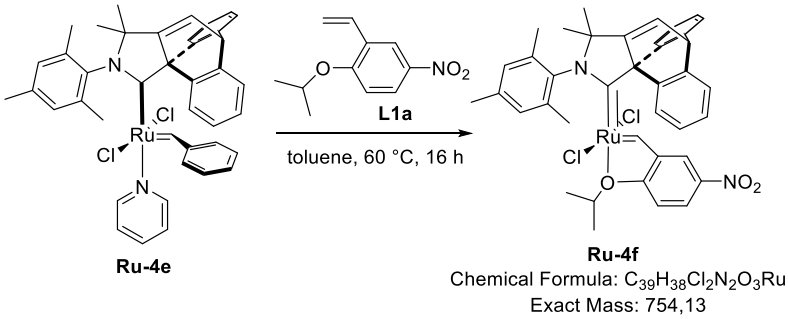


In an Ar-filled glove box, **CABC(d).PF$_6$** (206 mg, 0.385 mmol, 1.1 equiv.) was dissolved in Toluene (3 mL) in an oven-dried Schlenk tube with KHMDS (84 mg, 0.421 mmol, 1.2 equiv.). The mixture was allowed to stir for 5 minutes at 25 °C. **Pyr-GI** (243 mg, 0.347 mmol, 1.0 equiv.), prepared according to previously reported procedure starting from Grubbs I and excess pyridine in toluene, was then added.[2] The reaction was stirred for 16 hours at 25°C in the glovebox. The mixture was filtered, concentrated to a minimum volume of toluene and then purified by precipitation in pentane (ca. 10 volumes of pentane/volume of toluene) followed by washing with pentane to afford **Ru-4e** as a dark green solid (213 mg, 84% yield).

^{1}H NMR (400 MHz, C_6D_6) δ 20.92 (s, 1H), 9.09 (d, *J* = 7.6 Hz, 2H), 8.55 – 8.44 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.04 – 6.92 (m, 5H), 6.88 (t, *J* = 7.3 Hz, 2H), 6.67 (t, *J* = 7.6 Hz, 2H), 6.58 (t, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 6.0 Hz, 1H), 6.26 (t, *J* = 6.6 Hz, 2H), 4.95 (d, *J* = 6.0 Hz, 1H), 2.68 (s, 6H), 2.14 (s, 3H), 1.04 (s, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 315.7, 270.8, 159.6, 153.5, 152.8, 147.9, 145.6, 139.4, 138.8, 136.3, 136.0, 131.0, 129.8, 128.9, 125.5, 125.2, 124.9, 123.1, 122.9, 78.5, 77.3, 52.6, 30.2, 25.6, 21.0.

2.1.4 Synthesis of *N*-Mesityl CABC Grela type Ru complex (Ru-4f)



In an Ar-filled glove box, **Ru-4e** complex (50 mg, 0.068 mmol, 1.0 equiv.) was dissolved in dry and degassed Toluene (2 mL) in an oven-dried Schlenk tube, then Styrenyl **L1a** (17 mg, 0.082 mmol, 1.2 equiv.) was added and allowed to stir during 16 hours at 60°C outside of the glovebox. The mixture was purified by column chromatography (eluent: toluene), then washed with Hexane afford **Ru-4f** as a green solid (21 mg, 40% yield).

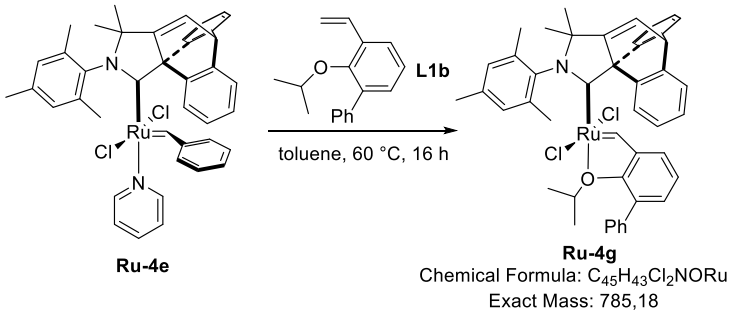
^{1}H NMR (400 MHz, $CDCl_3$) δ 18.24 (s, 1H), 8.50 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.11 (d, *J* = 2.7 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.17 (s, 2H), 7.11 (d, *J* = 9.2 Hz, 1H), 7.03 (td, *J* = 7.5, 1.1 Hz, 2H), 6.82 (td, *J* = 7.6, 1.3 Hz, 2H), 6.77 (d, *J* = 6.0 Hz, 1H), 5.31 (d, *J* = 6.0 Hz, 1H), 5.22 (sept, *J* = 6.2 Hz, 1H), 2.43 (s, 6H), 2.41 (s, 3H), 1.55 (d, *J* = 6.1 Hz, 6H), 1.34 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 292.2, 264.1, 158.9, 158.8, 147.0, 145.3, 143.0, 142.7, 139.3, 139.2, 135.5, 130.7, 128.2, 125.9, 125.2, 124.8, 123.7, 123.1, 118.5, 113.4, 78.1, 77.8, 75.6, 52.1, 30.7, 25.1, 21.6, 21.1.

X-ray diffraction: CCDC 2256504

HRMS/ESI for **(**C_{39} H_{38} N_2 O_3 $^{35}Cl_2$ ^{102}Ru**)** (M+.): calc.: 754.12975, found: 754.1301.

2.1.5 Synthesis of *N*-Mesityl CABC Blechert type Ru complex (Ru-4g)



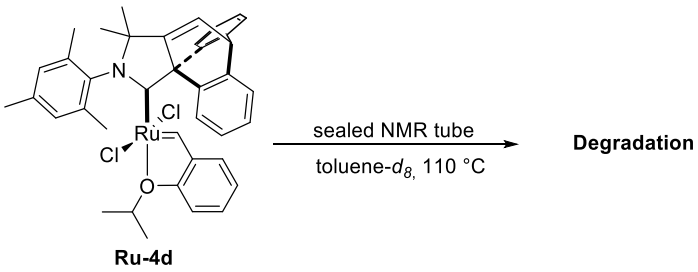
In an Ar-filled glove box, **Ru-4e** complex (213 mg, 0.29 mmol, 1.0 equiv.) was dissolved in Toluene (4 mL) in an oven-dried Schlenk tube, then Styrenyl **L1b** (84 mg, 0.35 mmol, 1.2 equiv.) was added and allowed to stir for 16 hours at 60 °C outside of the glovebox. The mixture was purified by column chromatography (eluent: toluene), then washed with Hexane to afford **Ru-4g** as a green solid (135 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 18.33 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 5H), 7.19 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.14 (s, 2H), 7.01 (td, *J* = 7.3, 1.1 Hz, 2H), 6.96 – 6.83 (m, 3H), 6.76 (d, *J* = 6.0 Hz, 1H), 5.28 (d, *J* = 6.0 Hz, 1H), 4.72 (sept, *J* = 6.3 Hz, 1H), 2.46 (s, 6H), 2.36 (s, 3H), 1.54 (s, 1H), 1.35 (s, 6H), 1.14 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 299.3, 266.9, 159.4, 151.7, 147.3, 146.3, 145.4, 140.0, 139.4, 139.1, 135.8, 135.7, 131.2, 130.6, 129.6, 128.4, 127.9, 127.7, 124.8, 124.7, 124.3, 123.7, 122.8, 122.5, 77.9, 75.8, 52.1, 30.8, 25.1, 21.1, 21.0.

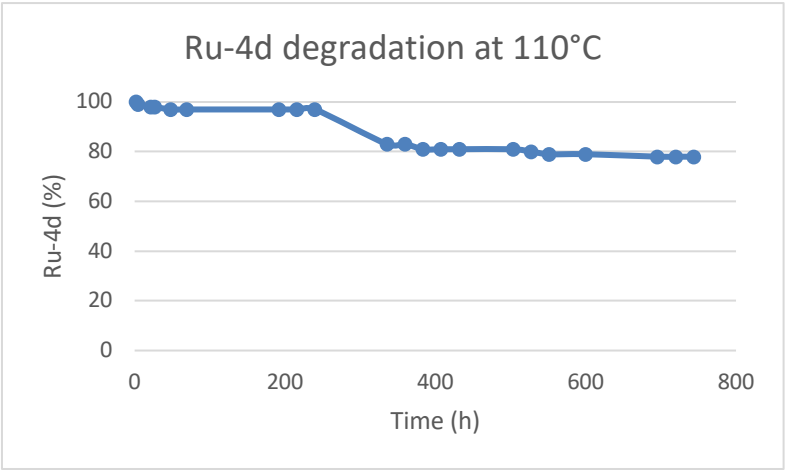
HRMS/ESI for **(**C_{45} H_{43} N O $^{35}Cl_2$ ^{102}Ru**)** (M+.): calc.: 785.17597, found: 785.1760 (0 ppm).

2.2 Thermal Stability of Ru-4d

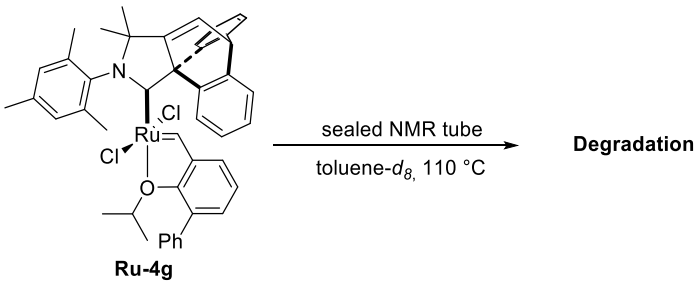


In a Wilmaud® tube equipped with J Young valve, The **Ru-4d** complex (15.2 mg, 0.021 mmol, 1.0 equiv.) was dissolved in dry and degassed toluene–d_8 (0.5 mL) and 1,3,5-trimethoxybenzene (ca. 2 mg, 0.0118 mmol, 3.3 equiv.) as an internal standard were introduced in the reaction mixture, which was heated at 110°C. The resulting solution was held at 110 °C and monitored by ^{1}H-NMR over time.

Time (h)	Ru-4d (%)
2	100
5	99
22	98
27	98
48	97
70	97
192	97
216	97
240	97
336	83
360	83
384	81
408	81
432	81
504	81
528	80
552	79
600	79
696	78
720	78
744	78



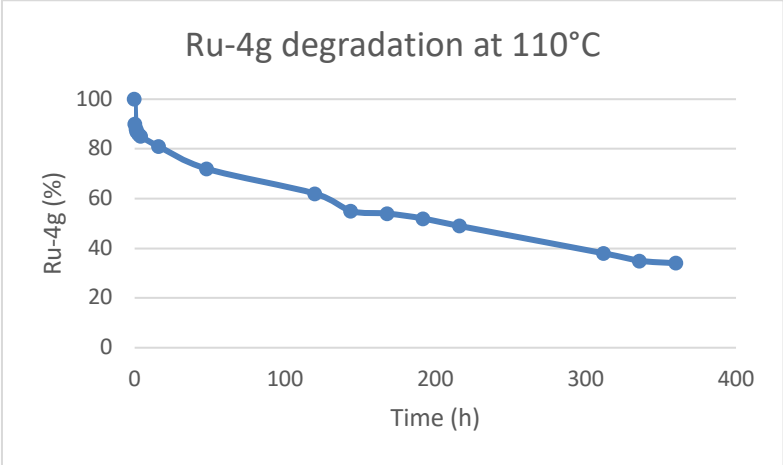
2.3 Thermal Stability of Ru-4g



Ru-4g

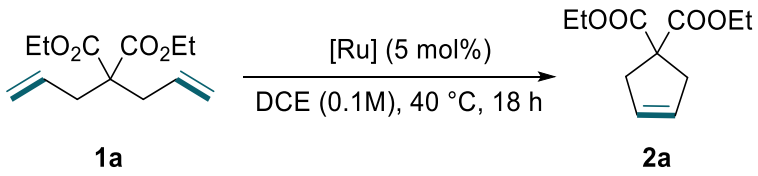
In a standard NMR tube, The **Ru-4g** complex (15 mg, 0.019 mmol, 1.0 equiv.) was dissolved in toluene–d_8 (0.5 mL) and 1,3,5-trimethoxybenzene (15.3 mg, 0.091 mmol, 5 equiv.) as an internal standard were introduced in the reaction mixture, which was heated at 110°C. The resulting solution was held at 110 °C and monitored by ^{1}H-NMR over time.

Time (h)	Ru-4d (%)
0	100
0.5	90
1	88
1.5	87
3	86
4	85
16	81
48	72
120	62
144	55
168	54
192	52
216	49
312	38
336	35
360	34



2.4 Evaluation of the complexes in catalysis

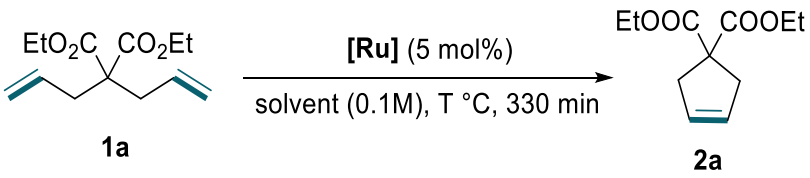
2.5 Ring-Closing Metathesis: Optimization Conditions



Into an Ar-filled glovebox, an oven-dried vial was charged with diethyl diallylmalonate **1a** (0.165 mmol, 40 µL, 1.0 equiv.) and 1,3,5-trimethoxybenzene as internal standard (0.055 or 0.068 mmol, 9.2 or 11.4 mg, 0.33 or 4.0 equiv.), diluted in dry and degassed DCE (1.7 mL in total with [Ru] solution). The [Ru] complex (5 mol%) was dissolved in DCE (1.0 mL) and the appropriate volume introduced in the reaction mixture, which was further stirred at 40 °C for 18 hours. The completion reaction completion was monitored by ^{1}H-NMR.

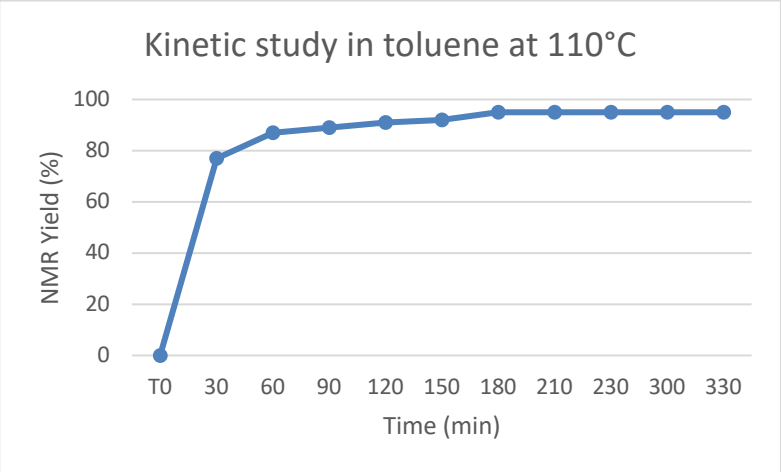
Entry	Catalyst	NMR conversion [%]	NMR Yield [%]
1	Ru-4a	5	1
2	Ru-4b	3	2
3	Ru-4c	7	5
4	Ru-4d	9	7
5	Ru-4e	45	41
6	Ru-4f	14	13
7	Ru-4g	75	73

2.5.1 Kinetic studies

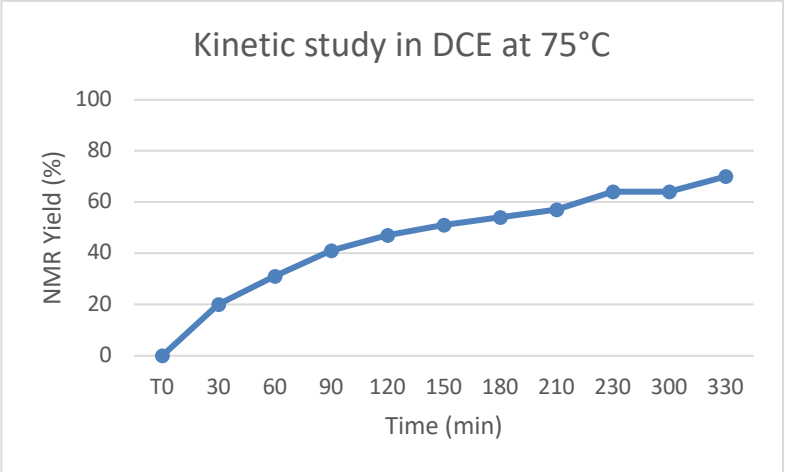


Diethyl diallylmalonate **1a** (0.17 mmol, 42 µL, 1.0 equiv.) and a solution of **Ru-4g** (0.0085 mmol, 6.6 mg, 5 mol%) in Dichloroethane or toluene were charged, under continuous Ar flow, into an oven-dried Wilmaud® NMR tube. The reaction was kept for 330 minutes at 75 or 110 °C and analyzed each 30 minutes at the ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.17 mmol, 28.8 mg, 1 equiv.).

Time (min)	Yield (%)
T0	0
30	77
60	87
90	89
120	91
150	92
180	95
210	95
230	95
300	95
330	95

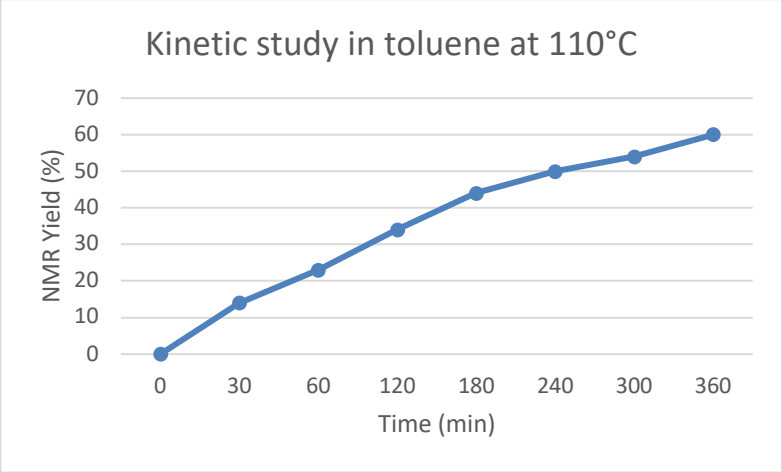


Time (min)	Yield (%)
T0	0
30	20
60	31
90	41
120	47
150	51
180	54
210	57
230	64
300	64
330	70



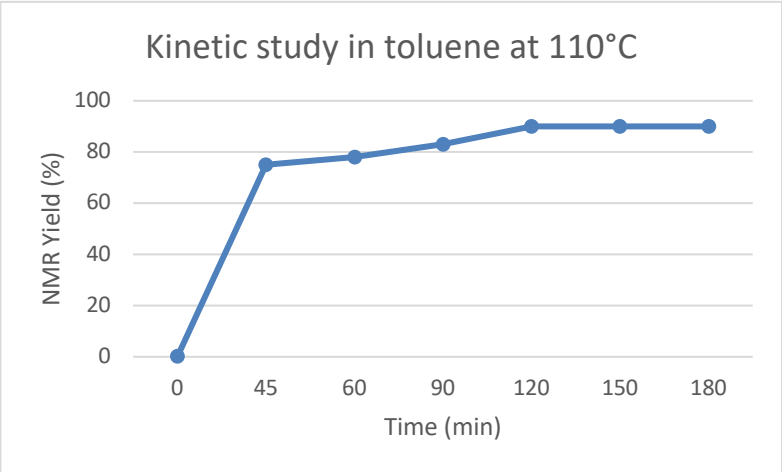
Diethyl diallylmalonate **1a** (0.17 mmol, 42 µL, 1.0 equiv.) and a solution of **Ru-4d** (0.0085 mmol, 6 mg, 5 mol%) in toluene were charged, under continuous Ar flow, into an oven-dried Wilmaud® NMR tube. The reaction was kept for 360 minutes at 110 °C and analyzed throughout the time at the ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.17 mmol, 28.8 mg, 1 equiv.).

Time (min)	Yield (%)
T0	0
30	14
60	23
120	34
180	44
240	50
300	54
360	60

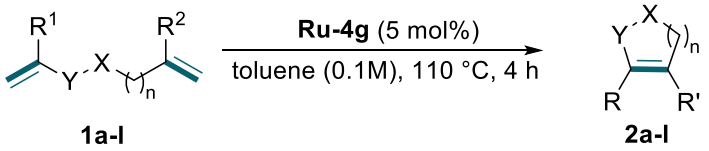


Diethyl diallylmalonate **1a** (0.12 mmol, 30 µL, 1.0 equiv.) and a solution of **Ru-4f** (0.0062 mmol, 4.6 mg, 5 mol%) in toluene–d_8 were charged, under continuous Ar flow, into an oven-dried Wilmaud® NMR tube. The reaction was kept for 3 hours at 110 °C and analyzed throughout the time at the ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard (0.12 mmol, 6.8 mg, 0.33 equiv.).

Time (min)	Yield (%)
T0	0
45	75
60	78
90	83
120	90
150	90
180	90



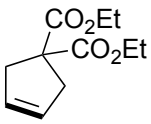
2.5.2 General procedure for ring closing metathesis reaction



1a-l **2a-l**

The substrate (0.1, 0.17 or 0.2 mmol, 1.0 equiv.) and a solution of catalyst **Ru-4g** (0.01 or 0.005 mmol, 7.8 or 3.9 mg, 5 mol%) in toluene (1, 1.7 or 2 mL) were sequentially loaded into an oven-dried vial. The reaction was stirred at 110 °C for 4 hours outside the glovebox then quenched with EVE. The final conversions and yields were measured by ^{1}H-NMR upon addition of 1,3,5-trimethoxybenzene as internal standard (IS; 0.066 or 0.1 mmol, 0.3 or 1.0 equiv.).

Diethyl cyclopent-3-ene-1,1-dicarboxylate (2a)

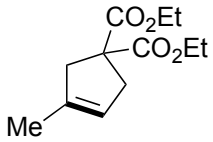


Chemical Formula: $C_{11}H_{16}O_4$
Molecular Weight: 212,24

The reaction was performed following the general procedure, stirring a solution of diethyl diallylmalonate **1a** (0.17 mmol, 41 mg, 1.0 equiv.) providing **diethyl cyclopent-3-ene-1,1-dicarboxylate (2a)** with 99% conversion and 97% NMR yield (IS = 0.17 mmol, 28.8 mg, 1.0 equiv.). The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, toluene–d_8) δ 5.69 – 5.61 (m, 2H), 4.19 (q, J = 7.1 Hz, 4H), 3.36 (s, 4H), 1.18 (t, J = 7.1 Hz, 6H).

diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (2b)

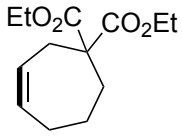


Chemical Formula: $C_{12}H_{18}O_4$
Molecular Weight: 226,27

The reaction was performed following the general procedure, stirring a solution of diethyl 2-allyl-2-(2-methylallyl)malonate **1b** (0.2 mmol, 49.8 mg, 1.0 equiv.) providing **diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (2b)** with 83% conversion and 79% NMR yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 – 5.15 (m, 1H), 4.19 (q, J = 7.1 Hz, 4H), 2.99 – 2.94 (m, 2H), 2.93 – 2.87 (m, 2H), 1.72 – 1.69 (m, 3H), 1.24 (t, J = 7.1Hz, 6H).

diethyl cyclohept-3-ene-1,1-dicarboxylate (2d)

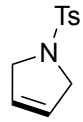


Chemical Formula: $C_{13}H_{20}O_4$
Molecular Weight: 240,30

The reaction was performed following the general procedure, stirring a solution of diethyl 2-allyl-2-(pent-4-en-1-yl)malonate **1d** (0.2 mmol, 53.7 mg, 1.0 equiv.), providing **diethyl cyclohept-3-ene-1,1-dicarboxylate (2d)** with 68% NMR yield. The data were consistent with the reported ones.[5].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.80 (m, 1H), 5.74 – 5.62 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 2.67 (d, *J* = 6.4 Hz, 2H), 2.27 – 2.21 (m, 2H), 2.18 – 2.16 (m, 2H), 1.65 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H).

1-tosyl-2,5-dihydro-1H-pyrrole (2e)

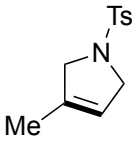


Chemical Formula: $C_{11}H_{13}NO_2S$
Molecular Weight: 223,29

The reaction was performed following the general procedure, stirring a solution of N,N-diallyl-tosylamide **1e** (0.2 mmol, 50.2 mg, 1.0 equiv.) providing **diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (2e)** with 78% isolated yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5, Hz, 2H), 7.37 – 7.29 (m, 2H), 5.62 (s, 2H), 4.11 (s, 4H), 2.40 (br s, *J* = 2.9 Hz, 3H).

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

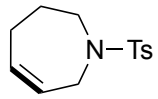


Chemical Formula: $C_{12}H_{15}NO_2S$
Molecular Weight: 237,32

The reaction was performed following the general procedure, stirring a solution of N-allyl-N-(2-methylallyl)tosylamide **1f** (0.2 mmol, 53.1 mg, 1.0 equiv.) providing **3-methyl-1-tosyl-2,5-dihydro-1H-pyrrole (2f)** with 72% isolated yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 2H), 7.39 – 7.37 (m, 2H), 5.23 – 5.21 (m, 1H), 4.08 – 4.06 (m, 2H), 4.00 – 3.98 (m, 2H), 2.41 (s, 3H), 1.64 (s, 3H).

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

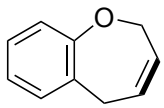


Chemical Formula: $C_{13}H_{17}NO_2S$
Molecular Weight: 251,34

The reaction was performed following the general procedure, stirring a solution of N-allyl N-allyl-N-(pent-4-en-1-yl)tosylamide **1h** (0.2 mmol, 55.9 mg, 1.0 equiv.) providing **1-tosyl-2,3,4,7-tetrahydro-1H-azepine (2h)** with 82% isolated yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.31 – 7.26 (m, 2H), 5.77 (dtt, *J* = 10.9, 5.4, 1.4 Hz, 1H), 5.65 (dtt, *J* = 11.3, 5.0, 1.5 Hz, 1H), 3.86 – 3.79 (m, 2H), 3.41 – 3.37 (m, 2H), 2.36 (s, 3H), 2.23 – 2.13 (m, 2H), 1.83 – 1.77 (m, 2H).

2,5-dihydrobenzo[b]oxepine (2i)

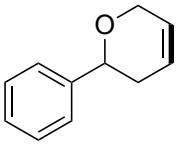


Chemical Formula: $C_{10}H_{10}O$
Molecular Weight: 146,19

The reaction was performed following the general procedure, stirring a solution of 1-allyl-2-(allyloxy)benzene **1i** (0.1 mmol, 17.4 mg, 1.0 equiv.), providing **2,5-dihydrobenzo[b]oxepine (2i)** with 83% NMR yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 1H), 7.14 – 6.97 (m, 3H), 5.86 (dtt, *J* = 11.5, 5.4, 2.2 Hz, 1H), 5.48 (dtt, *J* = 11.5, 3.0, 1.7 Hz, 1H), 4.64 – 4.55 (m, 2H), 3.50 – 3.48 (m, 2H).

2-phenyl-3,6-dihydro-2H-pyran (2j)

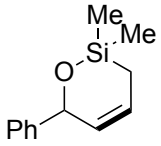


Chemical Formula: $C_{11}H_{12}O$
Molecular Weight: 160,22

The reaction was performed following the general procedure, stirring a solution of (1-(allyloxy)but-3-en-1-yl)benzene **1j** (0.1 mmol, 18.8 mg, 1.0 equiv.), providing **2-phenyl-3,6-dihydro-2H-pyran (2j)** with 81% NMR yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 5.98 – 5.88 (m, 1H), 5.86 – 5.78 (m, 1H), 4.56 (dd, *J* = 10.1, 3.6 Hz, 1H), 4.38 – 3.36 (m, 2H), 2.45 – 2.32 (m, 1H), 2.31 – 2.17 (m, 1H).

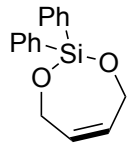
2,2-dimethyl-6-phenyl-3,6-dihydro-2H-1,2-oxasiline (2k)



Chemical Formula: $C_{12}H_{16}OSi$
Molecular Weight: 204,34

The reaction was performed following the general procedure, obtained from allyldimethyl((1-phenylallyl)oxy)silane **1k** (0.2 mmol, 46.5 mg, 1.0 equiv.) providing **2,2-dimethyl-6-phenyl-3,6-dihydro-2H-1,2-oxasiline (2k)** was with 22% NMR yield. NMR yield was attributed basing on the characteristic signal at 5.5 ppm (q, 1H). The data were consistent with the reported ones.[6]

2,2-diphenyl-4,7-dihydro-1,3,2-dioxasilepine (2l)

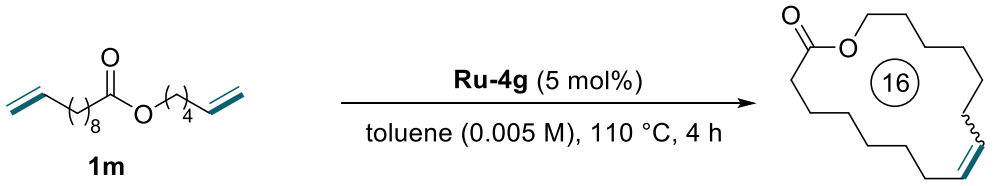


Chemical Formula: $C_{16}H_{16}O_2Si$
Molecular Weight: 268,39

The reaction was performed following the general procedure, stirring a solution of bis(allyloxy)diphenylsilane **1l** (0.2 mmol, 59.2 mg, 1.0 equiv.), providing **2,2-diphenyl-4,7-dihydro-1,3,2-dioxasilepine (2l)** with 35% NMR yield. The data were consistent with the reported literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 – 5.75 (m, 2H), 4.59 – 4.57 (m, 4H). Aromatic peaks fall into the toluene solvent peaks.

2.5.3 General procedure for macrocyclization



1m

2m

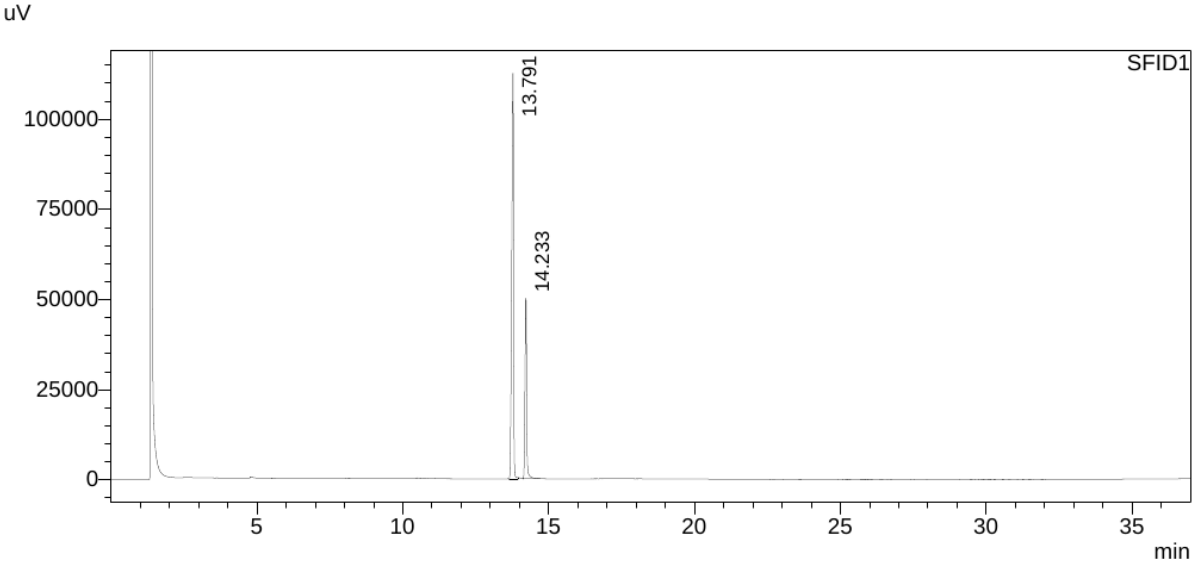
Chemical Formula: $C_{15}H_{26}O_2$

Molecular Weight: 238,37

Substrate hex-5-en-1-yl undec-10-enoate **1m** (84.7 mg, 0.318 mmol, 1.0 equiv.) and **Ru-4g** (5 mol%) were charged under continuous Ar flow into an oven-dried 100 mL Schlenk tube equipped with water refrigerator and solubilized in toluene (60 mL). The reaction was stirred at 110 °C for 4 hours then quenched with ethyl vinyl ether (EVE). The solvent was evaporated and the crude product was purified by chromatography on silica gel using pentane/diethyl ether = 95/5 as eluent to yield **oxacyclohexadec-9-en-2-one (2m)** with 65% isolated yield (49.3 mg). The data were consistent with the reported literature.[8] Selectivity and *E/Z* ratio were measured by GC analysis : *E/Z* 70/30, selectivity >99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ (*E/Z* isomers: 7/3) 5.54 – 5.30 (m, 2H), 4.27 – 4.12 (m, 2H), 2.42 – 2.34 (m, 2H), 2.11 (m, 4H), 1.78 – 1.64 (m, 4H), 1.53 – 1.27 (m, 12H).

<Chromatogram>



<Peak Table>

SFID1

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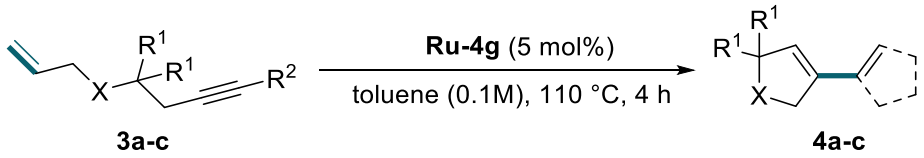
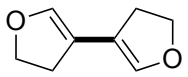
2	14.233	199732	49950	28.821			
Total		693018	162010				

2.5.4 General procedure for ring closing ene-yne metathesis



The substrate (0.1 or 0.2 mmol, 1.0 equiv.) and a solution of catalyst **Ru-4g** (0.01 or 0.005 mmol, 7.8 or 3.9 mg, 5 mol%) in toluene (1 or 2 mL) were sequentially loaded into an oven-dried vial. The reaction was stirred at 110 °C for 4 hours outside the glovebox then quenched with EVE. The final conversions and yields were measured by ^{1}H-NMR upon addition of 1,3,5-trimethoxybenzene as internal standard (IS; 0.066 or 0.1 mmol, 0.3 or 1.0 equiv.).

4,4',5,5'-tetrahydro-3,3'-bifuran (4a)

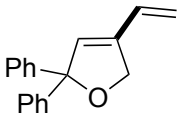


Chemical Formula: $C_8H_{10}O_2$
Molecular Weight: 138,17

The reaction was performed following the general procedure, stirring a solution of 1,4-bis(allyloxy)but-2-yne **3a** (0.1 mmol, 16.6 mg, 1.0 equiv.), providing **4,4',5,5'-tetrahydro-3,3'-bifuran (4a)** with 95% NMR yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 – 5.60 (m, 2H), 4.83 – 4.69 (m, 8H).

2,2-diphenyl-4-vinyl-2,5-dihydrofuran (4b)

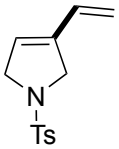


Chemical Formula: $C_{18}H_{16}O$
Molecular Weight: 248,32

The reaction was performed following the general procedure, stirring a solution of (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene **3b** (0.2 mmol, 49.6 mg, 1.0 equiv.), providing **2,2-diphenyl-4-vinyl-2,5-dihydrofuran (4b)** with 73% NMR yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 8H), 6.32 – 6.23 (m, 1H), 6.23 – 6.21 (m, 1H), 5.35 (d, J = 17.4 Hz, 1H), 5.13 (d, J = 11.1 Hz, 1H), 4.81 – 4.79 (m, 2H).

1-tosyl-3-vinyl-2,5-dihydro-1H-pyrrole (4c)

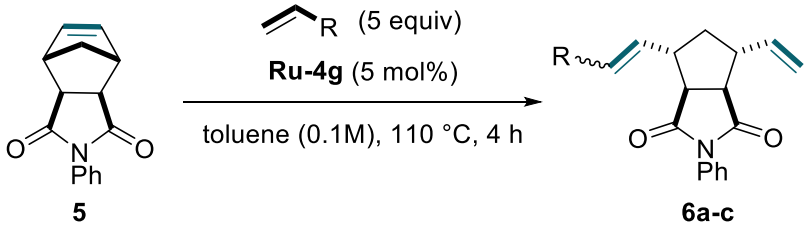


Chemical Formula: $C_{13}H_{15}NO_2S$
Molecular Weight: 249,33

The reaction was performed following the general procedure, stirring a solution of N-allyl-N-(prop-2-yn-1-yl)tosylamide **3c** (0.2 mmol, 49.8 mg, 1.0 equiv), providing **1-tosyl-3-vinyl-2,5-dihydro-1H-pyrrole (4c)** with 23% NMR yield. The data were consistent with the reported ones.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.27 (m, 2H), 6.39 – 6.31 (m, 1H), 5.58 – 5.54 (m, 1H), 5.15 (d, *J* = 11.4 Hz 1H), 5.01 (d, *J* = 17.6 Hz, 1H), 4.23 – 4.19 (m, 2H), 4.18 – 4.16 (m, 4H), 2.41 – 2.39 (m, 1H).

2.5.5 General Procedure for Ring-Opening Cross Metathesis



In an Ar-filled glovebox, the exo norbornene imide **5** (24 mg, 0.1 mmol, 1.0 equiv.) and the respective olefin (0.5 mmol, 5.0 equiv.) were charged into an oven-dried Schlenk tube and solubilized in toluene (0.1M). A solution of **Ru-4g** (0.005 mmol, 3.9 mg, 5 mol%) in toluene was added and the resulting solution stirred at 110 °C for 4 hours outside the glovebox. The mixture was quenched with EVE and the solvent evaporated under *vacuum*. Conversion and yield values were provided upon ^{1}H-NMR analysis of the crude in presence of 1,3,5-trimethoxybenzene as internal standard (0.1 mmol, 16.8 mg, 1.0 equiv.). The *E/Z* ratio was monitored by GC-MS.

Column Information: SH-Rxi-5ms (30.0 m x 0.25 mm ID; 0.25 µm thickness) (Shimadzu)

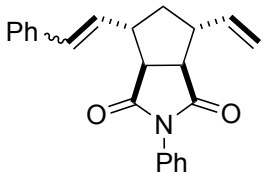
Carrier gas: Helium

Method: Linear velocity: constant = 40.0 cm/s

Temperature protocol:

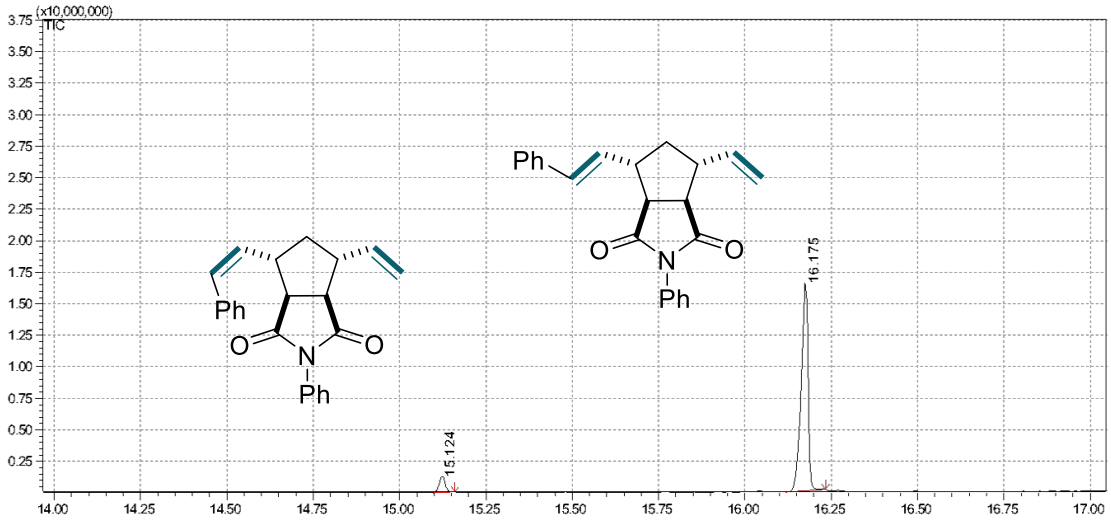
Rate [°C/min]	Temperature [°C]	Hold time [min]
-	80	0
15	300	20

2-phenyl-4-styryl-6-vinyltetrahydrocyclopenta[c]pyrrole-1,3(2H,3aH)-dione (6a)



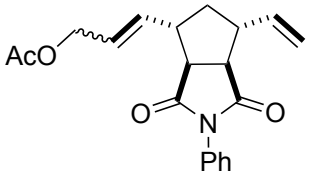
Chemical Formula: $C_{23}H_{21}NO_2$
Molecular Weight: 343,43

(6a) was obtained upon reaction with styrene (0.5 mmol, 60 µL, 5.0 equiv.) as olefin partner with 73% NMR yield, E/Z 95/5. Conversion and yield were attributed basing on the characteristic signal at 2.36 - 2.18 ppm (m, 1H). The data were consistent with the reported literature.[9]



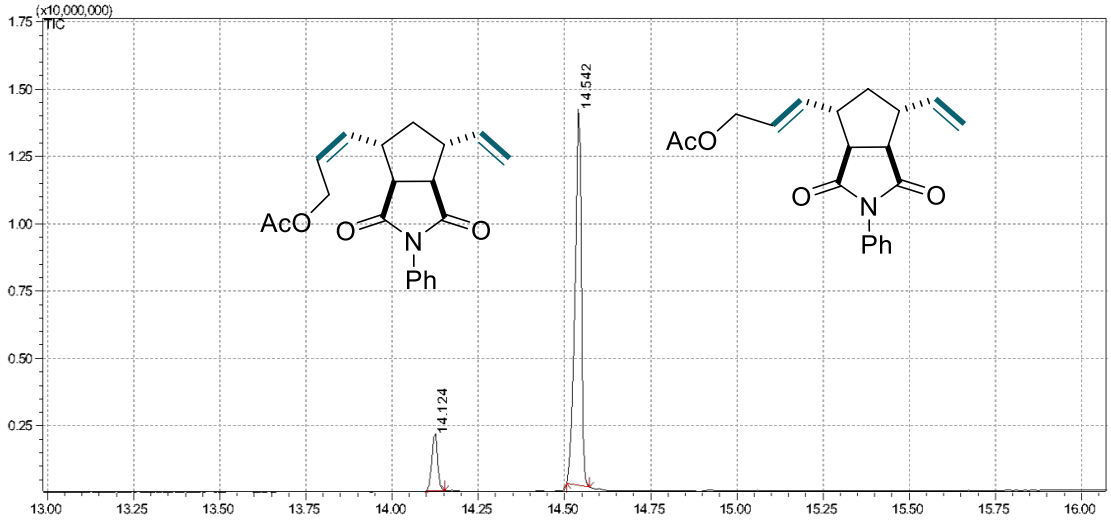
Peak	Retention time [min]	Area	Area [%]
1	15.124	1497562	6.14
2	16.175	22892639	93.86

3-(1,3-dioxo-2-phenyl-6-vinyloctahydrocyclopenta[c]pyrrol-4-yl)allyl acetate (6b)



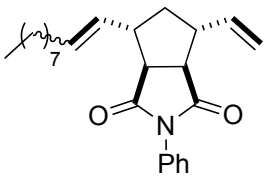
Chemical Formula: $C_{20}H_{21}NO_4$
Molecular Weight: 339,39

(6b) was obtained upon reaction with allyl acetate **10** (0.5 mmol, 55 µL, 5.0 equiv.) as CM partner with 88% NMR yield, E/Z 9/1. Conversion and yield were attributed based on the characteristic signal at 2.9 ppm (m, 2H). The data were consistent with the reported literature.[10]



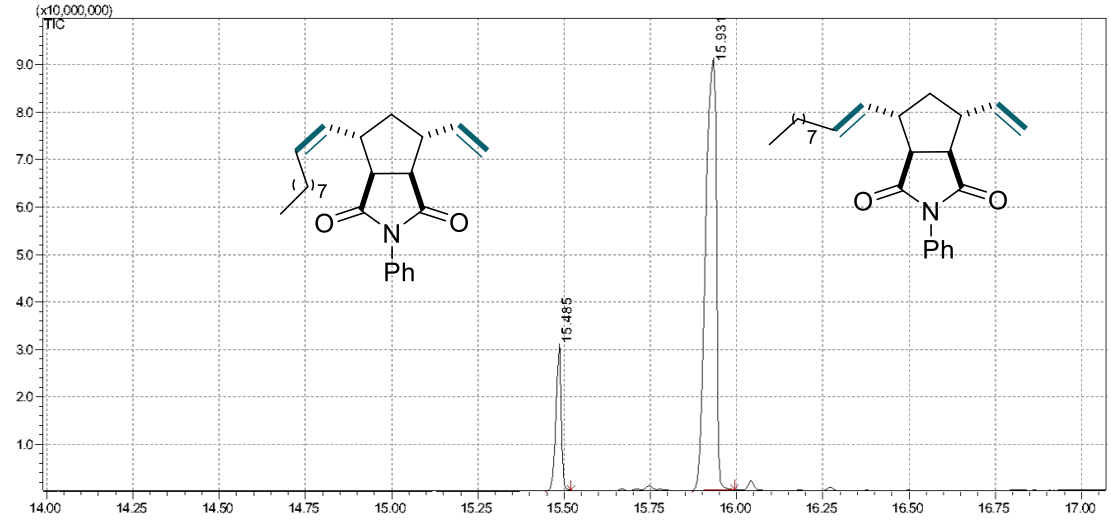
Peak	Retention time [min]	Area	Area [%]
1	14.124	2500314	12.09
2	14.542	18175095	87.91

4-(dec-1-en-1-yl)-2-phenyl-6-vinyltetrahydrocyclopenta[c]pyrrole-1,3(2H,3aH)-dione (6c)



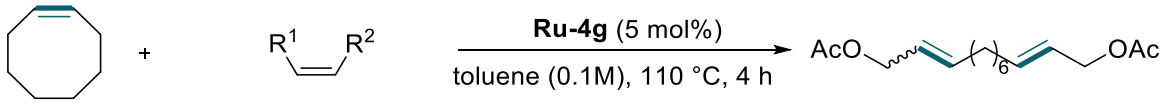
Chemical Formula: $C_{25}H_{33}NO_2$
Molecular Weight: 379,54

(6c) was obtained upon reaction with 1-decene (0.5 mmol, 85 µL, 5.0 equiv.) as CM partner with 71% NMR yield, E/Z 85/15. Conversion and yield were attributed based on the characteristic signal at 2.95-2.8 ppm (m, 2H). The data were consistent with the reported literature.[11]



Peak	Retention time [min]	Area	Area [%]
1	15.485	31926932	13.94
2	15.931	197073301	86.06

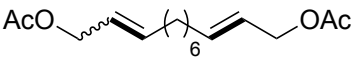
2.5.5.1 Ring opening cross metathesis of cyclooctene



7 **8 or 10** **9**

In the glovebox, in an oven-dried Schlenk, cyclooctene **7** (1.0 equiv.) and the olefin partner (4.0 equiv.) were diluted in toluene (1 mL). **Ru-4g** complex (0.005 mmol, 3.9 mg, 5 mol%) was dissolved in toluene (1 mL) and introduced in the reaction mixture, which was allowed to stir at 110°C during 4 hours. The completion was monitored by and ^{1}H-NMR. 1,3,5-trimethoxybenzene as internal standard (0.1 mmol, 16.8 mg, 1.0 equiv.)

dodeca-2,10-diene-1,12-diyl diacetate (9)



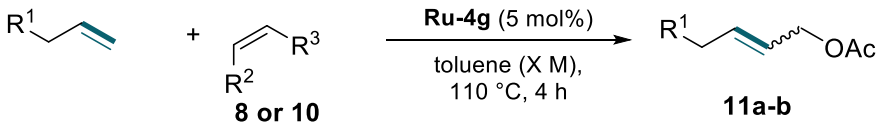
9
Chemical Formula: $C_{16}H_{26}O_4$
Molecular Weight: 282,38

(9) was obtained with cyclooctene **7** (0.1 mmol, 13 µL, 1.0 equiv.) and allyl acetate **8** as olefin partner (0.41 mmol, 44 µL, 4.0 equiv.) with 48% NMR yield, E,E/E,Z 8/2.

The same reaction with cyclooctene **7** (0.2 mmol, 25 µL, 1.0 equiv.) and cis-diacetoxybut-2-ene **10** (0.8 mmol, 130 µL, 4.0 equiv.) as olefin partner afforded 38% NMR yield, 25% isolated yield E,E/E,Z 8/2. The data were consistent with the reported literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 – 5.74 (m, 2H), 5.59 – 5.52 (m, 2H), 4.50 (dt, *J* = 6.4, 1.0 Hz, 4H), 2.08 – 2.06 (m, 10H), 1.44 – 1.27 (m, 8H).

2.5.6 General procedure for cross metathesis



In an Ar-filled glovebox, an oven-dried vial was filled with acetate derivative (1.0 equiv. or 4 equiv.), degassed CM partner (1.0 equiv. or 2.5 equiv.) and toluene (0.5 mL or 2 mL). The solution of **Ru-4g** complex (0.005 mmol, 3.9 mg, 5 mol%) in toluene was then added and the mixture was stirred for 4 hours at 110 °C. The conversion was monitored by ^{1}H NMR. 1,3,5-trimethoxybenzene as internal standard (0.1 mmol, 16.8 mg, 1.0 equiv.)

tridec-2-en-1-yl acetate (11a)

Chemical Formula: $C_{15}H_{28}O_2$
Molecular Weight: 240,39

(**11a)** was obtained from 1-dodecene (0.25 mmol, 56 µL, 2.5 equiv.) as olefin partner and cis-diacetoxybut-2-ene **10** (0.1 mmol, 16 µL, 1.0 equiv.) in toluene (0.2M) with 81% NMR yield 88% conversion, E/Z 8/2. The same experiment with allyl acetate **8** (0.1 mmol, 11 µL, 1.0 equiv.) as olefin partner afforded 51% NMR yield 75% conversion, E/Z 85/15. The data were consistent with the reported literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) given as *E/Z* mixture δ 5.82 – 5.71 (m, 2H, *Z* isomer), 5.68 – 5.47 (m, 2H, *E* isomer), 4.61 (dd, *J* = 6.9, 1.3 Hz, 2H, *Z* isomer), 4.50 (dd, *J* = 6.6, 1.1 Hz, 2H, *E* isomer), 2.05 (m, 5H), 1.42 – 1.19 (m, 16H), 0.91 – 0.83 (m, 3H).

4-phenylbut-2-en-1-yl acetate (11b)

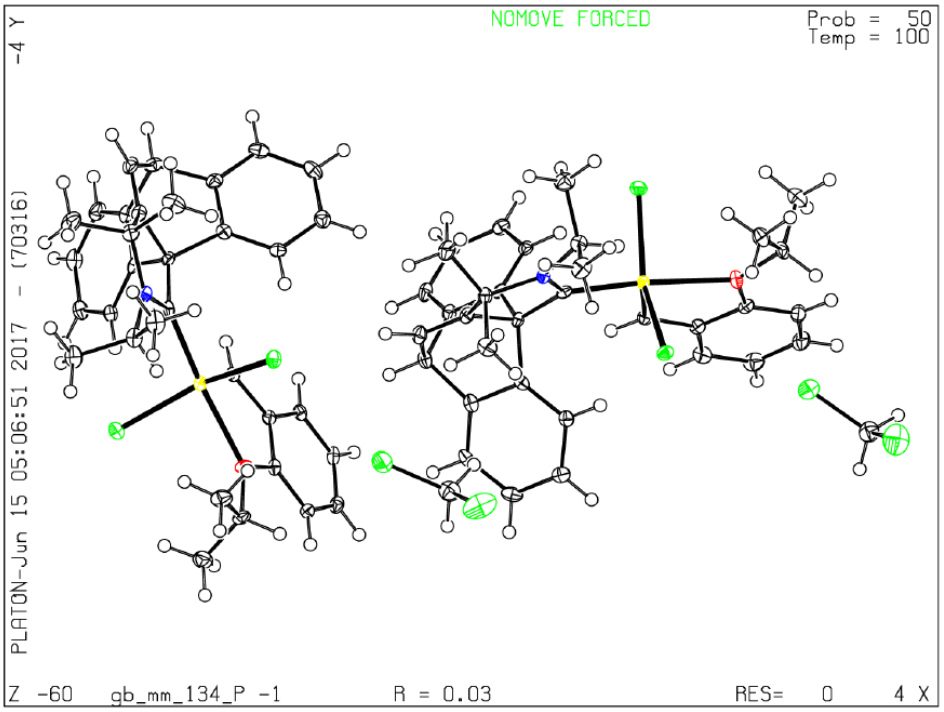
Chemical Formula: $C_{12}H_{14}O_2$
Molecular Weight: 190,24

(**11b)** was obtained from allyl benzene (0.2 mmol, 25 µL, 1.0 equiv.) as CM partner and cis-diacetoxybut-2-ene **10** (0.8 mmol, 130 µL, 4.0 equiv.) in toluene (0.1M) with 58% isolated yield (22 mg), E/Z 9/1. The data were consistent with the reported literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) (E/Z mixture) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 5.98 – 5.79 (m, 1H), 5.63 (dtt, *J* = 15.5, 6.4, 1.5 Hz, 1H), 4.77 – 4.52 (m, 2H), 3.50 – 3.37 (m, 2H), 2.07 (s, 3H).

2.6 Solid state structure obtained by X-ray diffraction

2.6.1 *N*-isopropyl CABC Hoveyda type Ru complex (Ru-4a) [JM-659]



Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=11.759(2) b=16.076(3) c=18.341(3)
alpha=110.149(6) beta=96.057(6) gamma=90.840(6)
Temperature: 100 K

	Calculated	Reported
Volume	3232.0(10)	3231.9(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C33 H35 Cl2 N O Ru, C H2 Cl2	C33 H35 Cl2 N O Ru, C H2 Cl2
Sum formula	C34 H37 Cl4 N O Ru	C34 H37 Cl4 N O Ru
Mr	718.52	718.51
Dx,g cm-3	1.477	1.477
Z	4	4
Mu (mm-1)	0.844	0.844
F000	1472.0	1472.0
F000'	1469.71	
h,k,lmax	15,20,23	15,20,23
Nref	14322	14226
Tmin,Tmax	0.859,0.881	0.468,0.491
Tmin'	0.852	

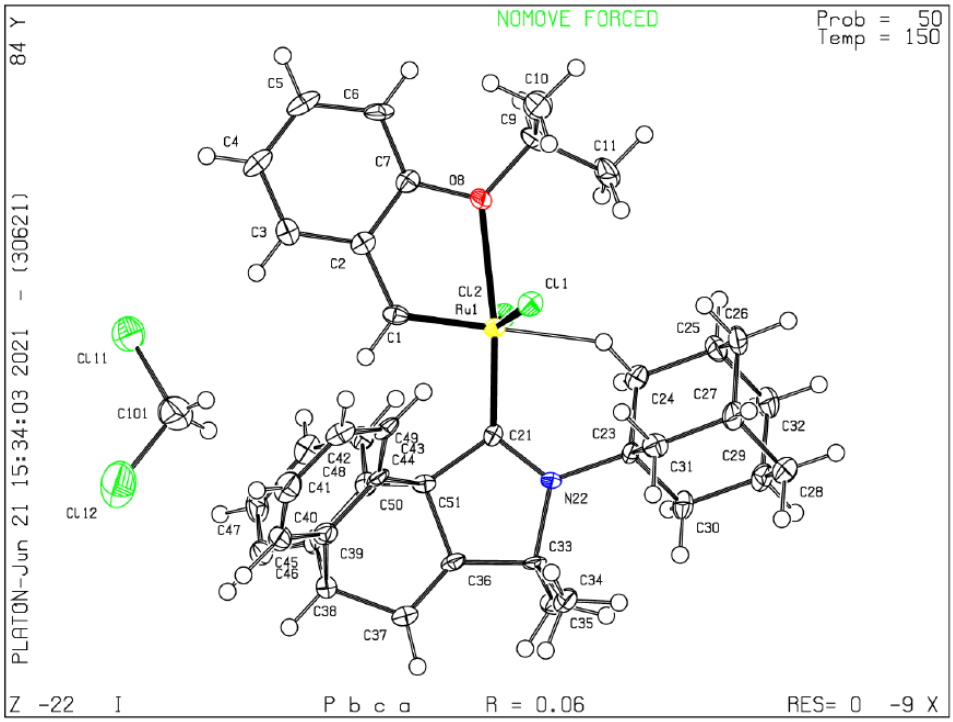
Correction method= # Reported T Limits: Tmin=0.468 Tmax=0.491
AbsCorr = MULTI-SCAN

Data completeness= 0.993 Theta(max)= 27.136

R(reflections)= 0.0290(11994) wR2(reflections)= 0.0683(14226)

S = 1.033 Npar= 751

2.6.2 *N*-Adamantyl CABC Hoveyda type Ru complex (Ru-4b) [JAT-168]



Bond precision: C-C = 0.0073 A Wavelength=0.71073

Cell: a=18.6545(12) b=16.0577(13) c=23.8797(16)
alpha=90 beta=90 gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	7153.1(9)	7153.1(9)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C40 H43 Cl2 N O Ru, C H2 Cl2	C40 H43 Cl2 N O Ru, C H2 Cl2
Sum formula	C41 H45 Cl4 N O Ru	C41 H45 Cl4 N O Ru
Mr	810.65	810.65
Dx,g cm-3	1.505	1.505
Z	8	8
Mu (mm-1)	0.772	0.772
F000	3344.0	3344.0
F000'	3339.56	
h,k,lmax	24,20,31	24,20,30
Nref	8202	8114
Tmin,Tmax	0.806,0.947	0.841,0.947
Tmin'	0.806	

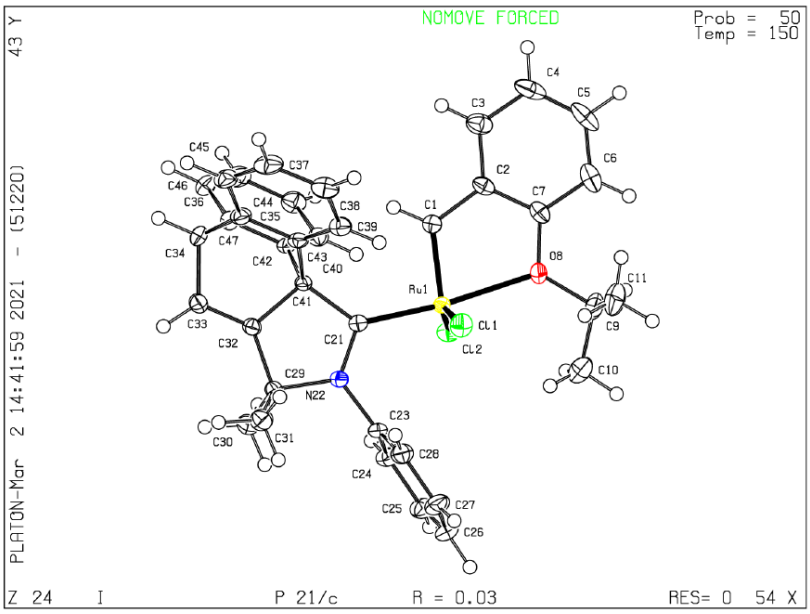
Correction method= # Reported T Limits: Tmin=0.841 Tmax=0.947
AbsCorr = MULTI-SCAN

Data completeness= 0.989 Theta(max)= 27.482

R(reflections)= 0.0576(4168) wR2(reflections)= 0.1307(8114)

S = 0.991 Npar= 437

2.6.3 *N*-Phenyl CABC Hoveyda type Ru complex (Ru-4c) [JAT-150]



Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=12.2592(11) b=14.8980(13) c=19.906(2)
alpha=90 beta=99.104(4) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	3589.8(6)	3589.7(6)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C36 H33 Cl2 N O Ru [+ solvent]	C36 H33 Cl2 N O Ru
Sum formula	C36 H33 Cl2 N O Ru [+ solvent]	C36 H33 Cl2 N O Ru
Mr	667.60	667.60
Dx,g cm-3	1.235	1.235
Z	4	4
Mu (mm-1)	0.611	0.611
F000	1368.0	1368.0
F000'	1364.54	
h,k,lmax	15,19,25	15,19,25
Nref	8275	8230
Tmin,Tmax	0.732,0.890	0.757,0.890
Tmin'	0.716	

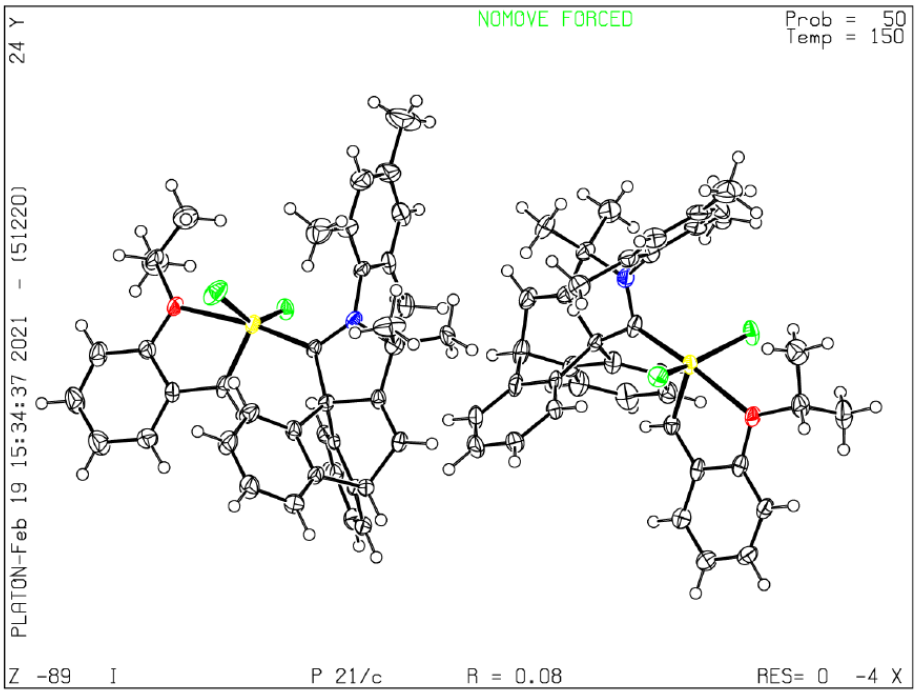
Correction method= # Reported T Limits: Tmin=0.757 Tmax=0.890
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 27.540

R(reflections)= 0.0334(6891) wR2(reflections)= 0.0874(8230)

S = 1.051 Npar= 374

2.6.4 N-Mesityl CABC Hoveyda type Ru complex (Ru-4d) [JAT-157]



Bond precision: C-C = 0.0098 A Wavelength=0.71073

Cell: a=19.3116(15) b=24.5754(19) c=16.7833(11)
alpha=90 beta=106.051(2) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	7654.7(10)	7654.7(10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C39 H39 Cl2 N O Ru [+ solvent]	C39 H39 Cl2 N O Ru
Sum formula	C39 H39 Cl2 N O Ru [+ solvent]	C39 H39 Cl2 N O Ru
Mr	709.68	709.68
Dx,g cm-3	1.232	1.232
Z	8	8
Mu (mm-1)	0.577	0.577
F000	2928.0	2928.0
F000'	2921.14	
h,k,lmax	25,32,21	25,31,21
Nref	17696	16790
Tmin,Tmax	0.735,0.989	0.723,0.989
Tmin'	0.708	

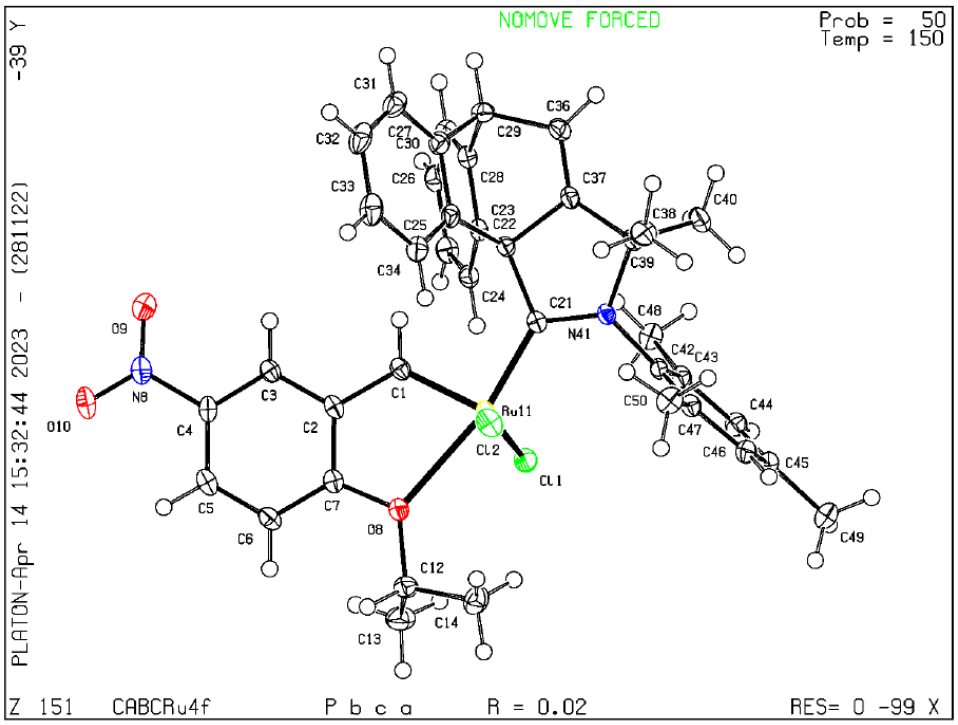
Correction method= # Reported T Limits: Tmin=0.723 Tmax=0.989
AbsCorr = MULTI-SCAN

Data completeness= 0.949 Theta(max)= 27.566

R(reflections)= 0.0819(12650) wR2(reflections)= 0.2096(16790)

S = 1.000 Npar= 807

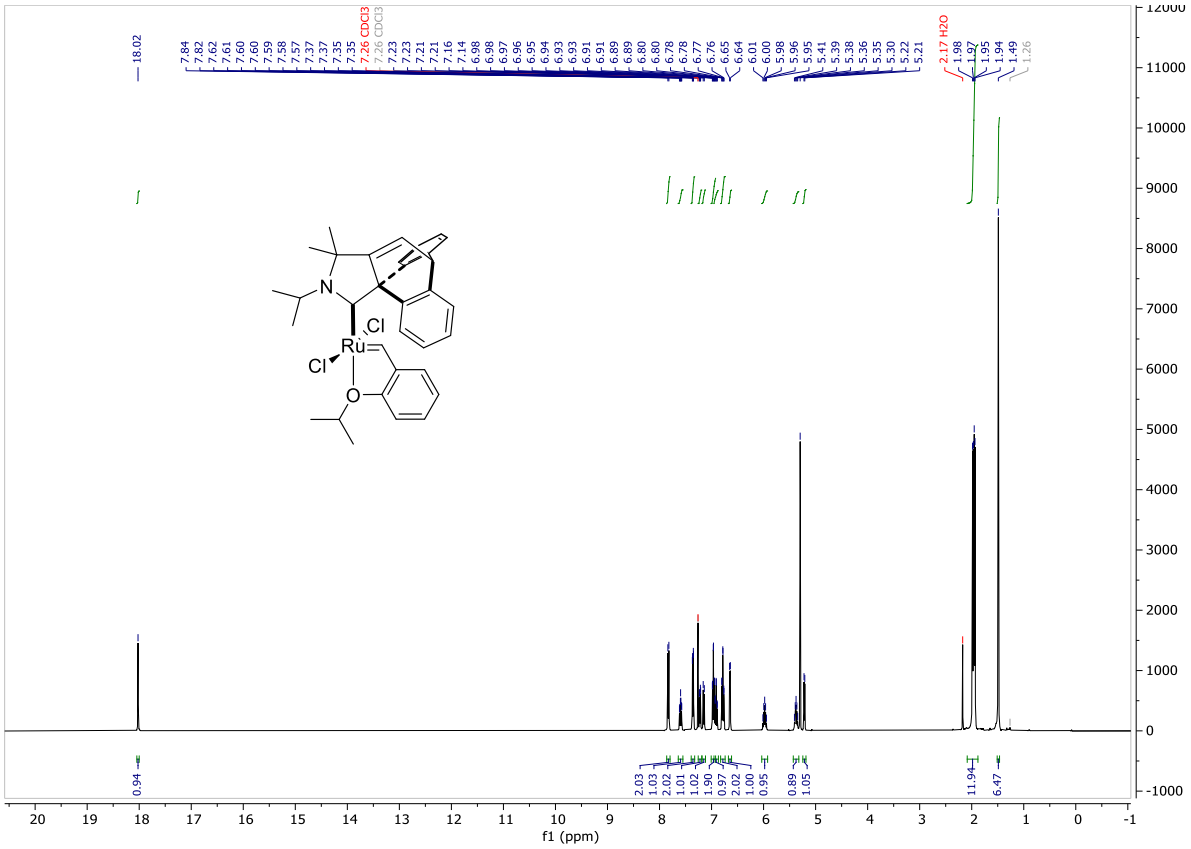
2.6.5 N-Mesityl CABC Grela type Ru complex (Ru-4f)



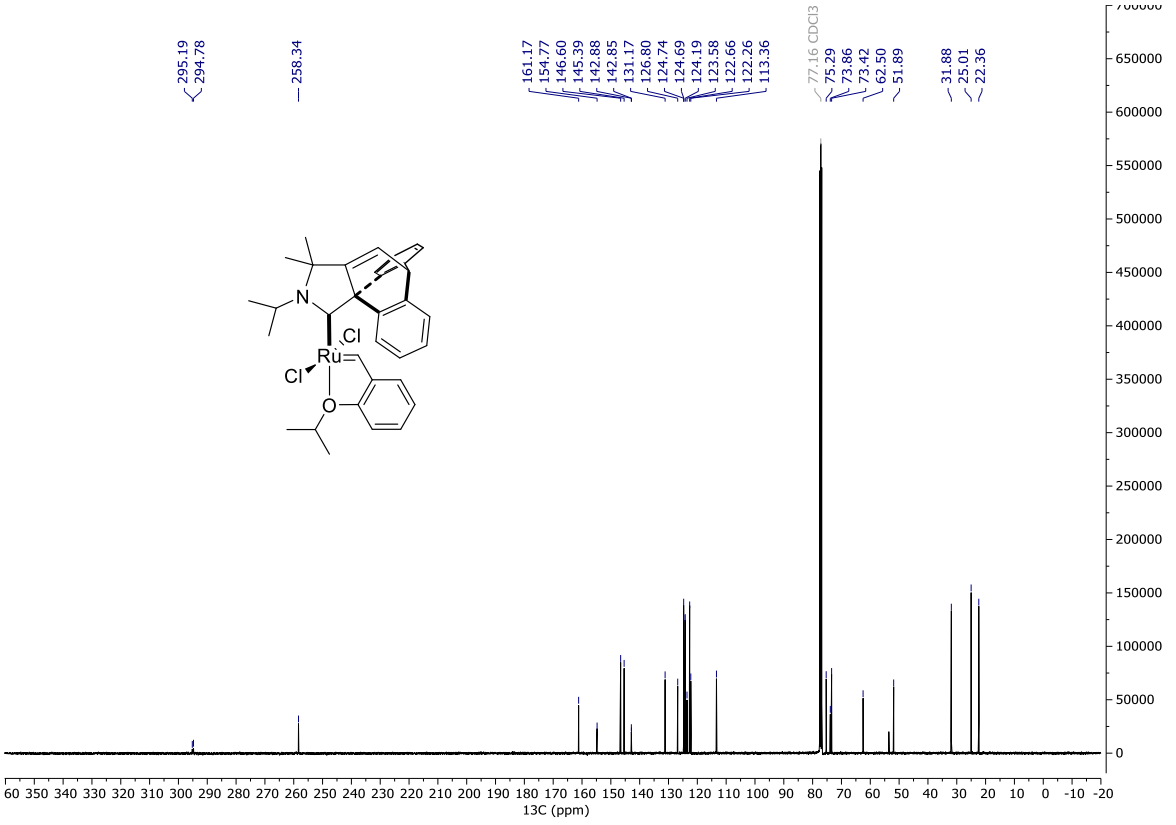

```
Bond precision:   C-C = 0.0022 A          Wavelength=0.71073

Cell:             a=17.4523(5)     b=18.7939(4)     c=20.0698(6)
                  alpha=90         beta=90          gamma=90
Temperature:      150 K

                  Calculated                  Reported
Volume            6582.8(3)                   6582.8(3)
Space group       P b c a                     P b c a
Hall group        -P 2ac 2ab                  -P 2ac 2ab
Moiety formula    C39 H38 Cl2 N2 O3 Ru        C39 H38 Cl2 N2 O3 Ru
Sum formula       C39 H38 Cl2 N2 O3 Ru        C39 H38 Cl2 N2 O3 Ru
Mr                754.68                      754.68
Dx,g cm-3         1.523                       1.523
Z                 8                           8
Mu (mm-1)         0.681                       0.681
F000              3104.0                      3104.0
F000'             3097.30
h,k,lmax          22,24,26                    22,24,26
Nref              7565                        7558
Tmin,Tmax         0.799,0.855                 0.785,0.855
Tmin'             0.799

Correction method= # Reported T Limits: Tmin=0.785 Tmax=0.855
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 27.491

R(reflections)= 0.0244( 7061)                 wR2(reflections)=
                                              0.0659( 7558)
S = 1.064                 Npar= 431
```

2.7 NMR spectra

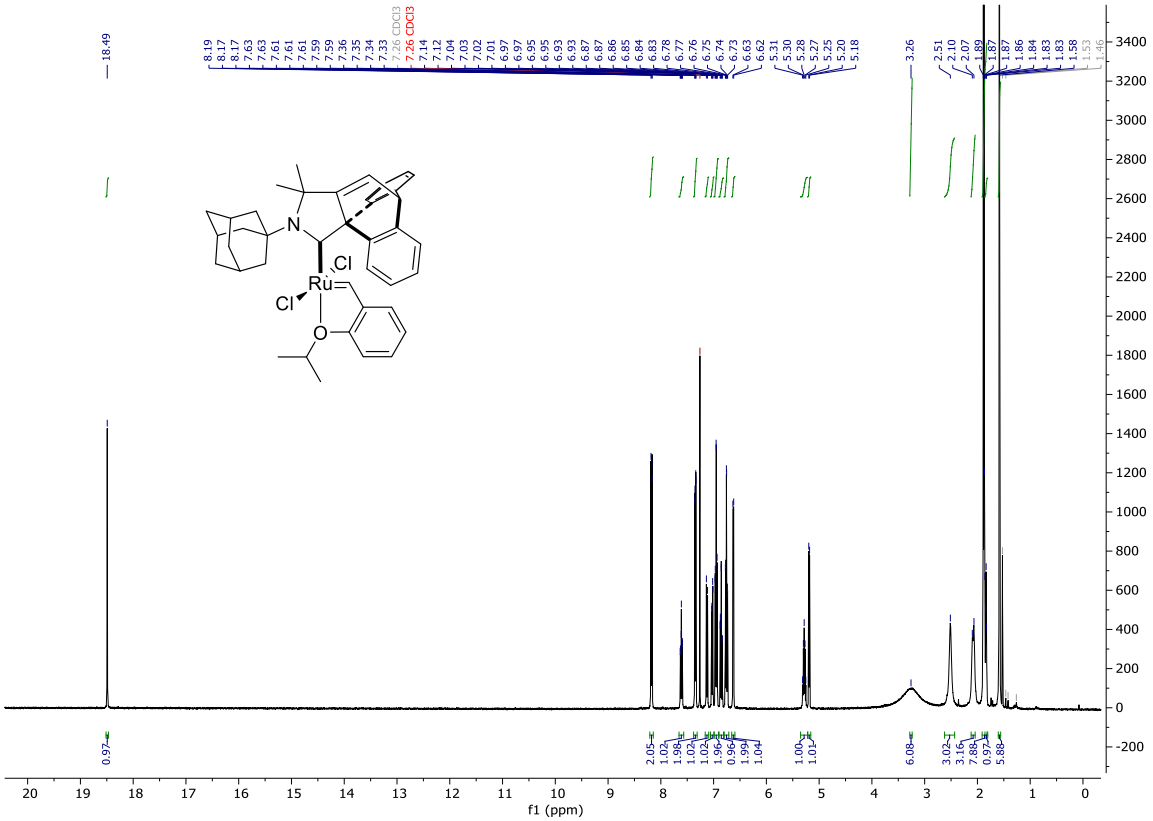
2.7.1 ^{1}H NMR (400 MHz, $CDCl_3$) of Ru-4a



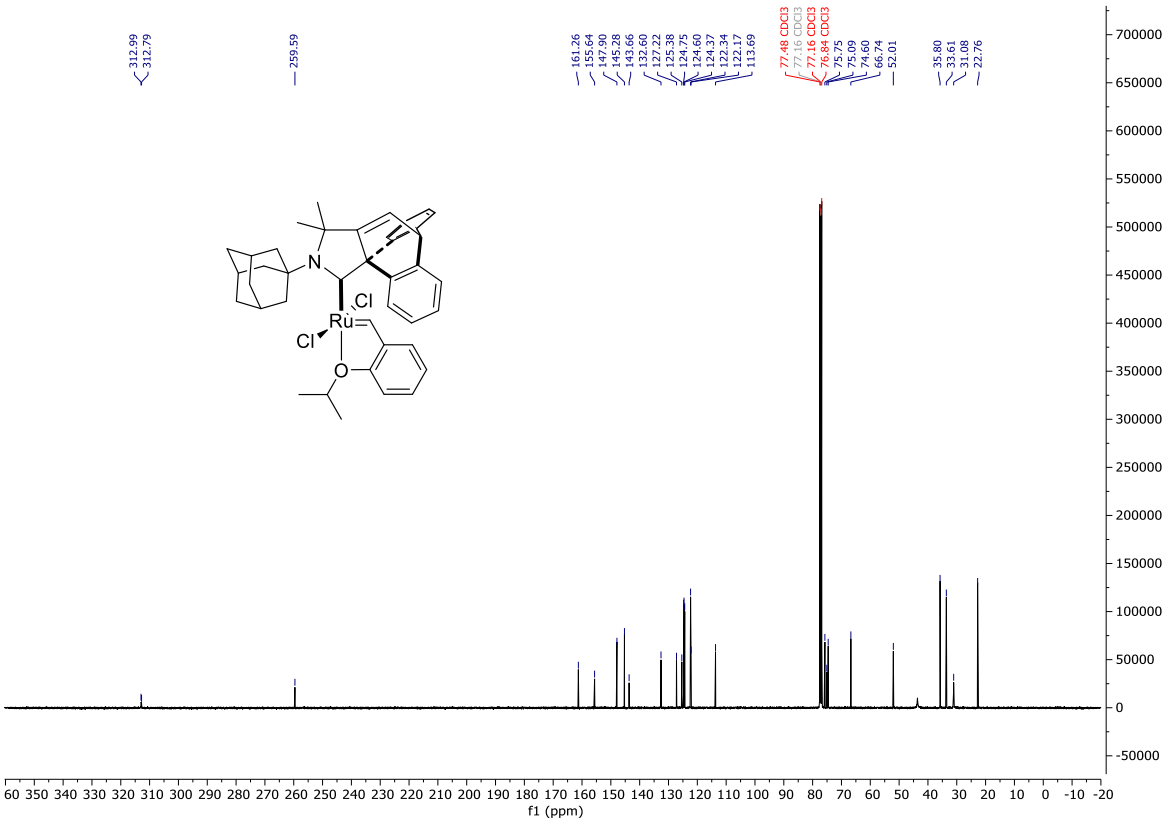
2.7.2 ^{13}C NMR (101 MHz, $CDCl_3$) of Ru-4a



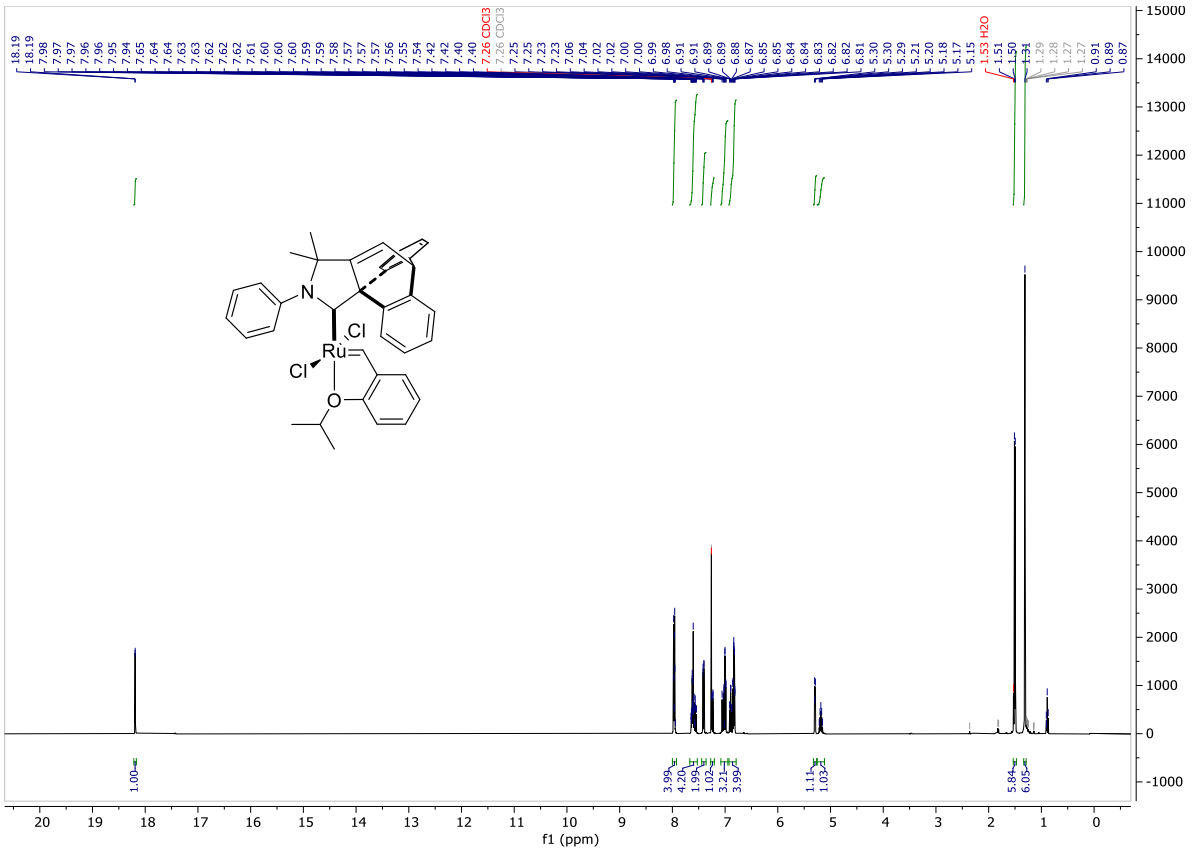
2.7.3 ^{1}H NMR (400 MHz, $CDCl_3$) of Ru-4b



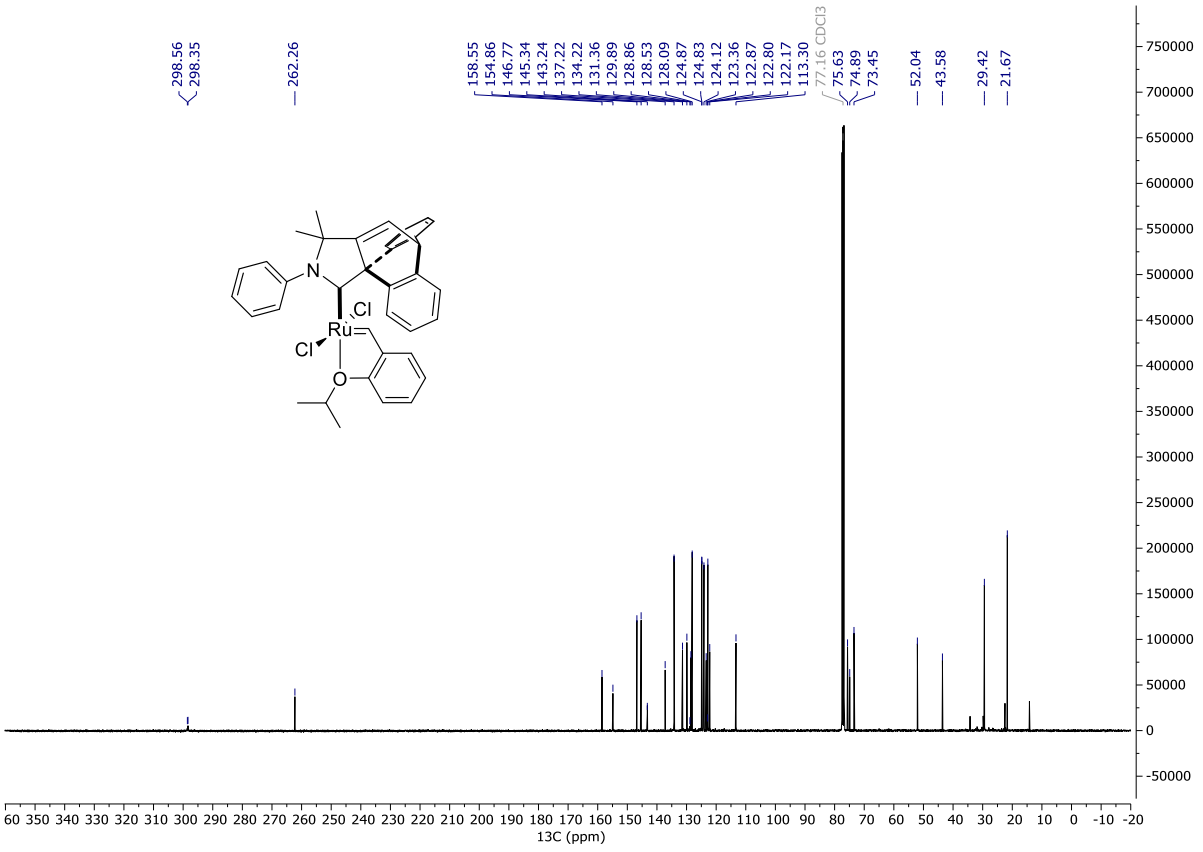
2.7.4 ^{13}C NMR (101 MHz, $CDCl_3$) of Ru-4b



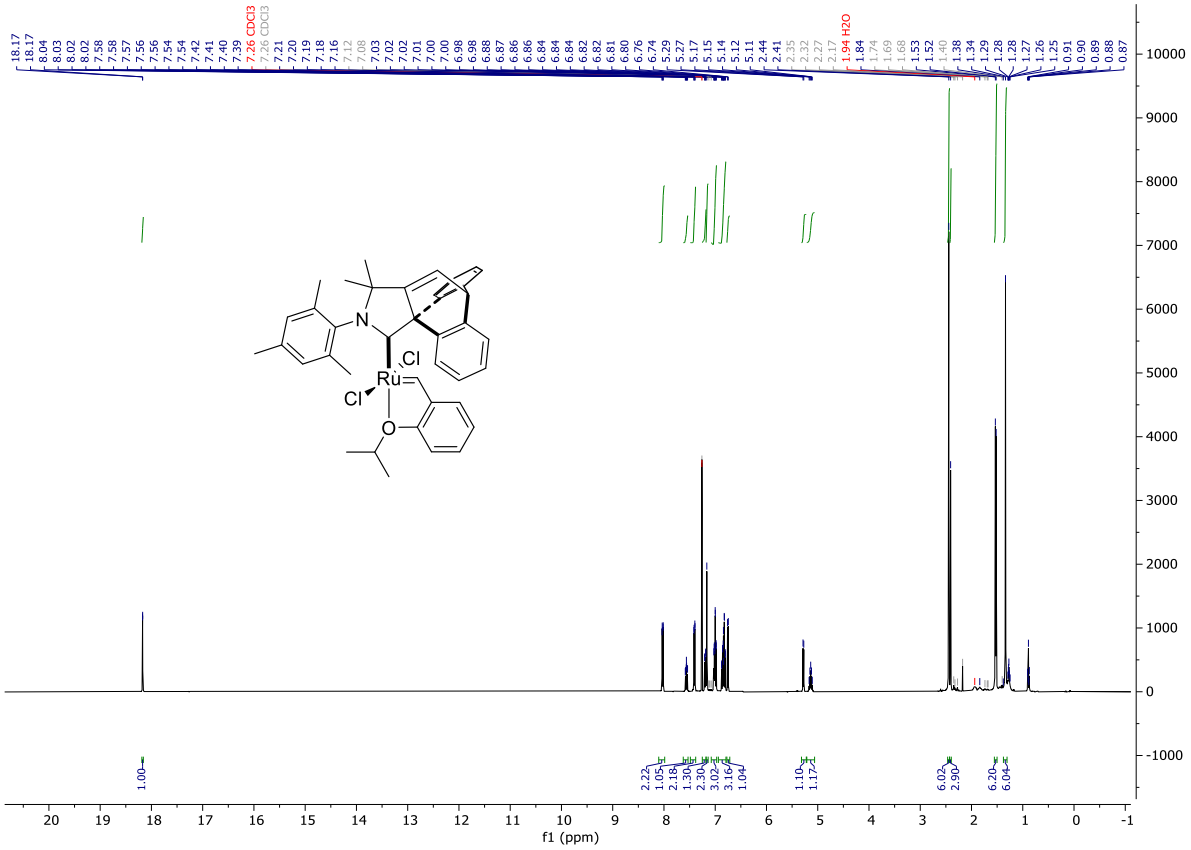
2.7.5 ^{1}H NMR (400 MHz, $CDCl_3$) of Ru-4c



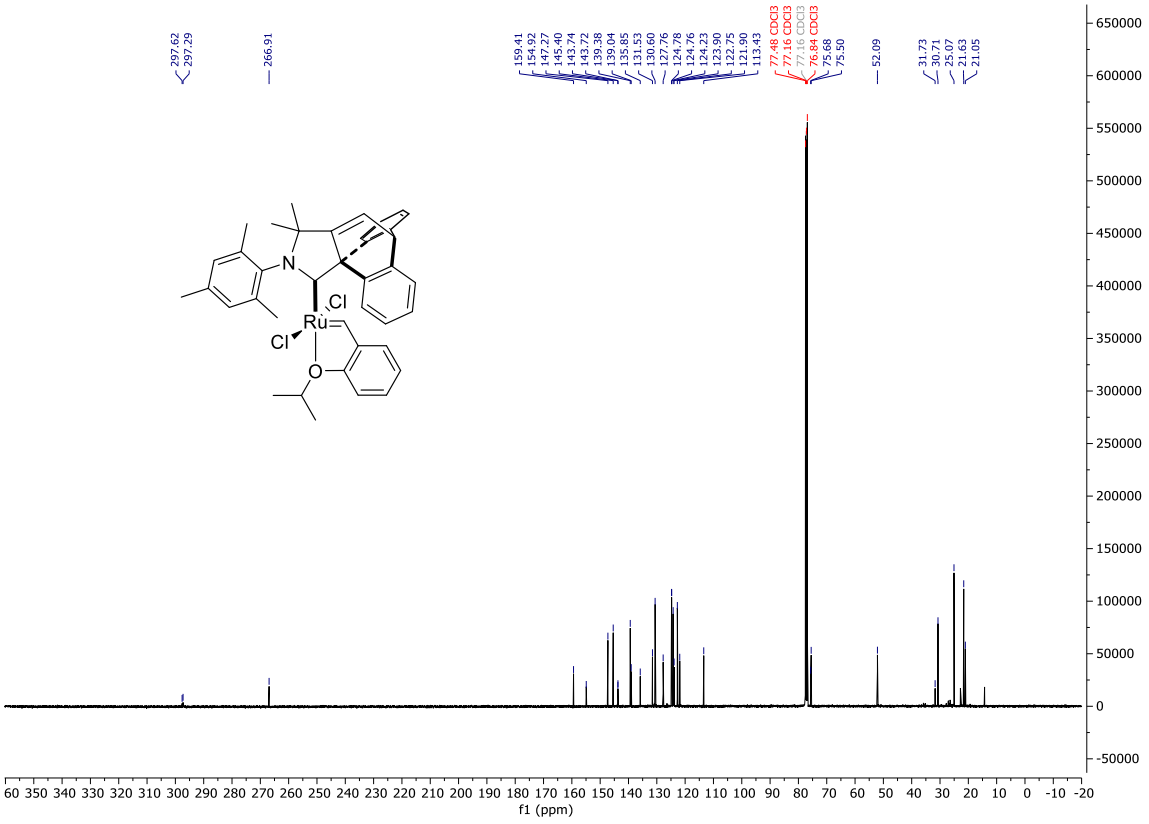
2.7.6 ^{13}C NMR (101 MHz, $CDCl_3$) of Ru-4c



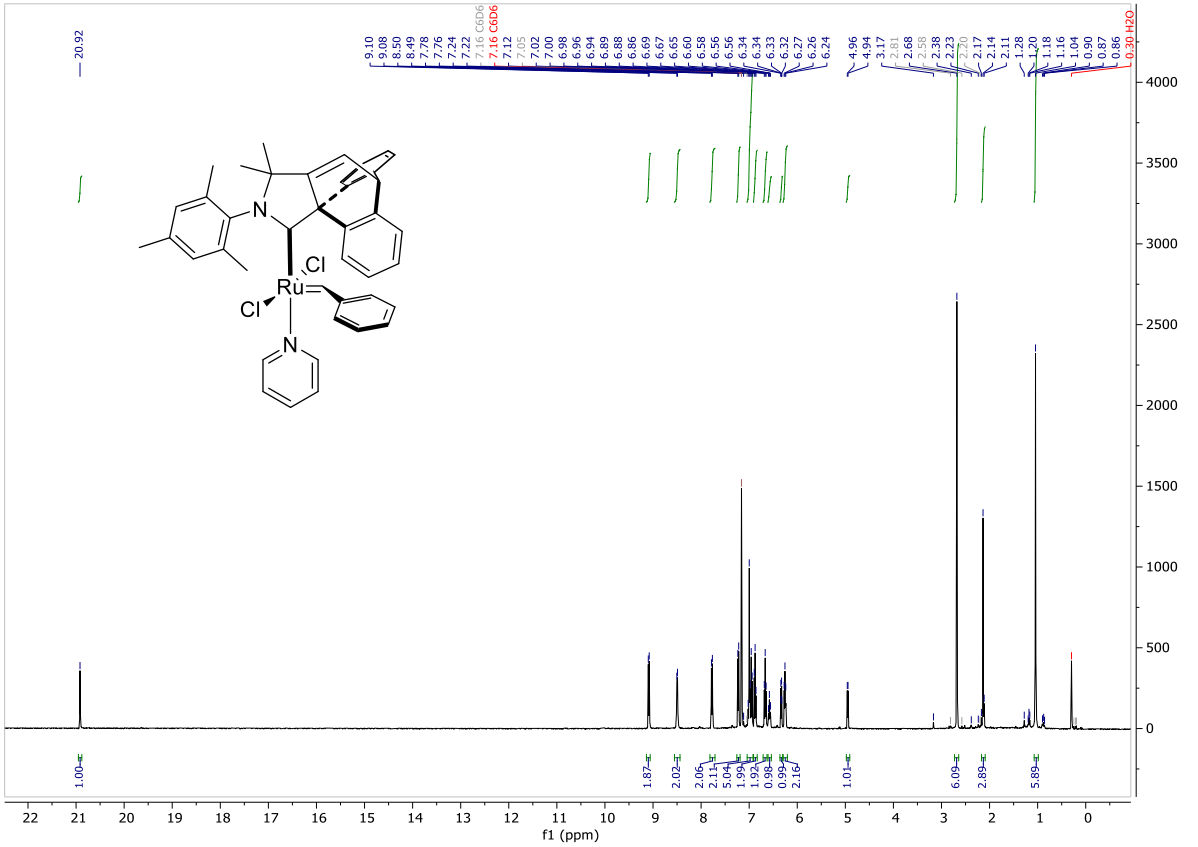
2.7.7 ^{1}H NMR (400 MHz, $CDCl_3$) of Ru-4d



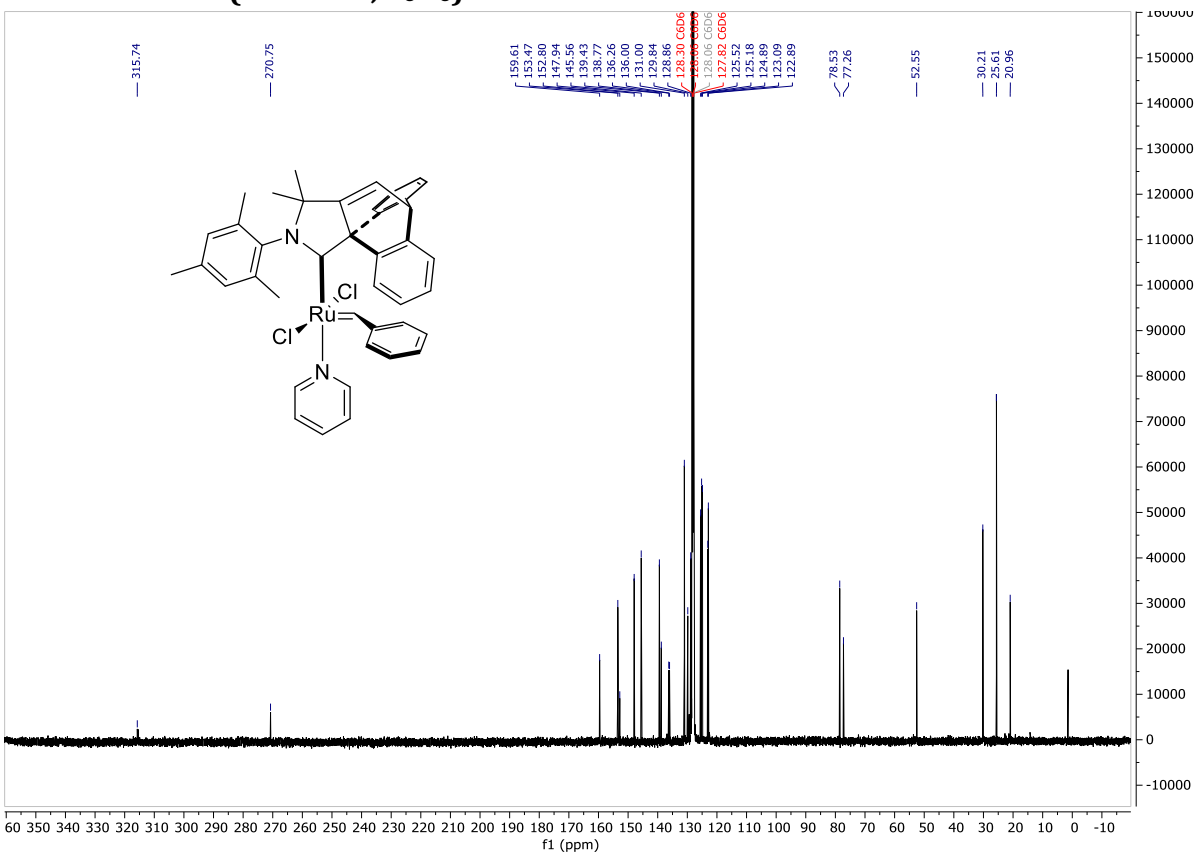
2.7.8 ^{13}C NMR (101 MHz, $CDCl_3$) of Ru-4d



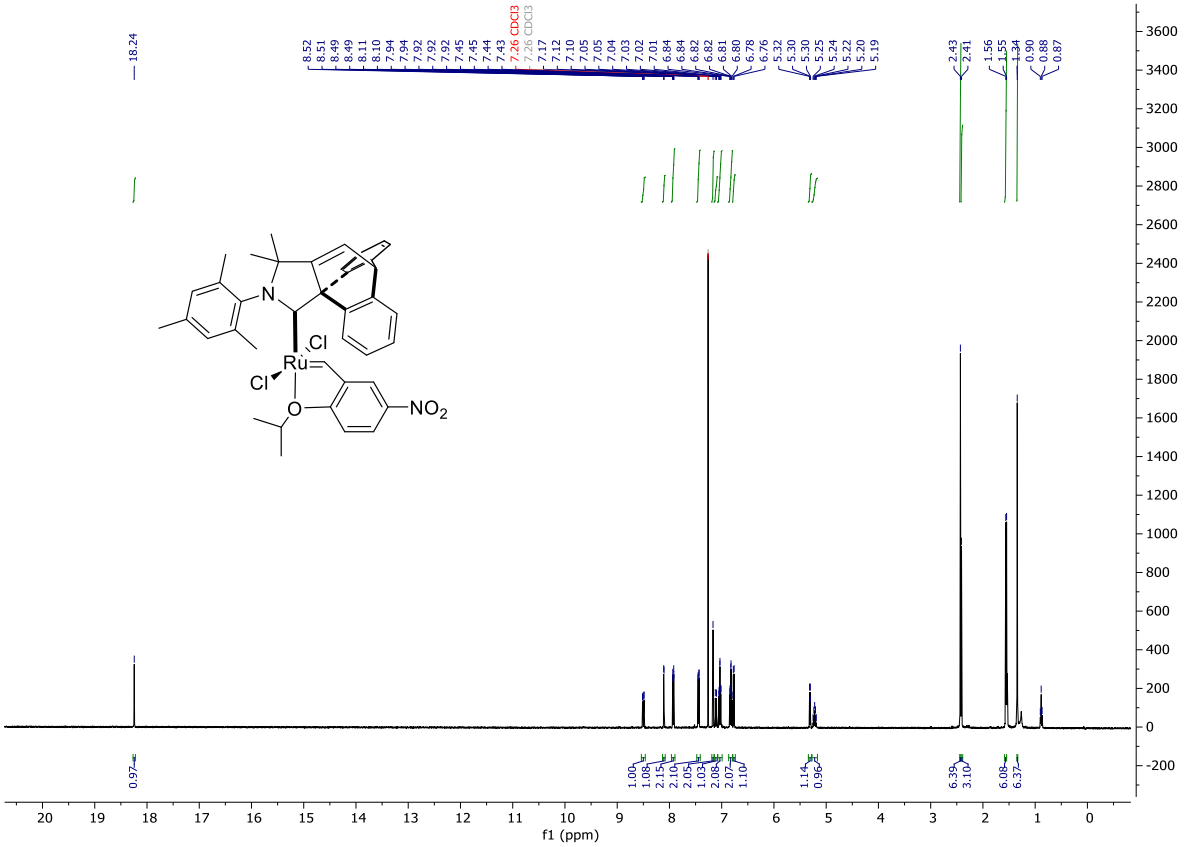
2.7.9 ^{1}H NMR (400 MHz, C_6D_6) of Ru-4e



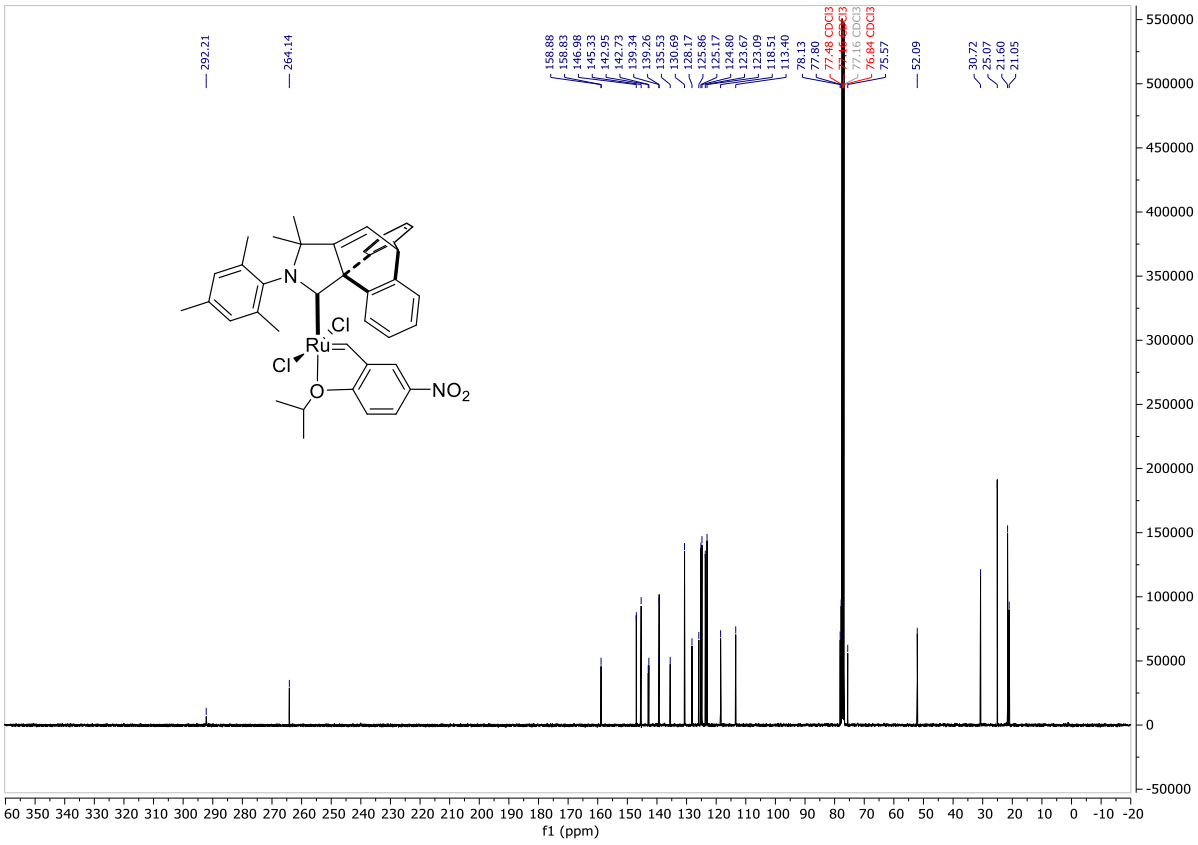
2.7.10 ^{13}C NMR (101 MHz, C_6D_6) of Ru-4e



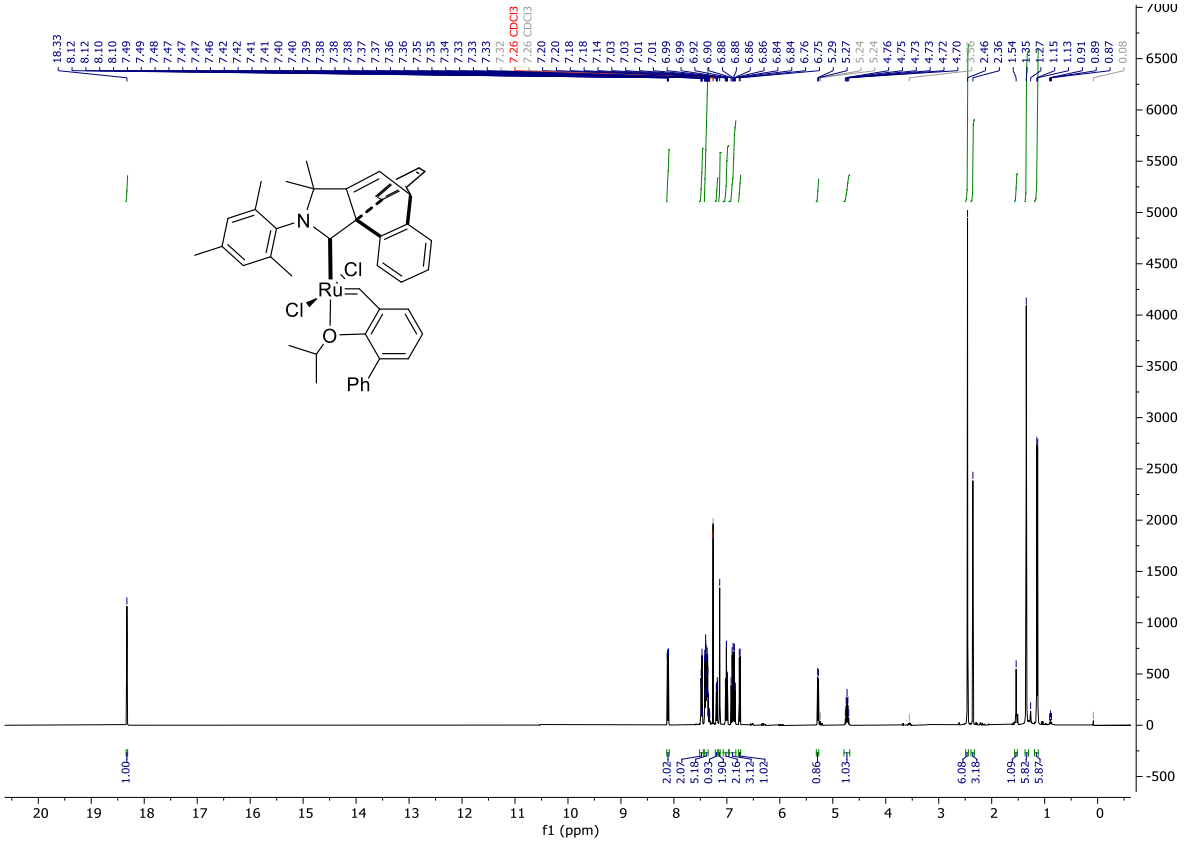
2.7.11 ^{1}H NMR (400 MHz, $CDCl_3$) of Ru-4f



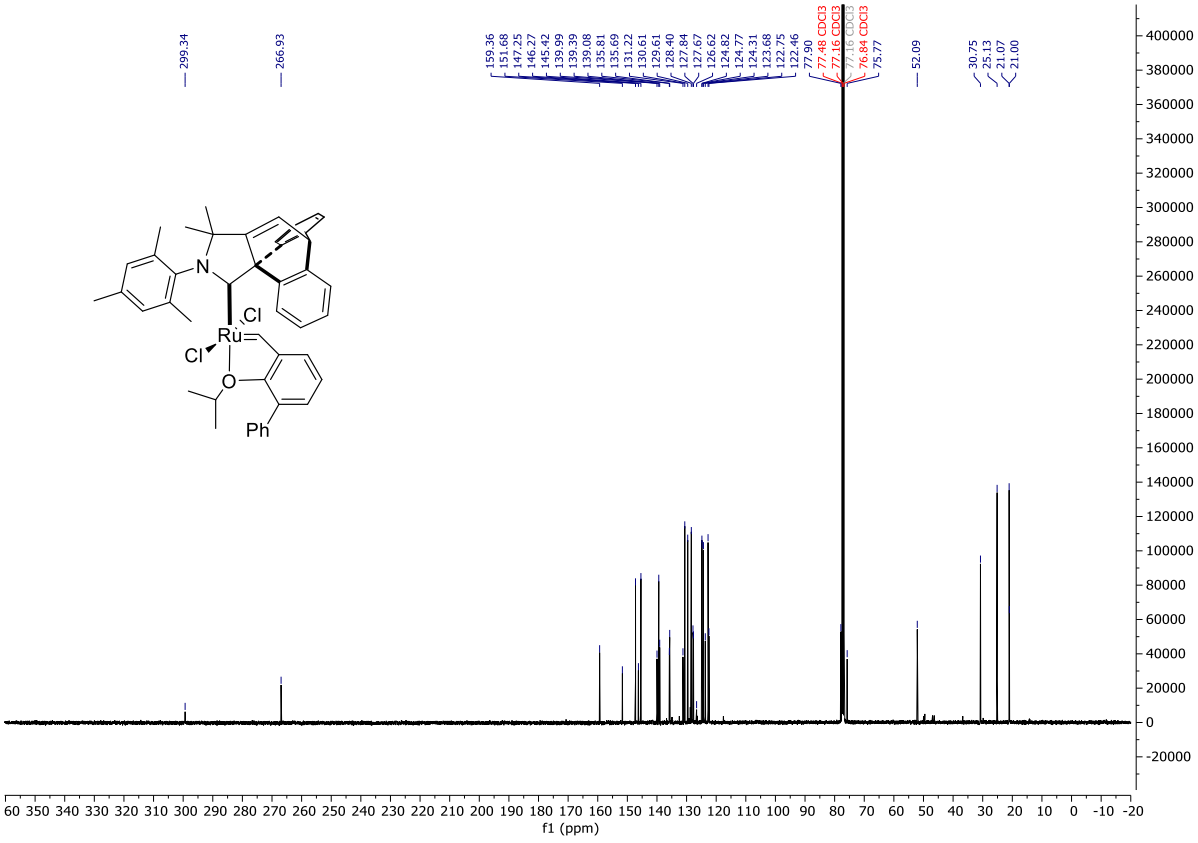
2.7.12 ^{13}C NMR (101 MHz, $CDCl_3$) of Ru-4f



2.7.13 ^{1}H NMR (400 MHz, $CDCl_3$) of Ru-4g

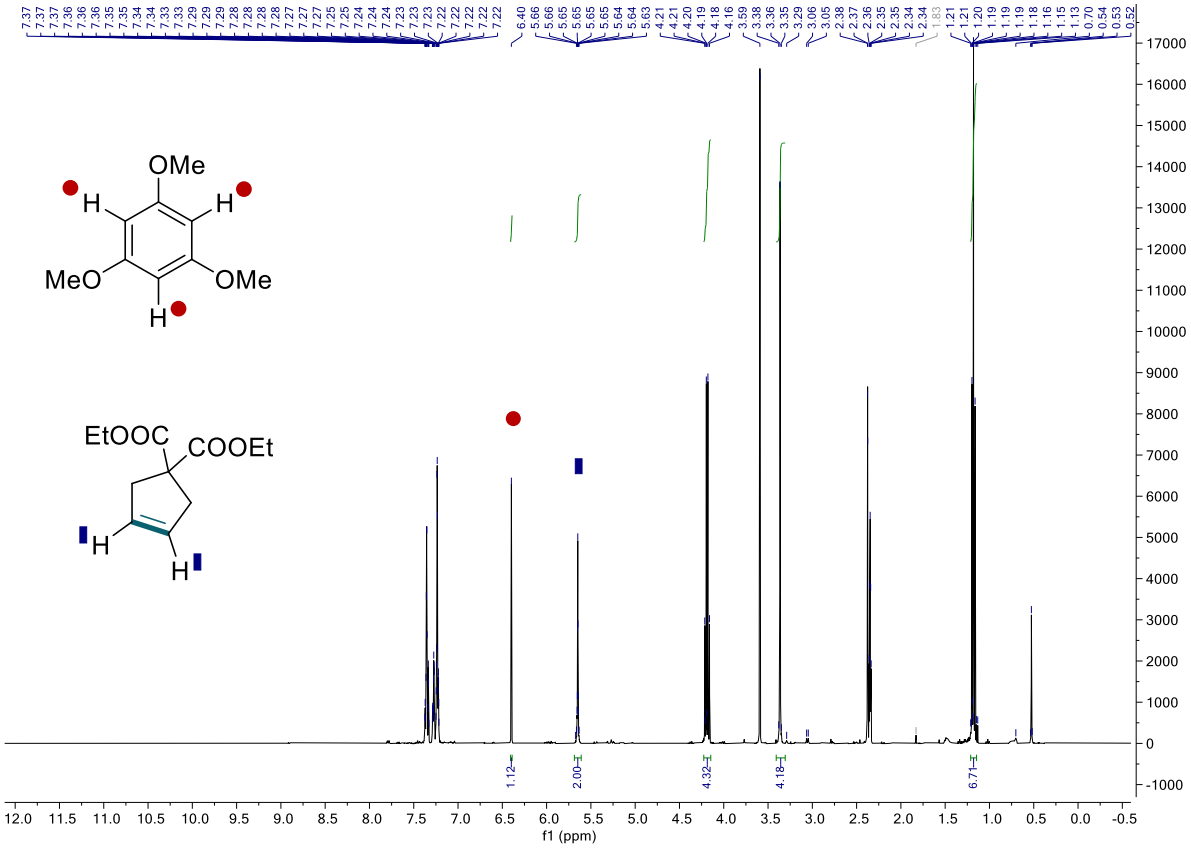


2.7.14 13C NMR (101 MHz, CDCl3) of Ru-4g

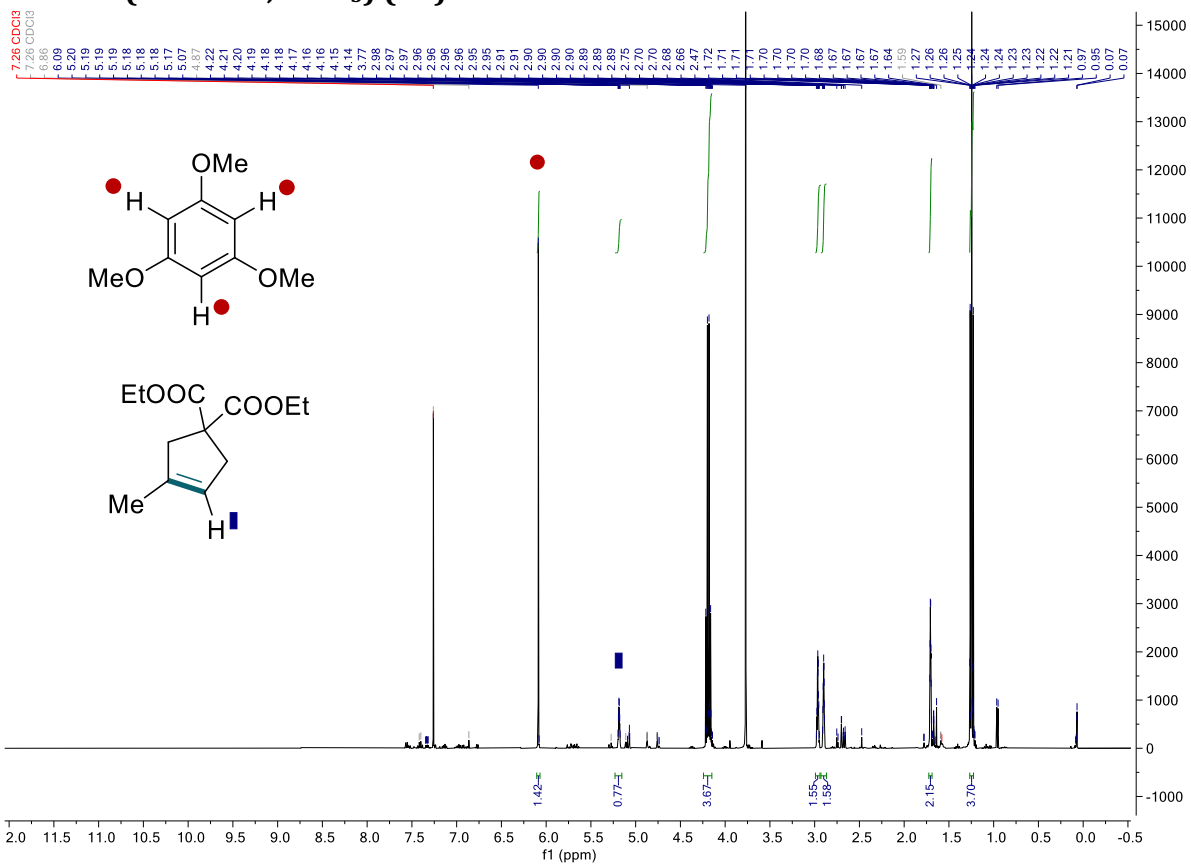


2.7.15 Catalytic products

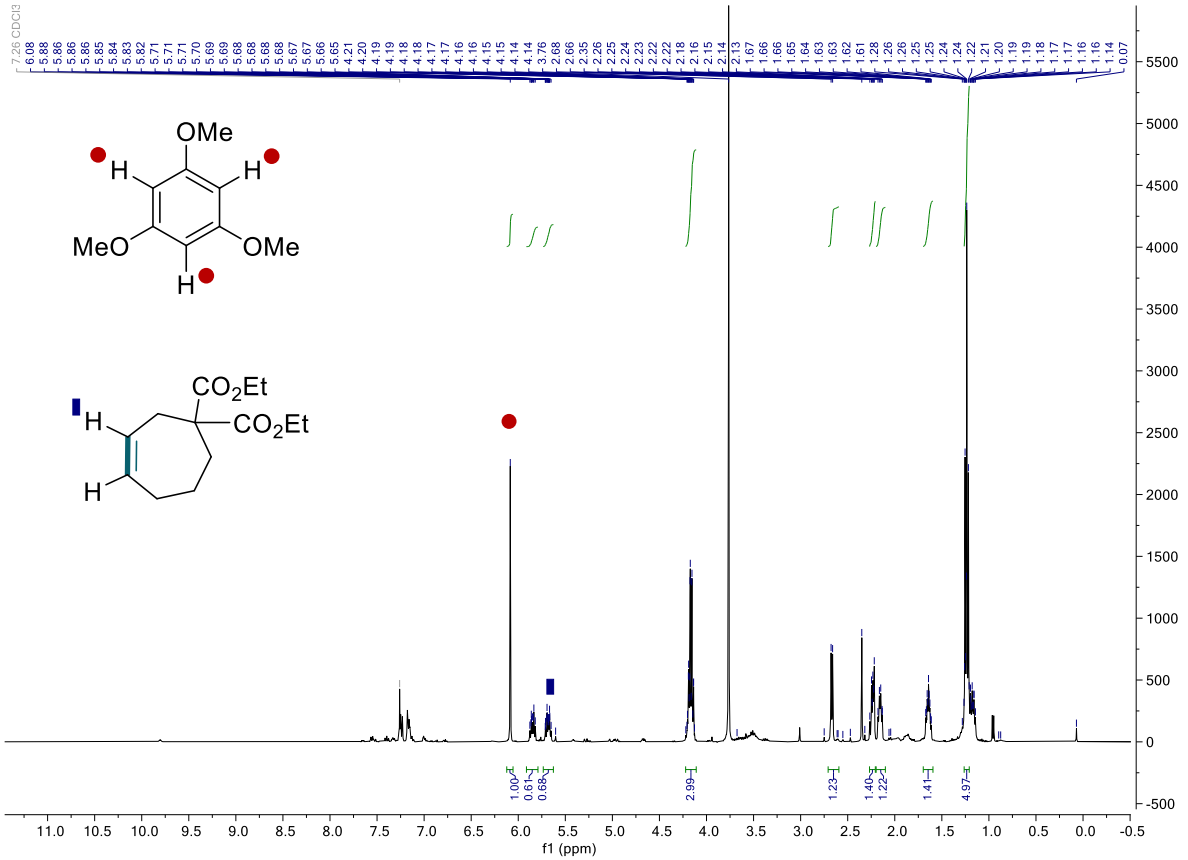
^{1}H NMR (400 MHz, toluene–d_8) (2a)



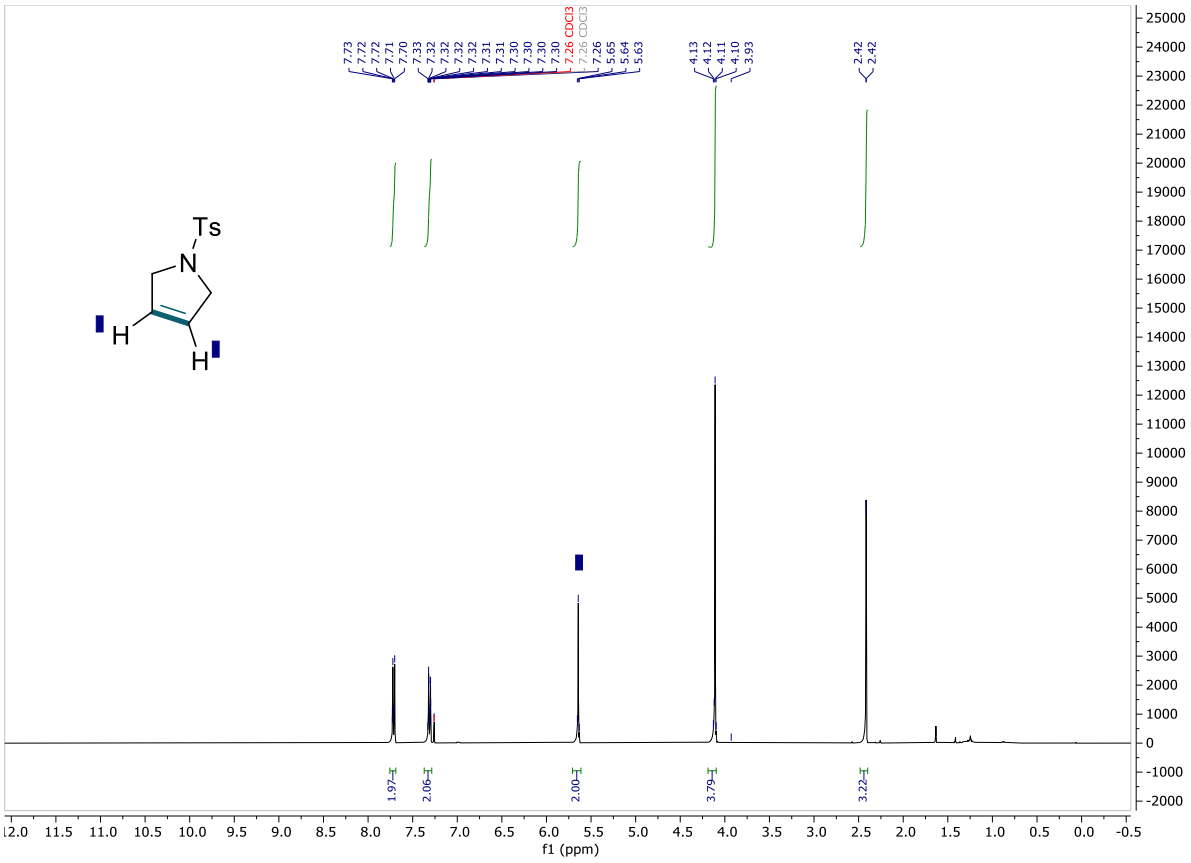
^{1}H NMR (400 MHz, $CDCl_3$) (2b)



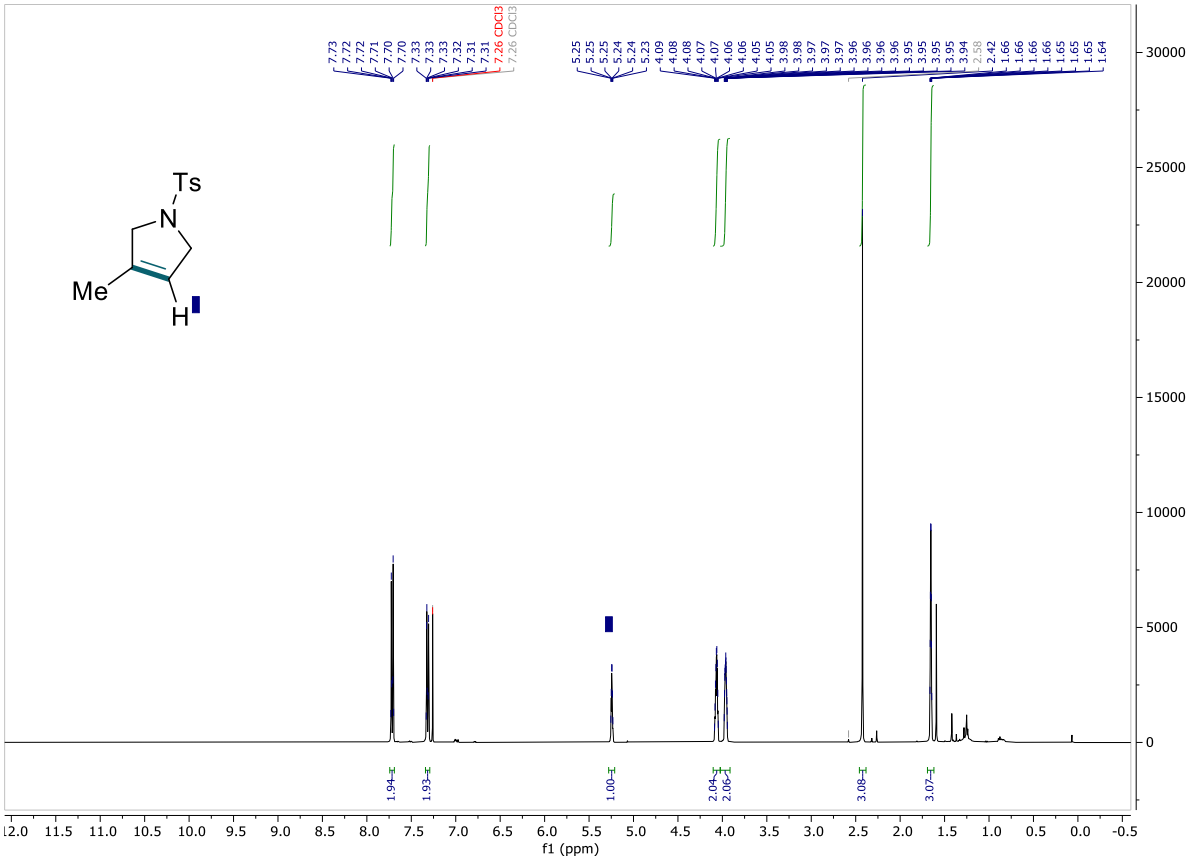
^{1}H NMR (400 MHz, $CDCl_3$) (2d)



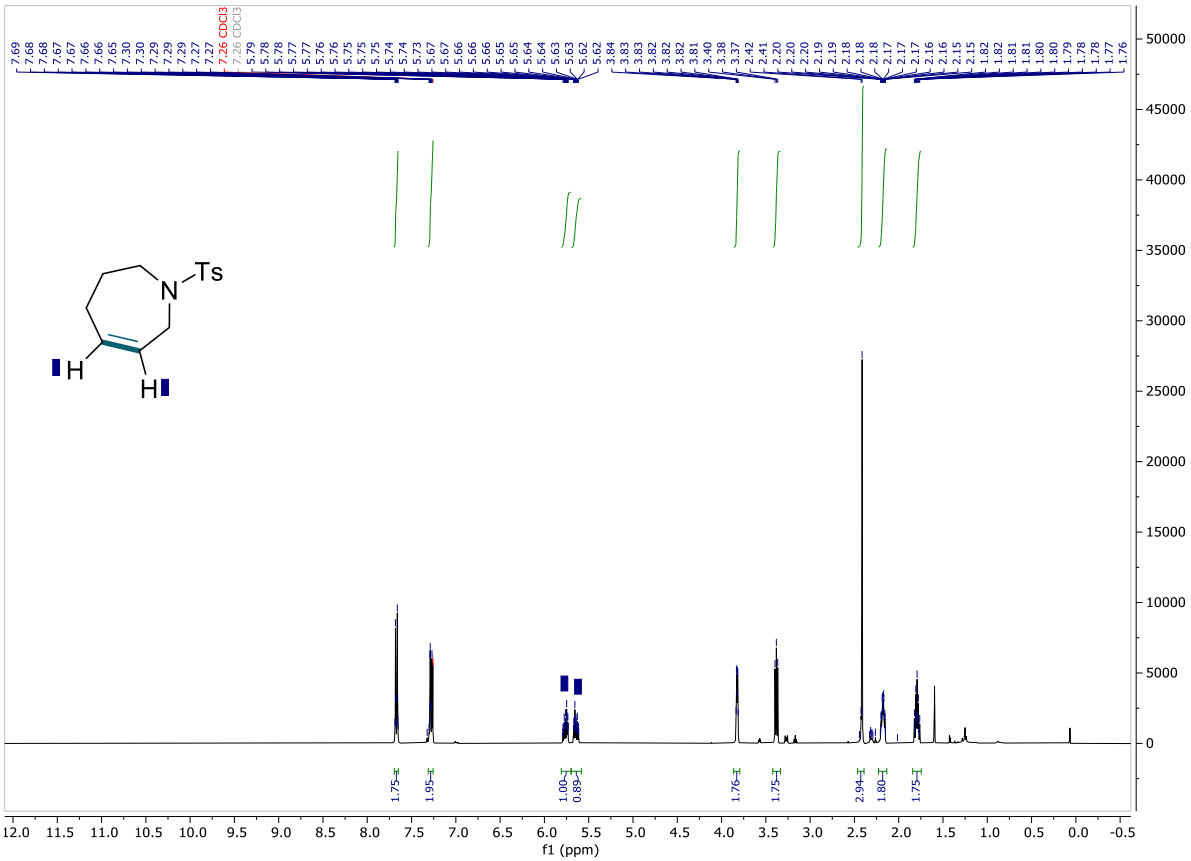
^{1}H NMR (400 MHz, $CDCl_3$) (2e)



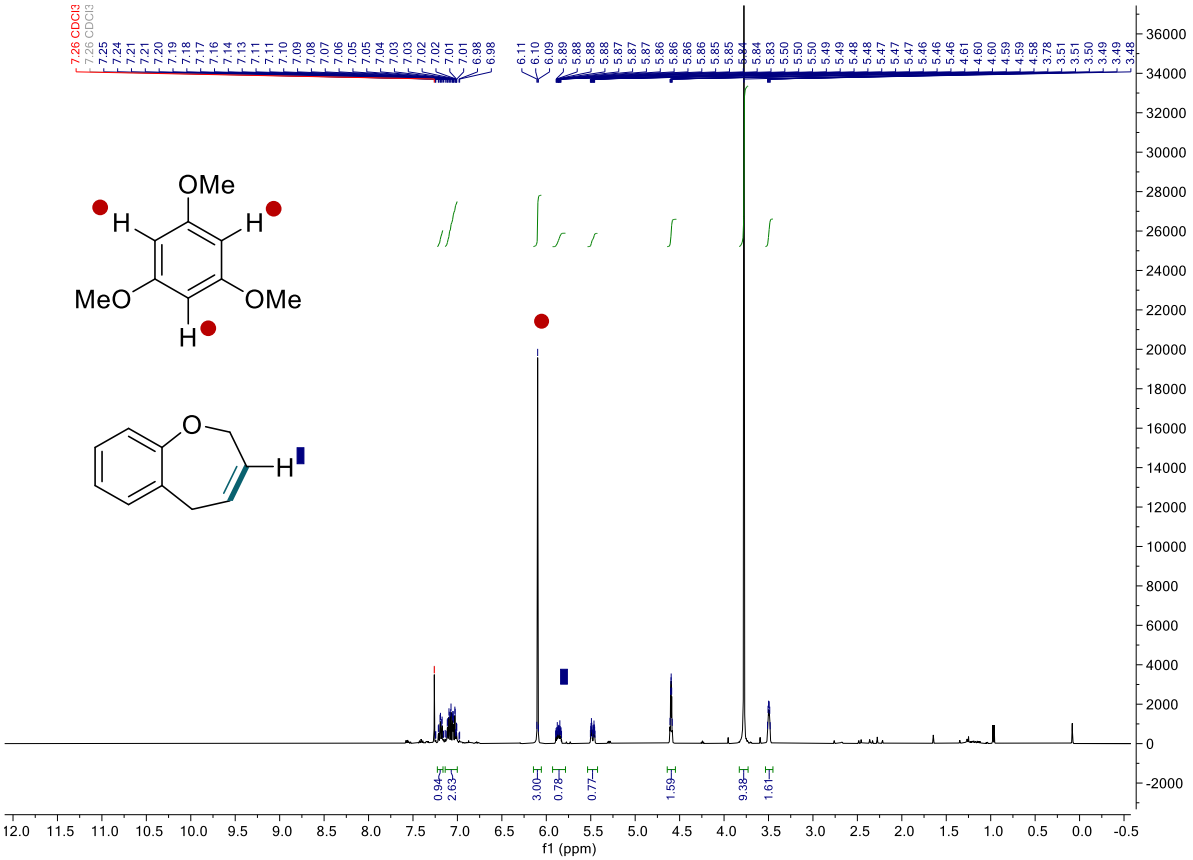
^{1}H NMR (400 MHz, $CDCl_3$) (2f)



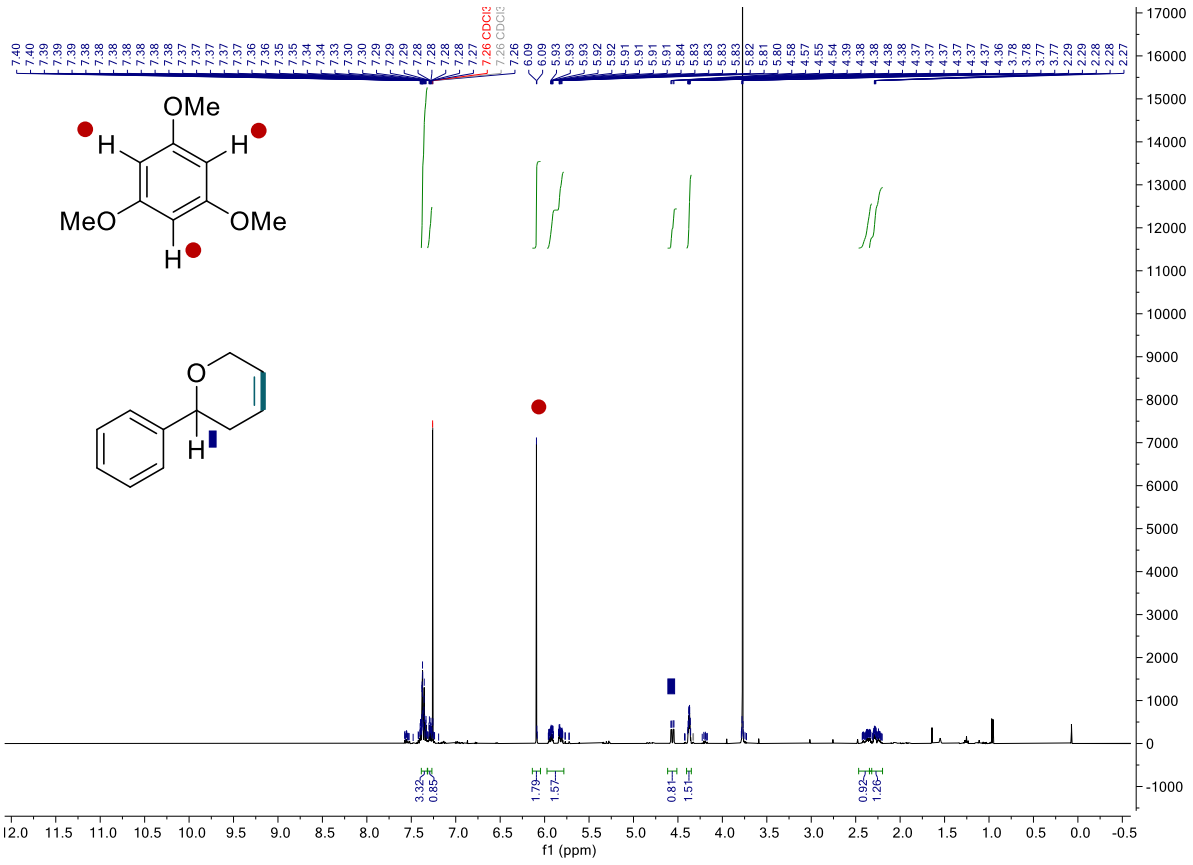
^{1}H NMR (400 MHz, $CDCl_3$) (2h)



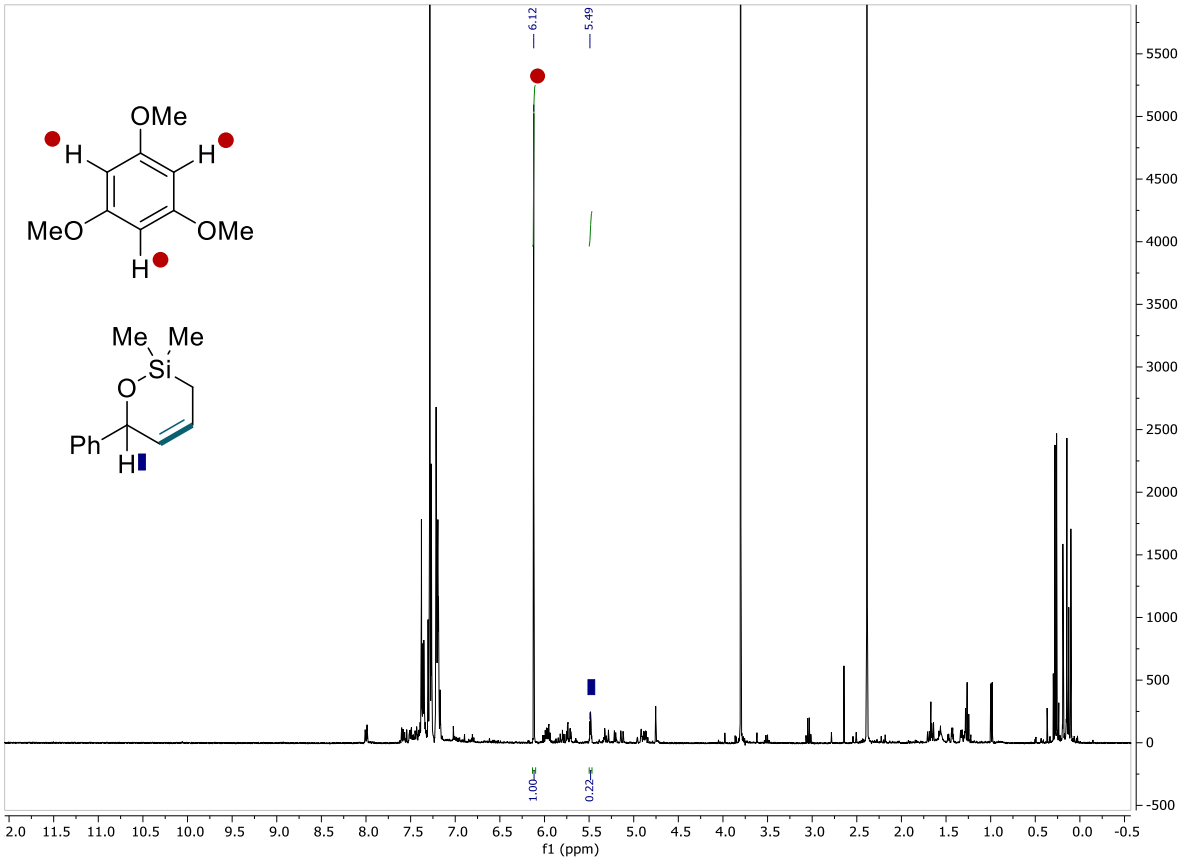
^{1}H NMR (400 MHz, $CDCl_3$) (2i)



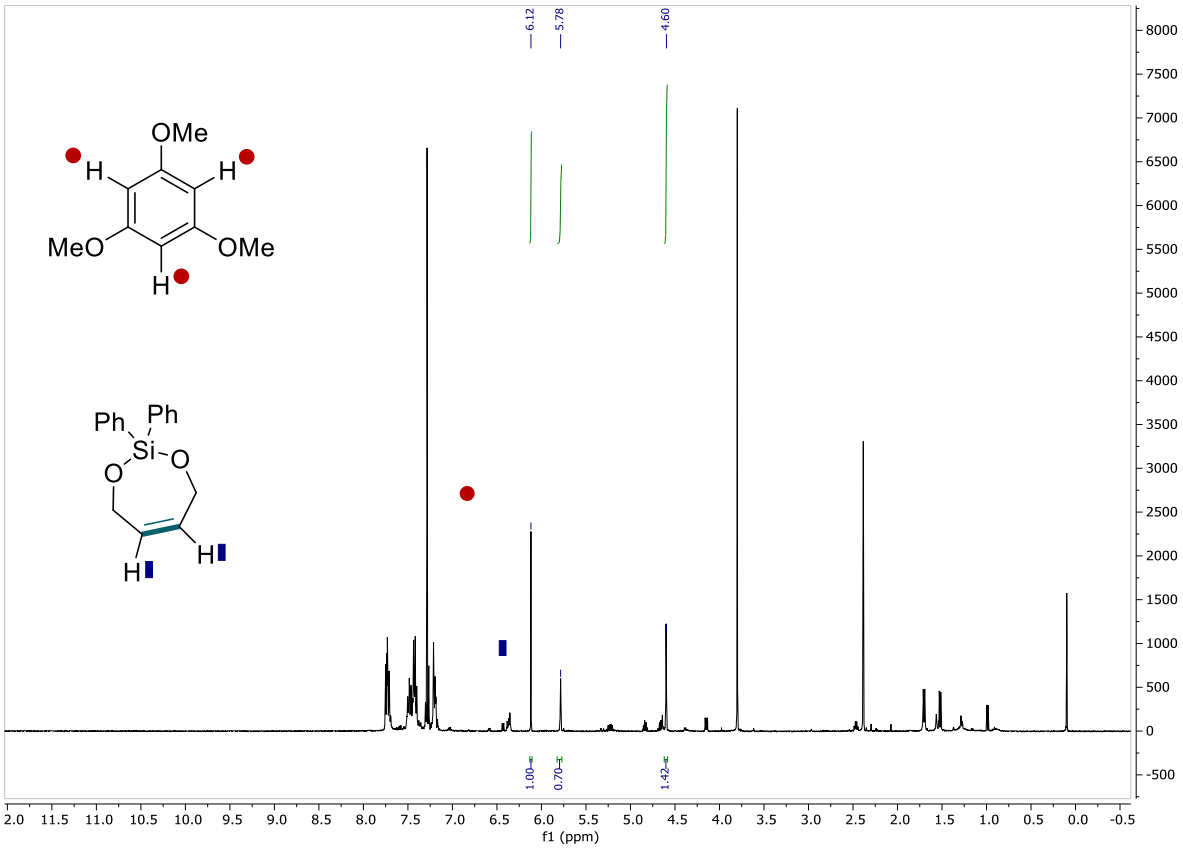
^{1}H NMR (400 MHz, $CDCl_3$) (2j)



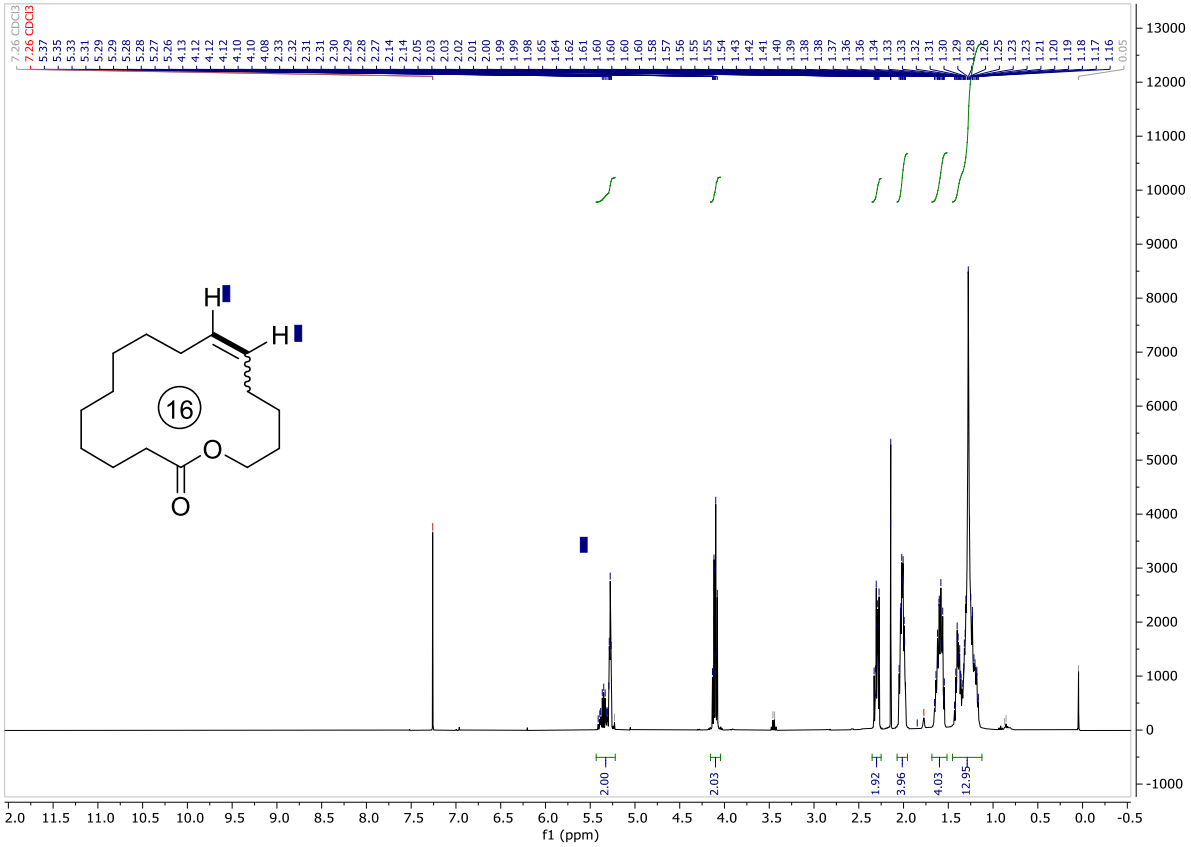
^{1}H NMR (400 MHz, $CDCl_3$) (2k)



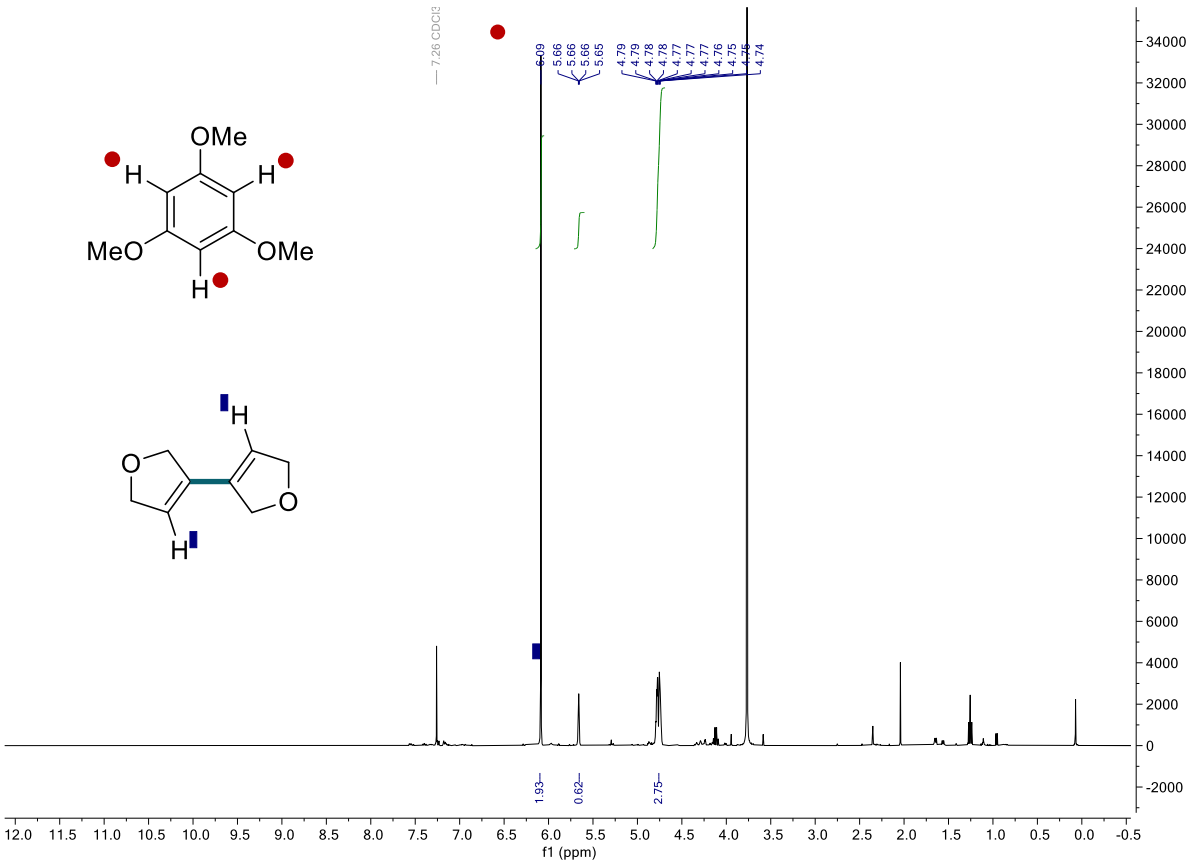
^{1}H NMR (400 MHz, $CDCl_3$) (2l)



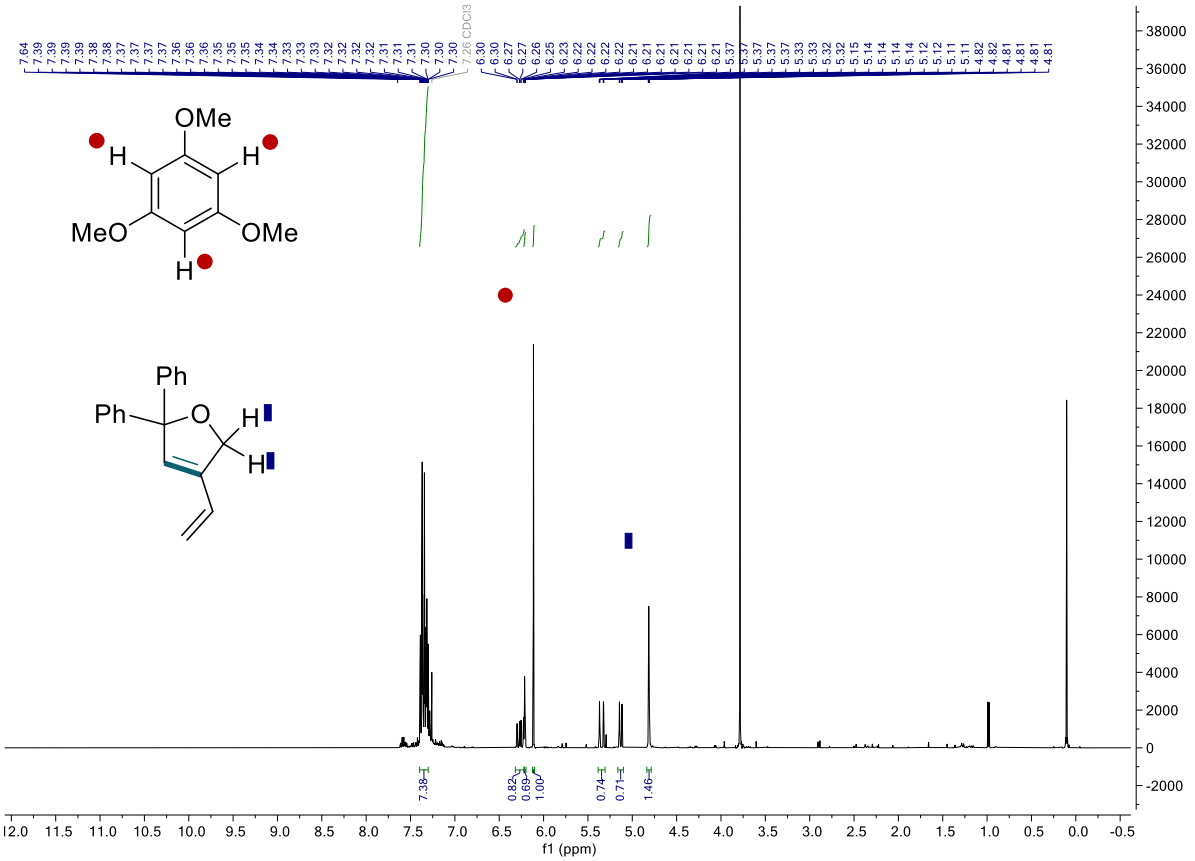
^{1}H NMR (400 MHz, $CDCl_3$) (2m)



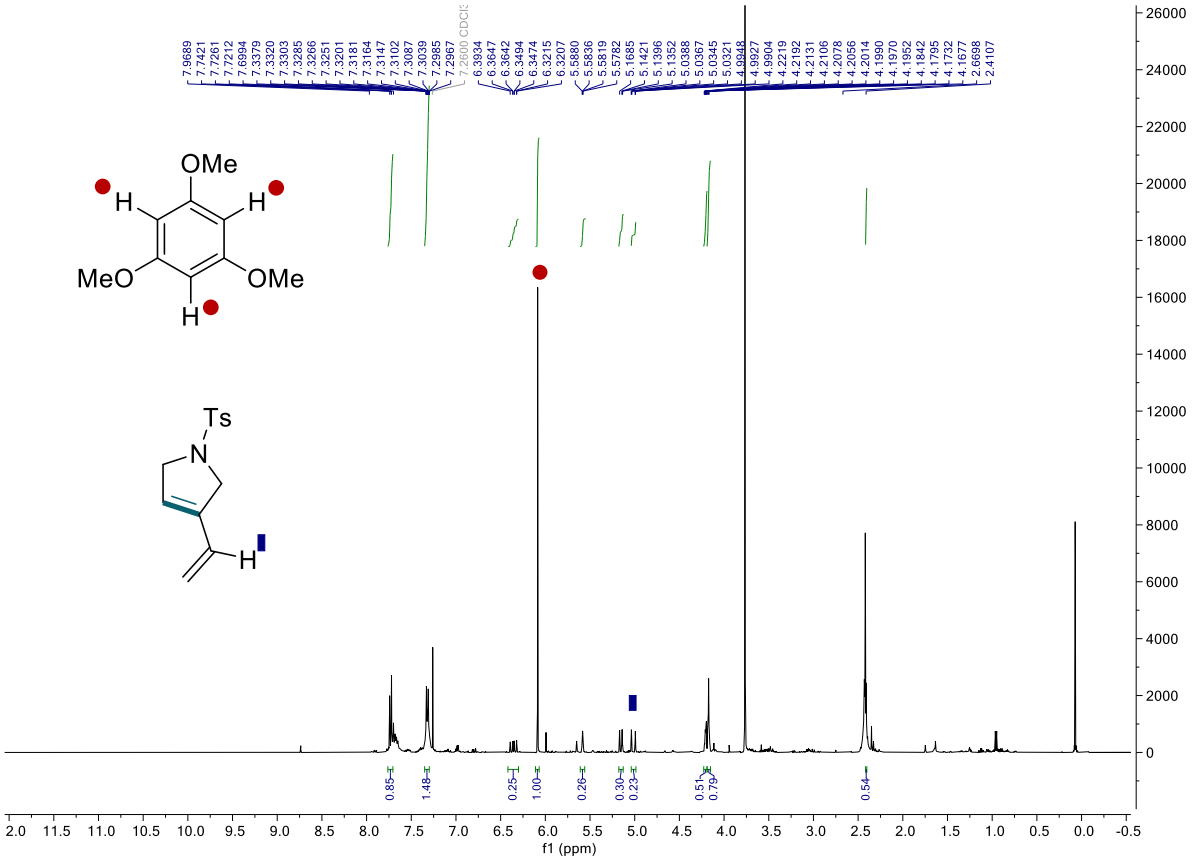
^{1}H NMR (400 MHz, $CDCl_3$) (4a)



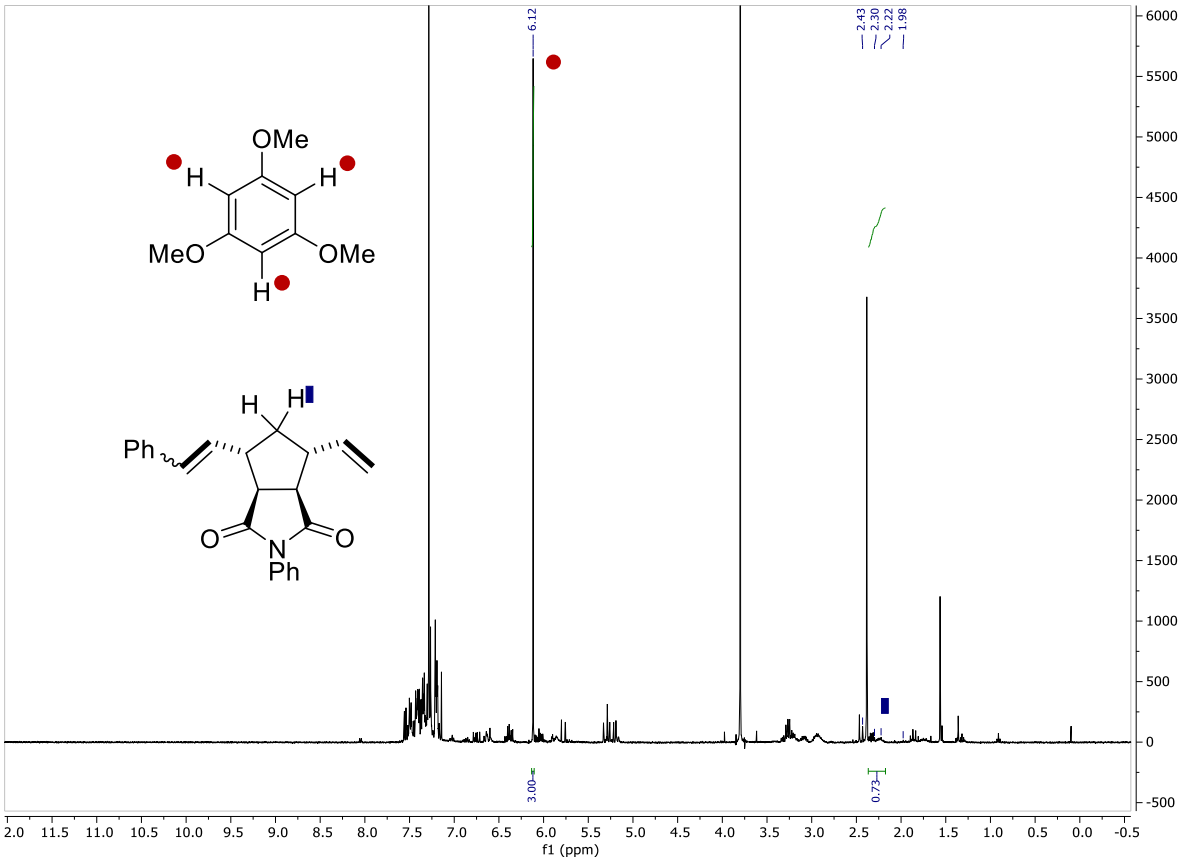
^{1}H NMR (400 MHz, $CDCl_3$) (4b)



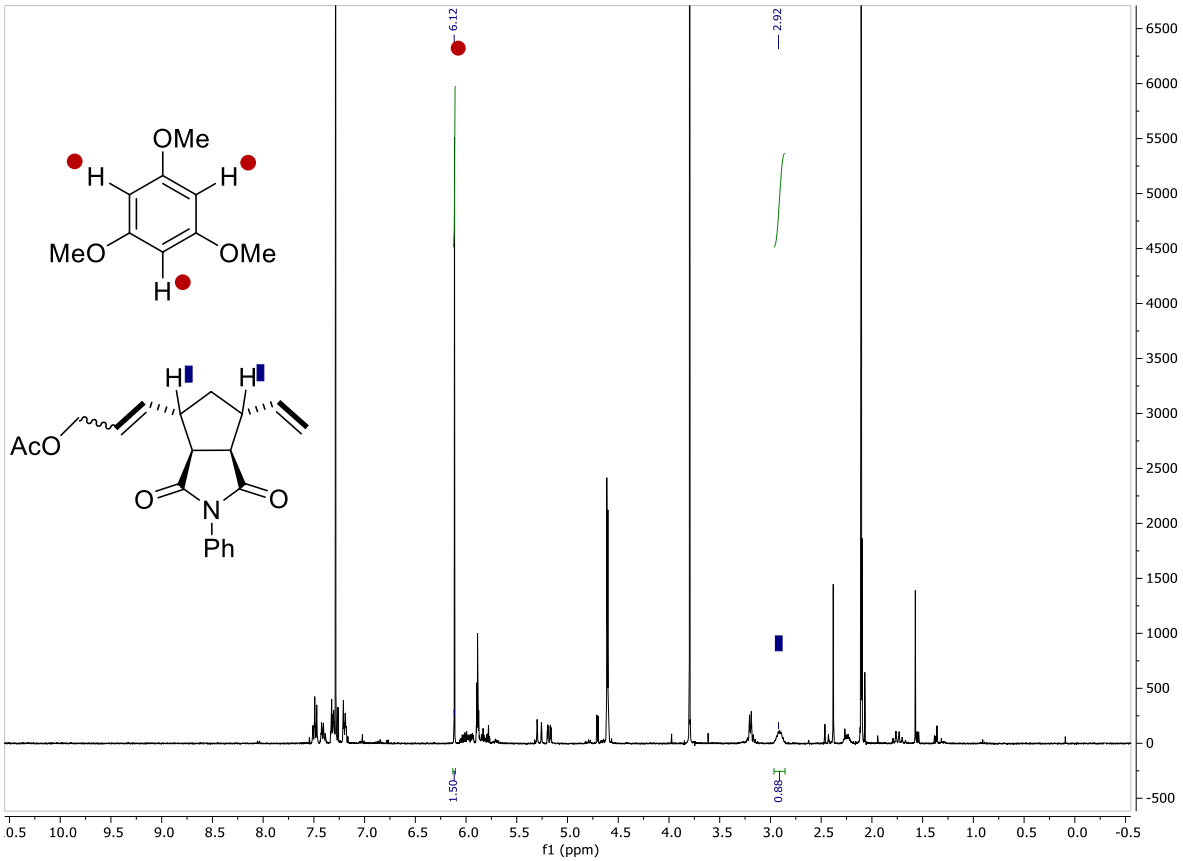
^{1}H NMR (400 MHz, $CDCl_3$) (4c)



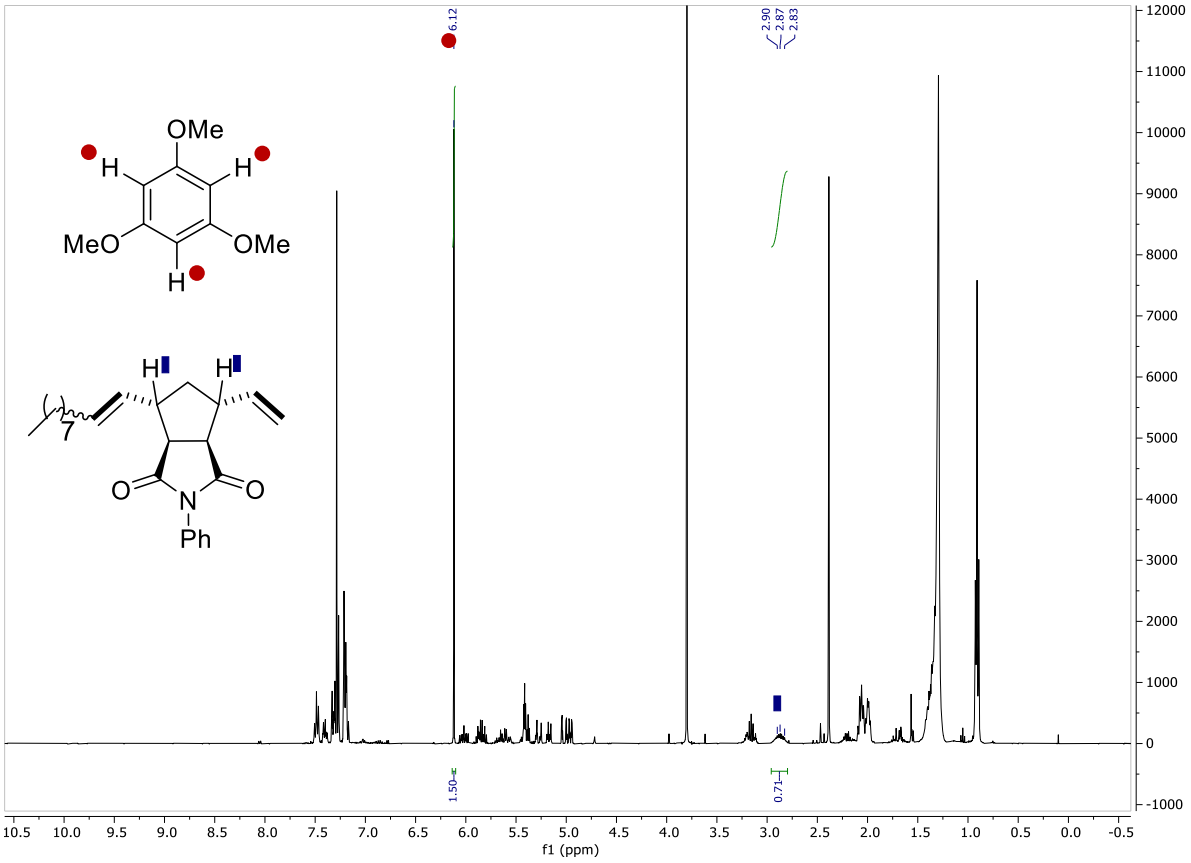
^{1}H NMR (400 MHz, $CDCl_3$) (6a)



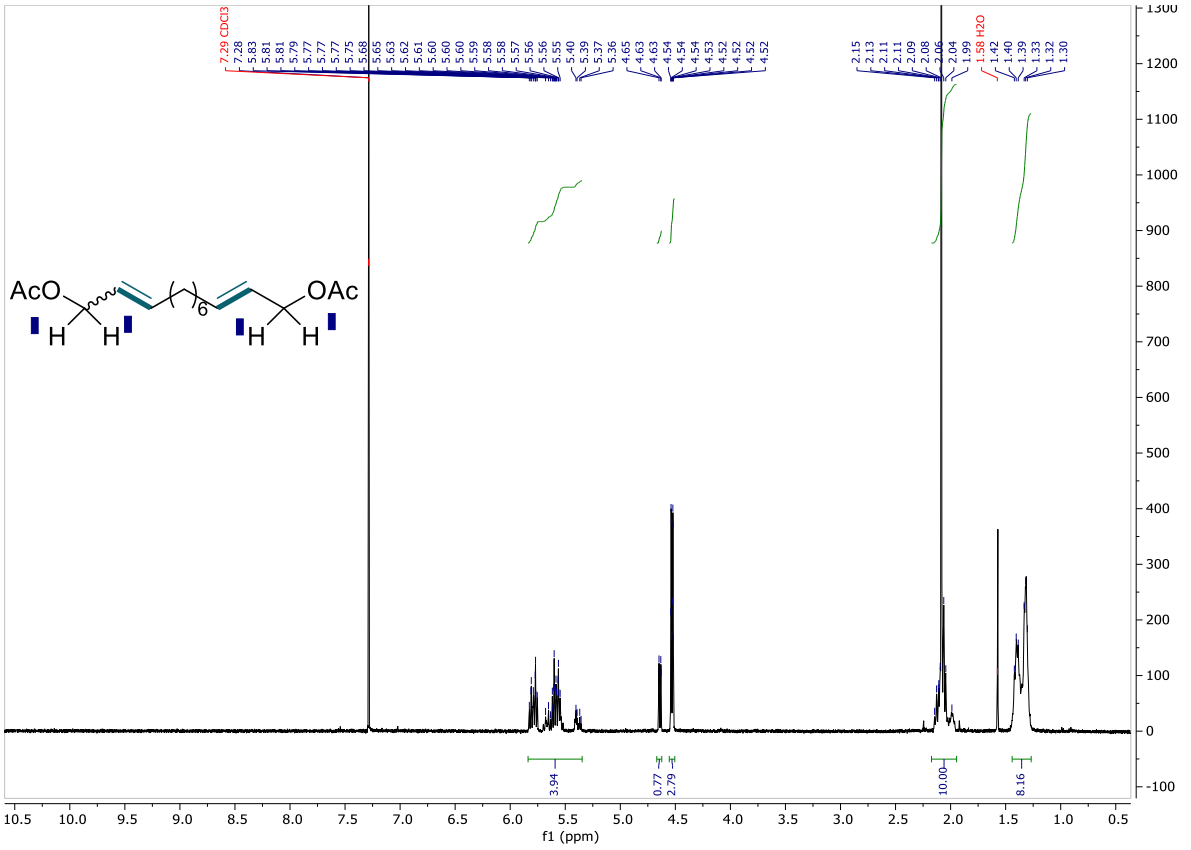
^{1}H NMR (400 MHz, $CDCl_3$) (6b)



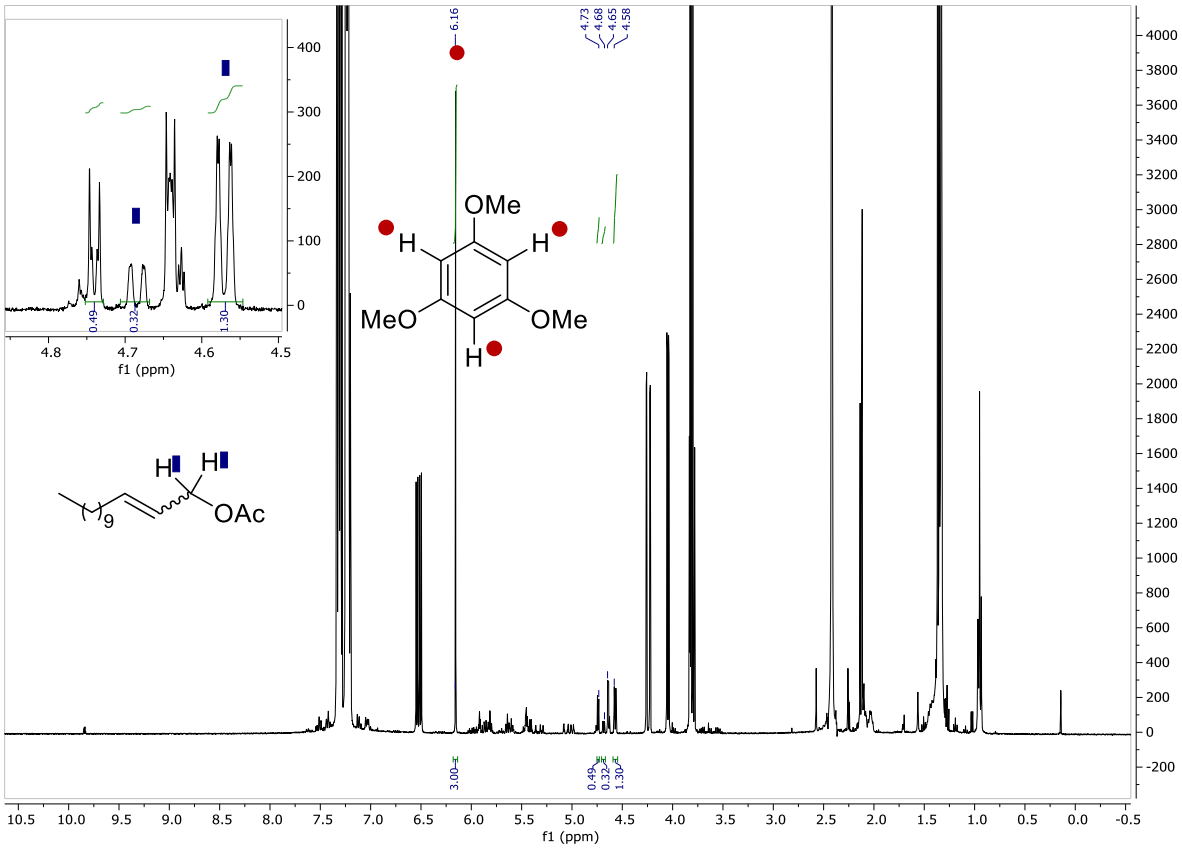
^{1}H NMR (400 MHz, $CDCl_3$) (6c)



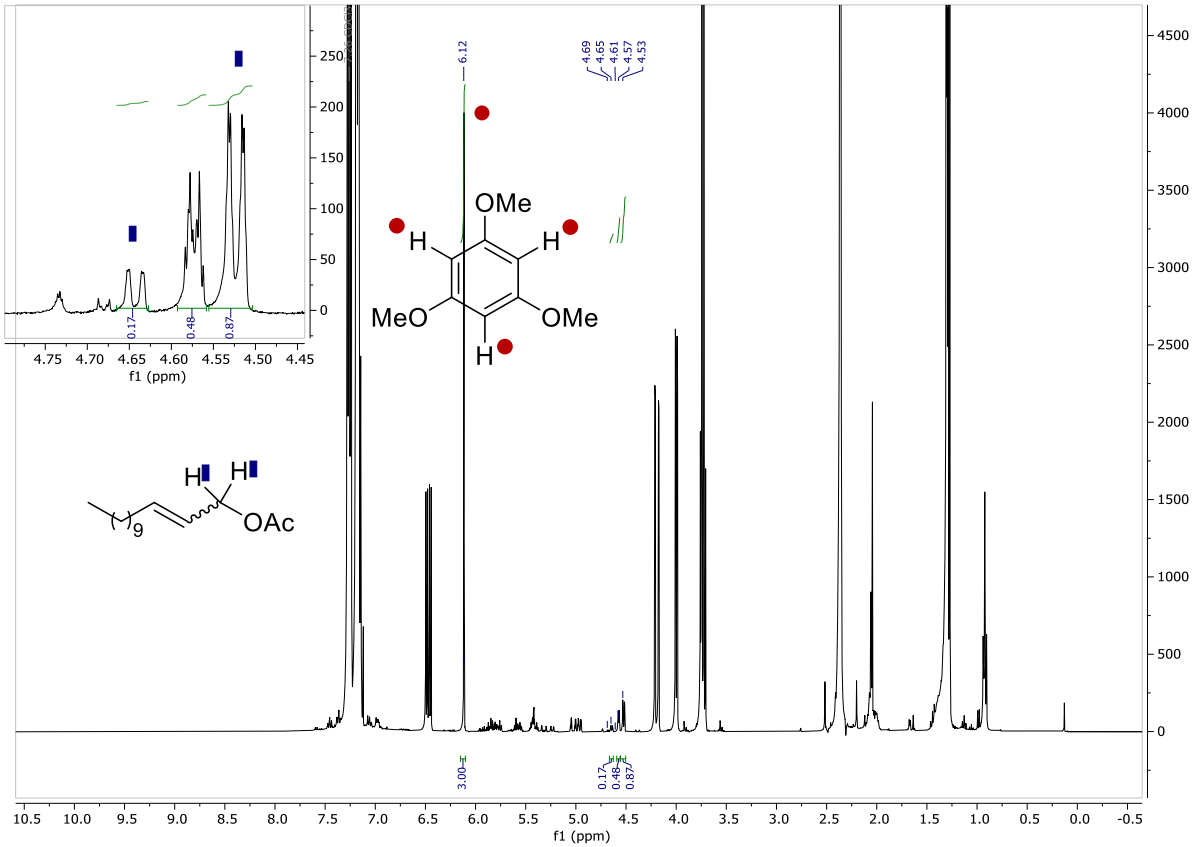
^{1}H NMR (400 MHz, $CDCl_3$) (9)



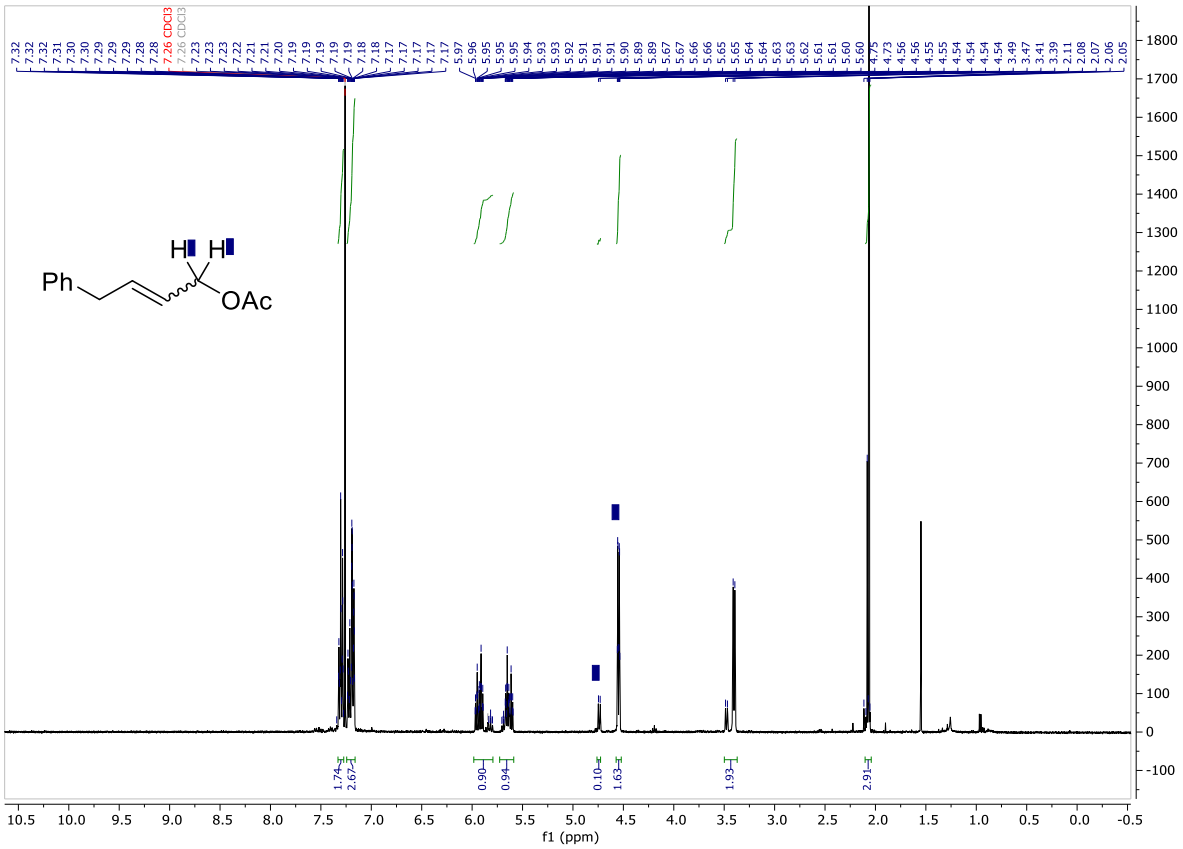
^{1}H NMR (400 MHz, $CDCl_3$) (11a) from allyl acetate 10



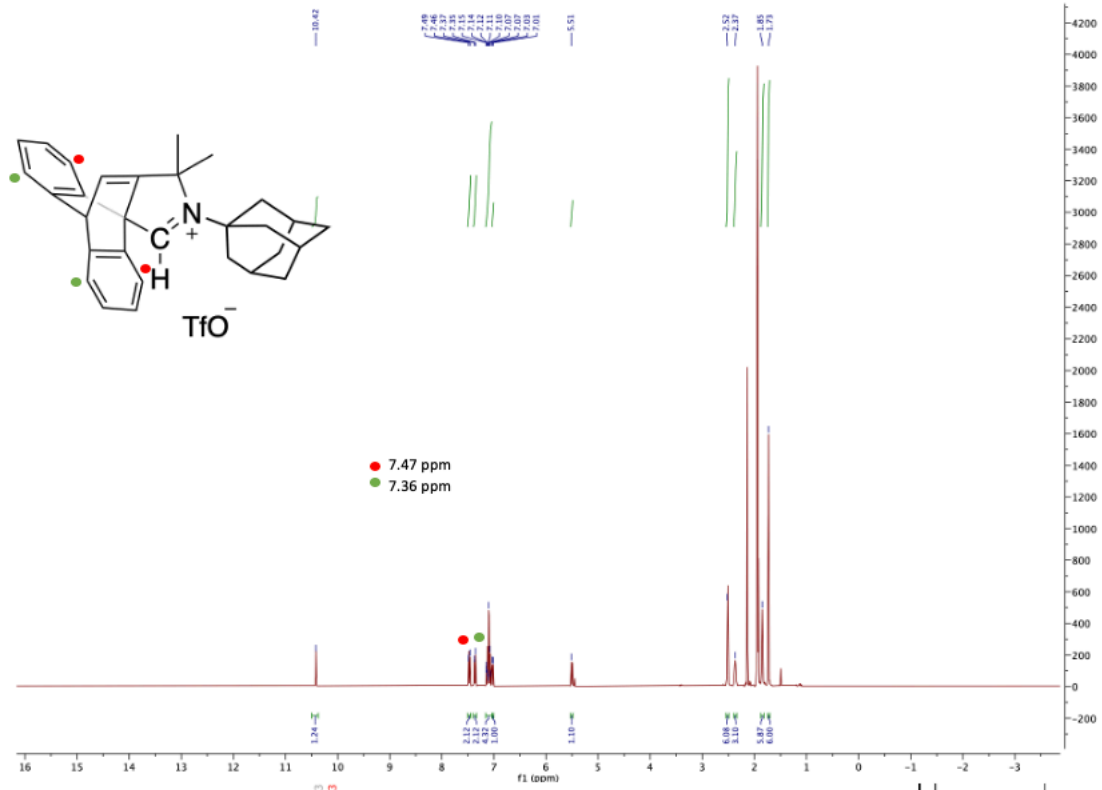
^{1}H NMR (400 MHz, $CDCl_3$) (11a) from diacetoxybutene 8

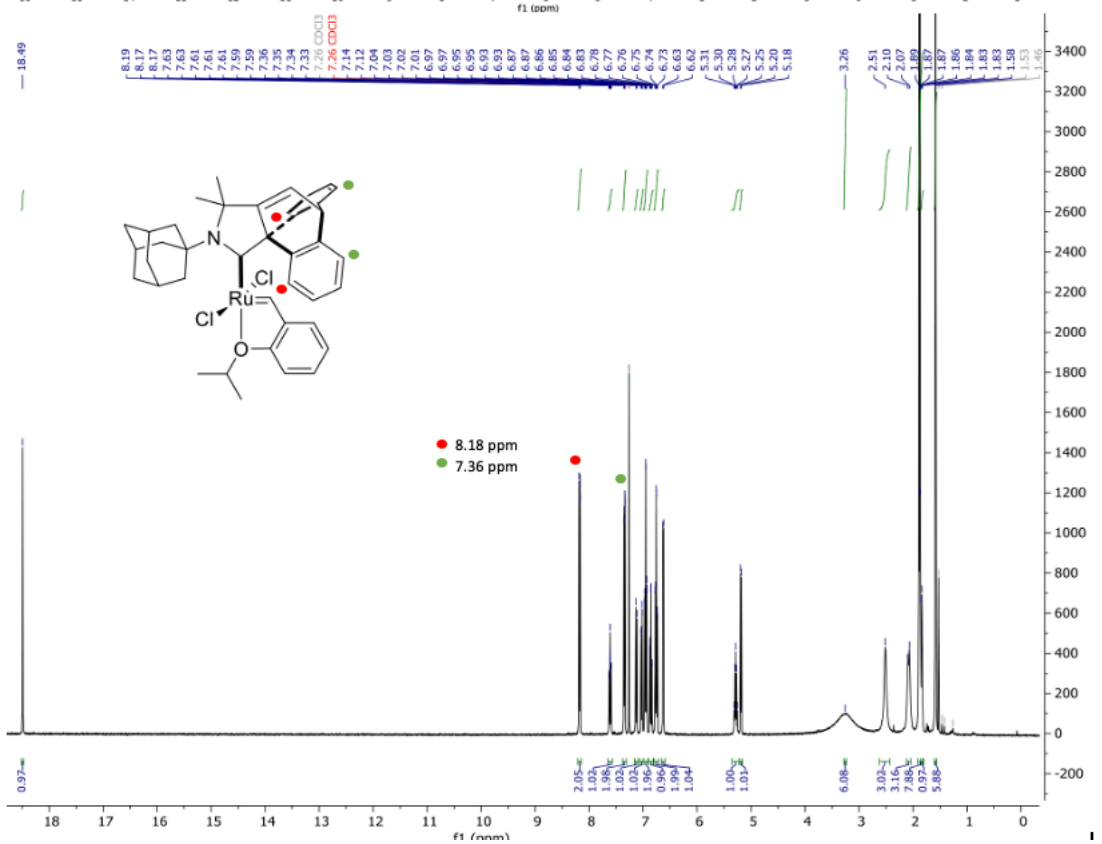


^{1}H NMR (400 MHz, $CDCl_3$) (11b)



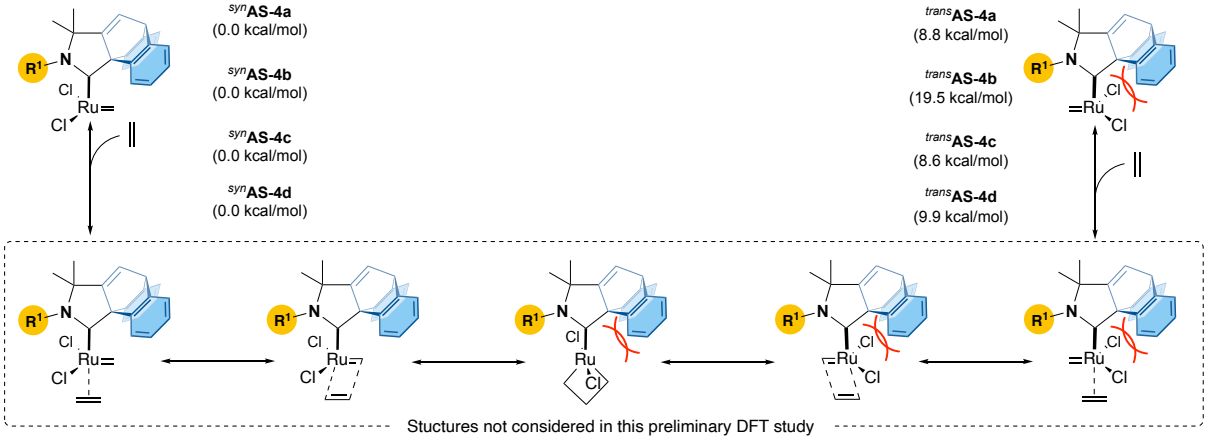
2.7.16 Highlighting weak hydrogen bond interactions by ^{1}H NMR in Ru-4b





3 Computational details

All calculations were performed using Gaussian 16, Revision C.01.[15] All structures were calculated without constraints using B3LYP and LACVP** basis set.[16] This method was chosen based for its accuracy for describing non-covalent interactions and outstanding performance for predicting structural parameters of related systems. The optimized geometric parameters were verified as true minima by the absence of negative eigenvalues in the harmonic vibrational frequency analysis. Energy reported for all molecules in this manuscript were the Gibbs free energies corrected with the zero-point energies. Geometry optimizations were benchmarked using B3LYP-d3 and several functionals comparing with X-ray structures. Based on these results, B3LYP-d3 and LACVP** basis set showed the best accuracy and were selected to perform analyze all other compounds. Gibbs free energies reported in this manuscript were corrected with the zero-point energies obtained from frequency calculations.



	R	N-C1-Ru-C4 °	C1-Ru-C4-H °	G (Hartree)	G (kCal)	ΔG (kCal)
SynAS-4a	**^{i}Pr**	177.17	4.21	-1107.641401	-694657.3046	0
AntiAS-4a	**^{i}Pr**	59.81	5.65	-1107.627295	-694648.4581	8.847
SynAS-4b	**Ad**	177.74	1.93	-1379.02862	-864857.799	0
AntiAS-4b	**Ad**	56.16	3.1	-1378.997547	-864838.3116	**19.487**
SynAS-4c	**Ph**	179.98	0.09	-1220.739806	-765586.9693	0
AntiAS-4c	**Ph**	45.94	3.62	-1220.726062	-765578.3498	**8.62**
SynAS-4d	**Mes**	179.95	0.08	-1338.589978	-839496.7047	0
AntiAS-4d	**Mes**	45.07	3.23	-1338.574117	-839486.7575	**9.947**

3.1 **SynAS-4a**

Ru	9.939000	2.326000	12.710000
Cl	8.751000	0.779000	14.084000
Cl	11.983000	3.512000	12.404000
N	8.790000	4.312000	14.397000
C	8.768000	3.779000	13.172000
C	7.103000	5.486000	13.325000
C	9.465000	5.345000	10.594000
H	10.274000	4.759000	11.011000
C	6.481000	3.654000	11.854000
C	6.263000	2.284000	11.949000
H	6.993000	1.634000	12.416000
C	8.186000	5.295000	11.138000
C	6.153000	6.277000	12.832000
H	5.607000	7.038000	13.378000
C	9.340000	2.059000	11.026000
H	8.589000	2.664000	10.513000
C	7.697000	4.468000	12.347000
C	5.490000	4.491000	11.307000
C	7.163000	6.101000	10.611000
C	7.403000	6.925000	9.519000
H	6.604000	7.539000	9.114000
C	5.065000	1.748000	11.454000
H	4.893000	0.680000	11.529000
C	9.859000	3.932000	15.361000
H	10.319000	3.035000	14.920000
C	7.671000	5.284000	14.702000
C	4.311000	3.956000	10.809000
H	3.555000	4.607000	10.380000
C	5.845000	5.974000	11.361000
H	5.061000	6.609000	10.945000
C	6.596000	4.608000	15.578000
H	6.927000	4.469000	16.608000
H	6.323000	3.636000	15.156000
H	5.706000	5.244000	15.583000
C	9.706000	6.183000	9.497000
H	10.703000	6.222000	9.072000
C	8.161000	6.591000	15.322000
H	8.944000	7.045000	14.711000
H	8.532000	6.444000	16.340000
H	7.317000	7.287000	15.371000
C	4.101000	2.572000	10.879000
H	3.179000	2.147000	10.496000
C	8.685000	6.961000	8.957000
H	8.882000	7.604000	8.105000
C	9.340000	3.498000	16.726000
H	8.580000	2.720000	16.625000
H	8.939000	4.337000	17.303000
H	10.178000	3.082000	17.294000
C	10.956000	4.995000	15.441000
H	10.637000	5.876000	16.001000
H	11.277000	5.288000	14.440000
H	11.822000	4.565000	15.955000
H	9.778000	1.224000	10.460000

3.2 **AntiAS-4a**

Ru	10.125000	2.457000	13.378000
Cl	12.046000	3.628000	14.108000
Cl	9.095000	1.436000	11.481000
N	7.392000	3.607000	13.449000
C	8.718000	3.785000	13.461000
C	7.643000	5.904000	13.151000
C	9.891000	5.301000	15.851000
H	9.892000	4.221000	15.931000
C	9.889000	5.771000	12.216000
C	10.559000	5.020000	11.260000
H	10.501000	3.935000	11.245000
C	9.536000	5.922000	14.662000
C	7.632000	7.233000	13.062000
H	6.761000	7.859000	12.907000
C	9.694000	1.508000	14.859000
H	8.920000	1.753000	15.590000
C	9.013000	5.266000	13.366000
C	9.907000	7.175000	12.156000
C	9.551000	7.322000	14.560000
C	9.965000	8.102000	15.632000
H	9.985000	9.184000	15.545000
C	11.296000	5.677000	10.267000
H	11.826000	5.093000	9.523000
C	6.756000	2.300000	13.766000
H	7.580000	1.588000	13.688000
C	6.589000	4.840000	13.057000
C	10.643000	7.826000	11.176000
H	10.663000	8.911000	11.138000
C	9.036000	7.836000	13.220000
H	9.046000	8.925000	13.154000
C	6.134000	4.724000	11.588000
H	5.312000	4.019000	11.459000
H	6.972000	4.415000	10.957000
H	5.798000	5.712000	11.257000
C	10.296000	6.088000	16.937000
H	10.588000	5.607000	17.864000
C	5.416000	5.120000	13.994000
H	5.751000	5.181000	15.033000
H	4.630000	4.366000	13.906000
H	4.983000	6.087000	13.720000
C	11.348000	7.069000	10.231000

H	11.926000	7.570000	9.461000
C	10.342000	7.477000	16.828000
H	10.665000	8.078000	17.671000
C	5.702000	1.837000	12.767000
H	6.108000	1.834000	11.753000
H	4.787000	2.436000	12.801000
H	5.428000	0.808000	13.021000
C	6.239000	2.277000	15.210000
H	5.279000	2.786000	15.319000
H	6.953000	2.749000	15.893000
H	6.101000	1.236000	15.521000
H	10.301000	0.618000	15.073000

3.3 **SynAS-4b**

Ru	6.967000	8.562000	4.586000
Cl	9.286000	8.744000	3.910000
Cl	4.625000	8.692000	4.037000
C	7.017000	9.720000	5.985000
H	7.060000	9.468000	7.046000
C	6.960000	6.916000	5.593000
N	6.968000	5.672000	5.070000
C	7.239000	5.369000	3.612000
C	6.751000	6.512000	2.703000
H	7.301000	7.451000	2.902000
H	5.679000	6.675000	2.836000
C	7.083000	6.233000	1.221000
H	6.731000	7.090000	0.633000
C	8.605000	6.077000	1.067000
H	9.111000	7.002000	1.371000
H	8.856000	5.890000	0.014000
C	9.081000	4.907000	1.941000
H	10.167000	4.785000	1.836000
C	8.366000	3.614000	1.511000
H	8.707000	2.771000	2.128000
H	8.613000	3.374000	0.468000
C	6.846000	3.798000	1.657000
H	6.332000	2.871000	1.371000
C	6.496000	4.104000	3.127000
H	6.765000	3.232000	3.726000
H	5.415000	4.261000	3.222000
C	8.764000	5.196000	3.420000
H	9.264000	6.115000	3.747000
H	9.133000	4.372000	4.037000
C	6.373000	4.953000	0.767000
H	5.284000	5.073000	0.845000
H	6.607000	4.746000	-0.285000
C	6.784000	4.552000	6.096000
C	7.895000	3.494000	6.085000
H	8.872000	3.965000	6.219000
H	7.909000	2.881000	5.183000
H	7.725000	2.828000	6.938000
C	5.375000	3.931000	5.999000
H	5.188000	3.372000	6.920000
H	5.261000	3.249000	5.157000
H	4.624000	4.723000	5.924000
C	6.867000	5.319000	7.381000
C	6.882000	4.937000	8.657000
H	6.839000	3.916000	9.019000
C	6.968000	6.123000	9.619000
H	6.980000	5.828000	10.670000
C	8.210000	6.901000	9.213000
C	9.276000	7.216000	10.046000
H	9.250000	6.930000	11.093000
C	10.384000	7.891000	9.518000
H	11.223000	8.138000	10.161000
C	10.412000	8.229000	8.168000
H	11.276000	8.736000	7.750000
C	9.333000	7.921000	7.327000
H	9.382000	8.184000	6.279000
C	8.222000	7.275000	7.858000
C	5.793000	7.027000	9.276000
C	4.815000	7.447000	10.167000
H	4.871000	7.156000	11.212000
C	3.754000	8.234000	9.703000
H	2.983000	8.563000	10.392000
C	3.684000	8.577000	8.355000
H	2.853000	9.168000	7.985000
C	4.676000	8.162000	7.455000
H	4.590000	8.424000	6.409000
C	5.745000	7.404000	7.920000
C	6.935000	6.817000	7.121000
H	7.018000	10.796000	5.749000

3.4 **AntiAS-4b**

Ru	3.998000	6.754000	5.874000
Cl	3.887000	6.465000	3.512000
Cl	2.906000	6.060000	7.894000
C	4.151000	8.558000	5.841000
H	5.050000	9.150000	6.011000
C	5.790000	6.177000	6.411000
N	6.657000	6.388000	7.424000
C	6.690000	7.596000	8.355000
C	7.384000	8.739000	7.577000
H	6.841000	8.918000	6.643000
H	8.398000	8.438000	7.295000
C	7.443000	10.016000	8.431000

H	7.926000	10.810000	7.846000
C	6.021000	10.447000	8.824000
H	5.425000	10.653000	7.924000
H	6.057000	11.377000	9.407000
C	5.360000	9.331000	9.651000
H	4.334000	9.619000	9.909000
C	6.174000	9.087000	10.927000
H	5.686000	8.322000	11.545000
H	6.238000	10.005000	11.527000
C	7.574000	8.623000	10.511000
H	8.173000	8.392000	11.403000
C	7.469000	7.333000	9.670000
H	6.940000	6.569000	10.251000
H	8.481000	6.976000	9.487000
C	5.290000	8.037000	8.820000
H	4.631000	8.209000	7.975000
H	4.834000	7.229000	9.399000
C	8.266000	9.729000	9.698000
H	9.285000	9.420000	9.423000
H	8.355000	10.638000	10.306000
C	7.802000	5.346000	7.490000
C	7.709000	4.466000	8.749000
H	6.665000	4.215000	8.954000
H	8.152000	4.918000	9.634000
H	8.245000	3.533000	8.542000
C	9.197000	5.961000	7.272000
H	9.914000	5.135000	7.211000
H	9.525000	6.629000	8.067000
H	9.224000	6.494000	6.318000
C	7.518000	4.506000	6.282000
C	8.183000	3.515000	5.688000
H	9.074000	3.025000	6.065000
C	7.624000	3.196000	4.296000
H	8.169000	2.401000	3.783000
C	6.151000	2.872000	4.480000
C	5.514000	1.710000	4.064000
H	6.069000	0.948000	3.526000
C	4.157000	1.527000	4.358000
H	3.651000	0.624000	4.035000
C	3.465000	2.496000	5.080000
H	2.420000	2.348000	5.331000
C	4.110000	3.667000	5.497000
H	3.552000	4.366000	6.115000
C	5.443000	3.870000	5.169000
C	7.670000	4.524000	3.543000
C	8.350000	4.772000	2.358000
H	8.864000	3.965000	1.845000
C	8.381000	6.076000	1.846000
H	8.913000	6.280000	0.923000
C	7.739000	7.110000	2.523000
H	7.767000	8.119000	2.126000
C	7.036000	6.857000	3.708000
H	6.504000	7.656000	4.210000
C	6.989000	5.560000	4.202000
C	6.337000	5.066000	5.520000
H	3.250000	9.124000	5.562000

3.5 **SynAS-4c**

Ru	7.188000	8.199000	13.600000
Cl	9.266000	7.167000	14.156000
Cl	5.951000	9.629000	12.144000
C	6.500000	8.600000	15.223000
H	5.745000	8.022000	15.759000
C	6.168000	6.599000	13.325000
N	6.322000	5.889000	12.203000
C	7.234000	6.262000	11.155000
C	6.792000	7.088000	10.117000
H	5.785000	7.485000	10.144000
C	7.673000	7.426000	9.091000
H	7.338000	8.079000	8.292000
C	8.983000	6.944000	9.103000
H	9.667000	7.215000	8.306000
C	9.420000	6.129000	10.149000
H	10.444000	5.772000	10.174000
C	8.548000	5.784000	11.181000
H	8.882000	5.186000	12.019000
C	5.484000	4.642000	12.059000
C	4.562000	4.770000	10.843000
H	3.912000	3.892000	10.792000
H	5.143000	4.829000	9.917000
H	3.933000	5.661000	10.931000
C	6.392000	3.413000	11.950000
H	7.053000	3.347000	12.819000
H	6.997000	3.453000	11.039000
H	5.772000	2.512000	11.918000
C	4.726000	4.677000	13.353000
C	3.807000	3.883000	13.899000
H	3.403000	2.979000	13.459000
C	3.342000	4.381000	15.272000
H	2.588000	3.740000	15.730000
C	4.599000	4.511000	16.123000
C	4.819000	3.894000	17.347000
H	4.047000	3.273000	17.791000
C	6.048000	4.074000	17.995000
H	6.230000	3.592000	18.950000
C	7.039000	4.856000	17.407000
H	7.998000	4.981000	17.898000
C	6.817000	5.488000	16.174000
H	7.606000	6.076000	15.721000

C	5.588000	5.327000	15.545000
C	5.128000	5.903000	14.189000
C	3.804000	6.649000	14.462000
C	3.478000	7.963000	14.147000
H	4.186000	8.612000	13.645000
C	2.200000	8.443000	14.468000
H	1.945000	9.469000	14.222000
C	1.265000	7.619000	15.089000
H	0.280000	8.003000	15.336000
C	1.588000	6.289000	15.385000
H	0.860000	5.635000	15.855000
C	2.849000	5.808000	15.061000
H	6.873000	9.507000	15.722000

3.6 **AntiAS-4c**

Ru	6.702000	8.480000	12.936000
Cl	8.745000	7.997000	11.837000
Cl	4.558000	9.522000	12.736000
C	7.271000	8.848000	14.614000
H	7.227000	8.184000	15.477000
C	5.933000	6.745000	13.215000
N	5.125000	6.328000	14.198000
C	4.945000	6.961000	15.475000
C	5.720000	6.506000	16.547000
H	6.447000	5.718000	16.379000
C	5.561000	7.079000	17.808000
H	6.166000	6.731000	18.638000
C	4.629000	8.104000	17.995000
H	4.509000	8.554000	18.975000
C	3.858000	8.549000	16.921000
H	3.142000	9.352000	17.060000
C	4.007000	7.977000	15.656000
H	3.444000	8.342000	14.807000
C	4.276000	5.103000	13.885000
C	4.398000	4.044000	14.980000
H	3.824000	3.162000	14.681000
H	4.002000	4.408000	15.933000
H	5.441000	3.743000	15.111000
C	2.824000	5.560000	13.699000
H	2.767000	6.346000	12.940000
H	2.411000	5.939000	14.639000
H	2.221000	4.709000	13.371000
C	4.907000	4.656000	12.602000
C	4.791000	3.562000	11.849000
H	4.097000	2.746000	12.012000
C	5.838000	3.512000	10.729000
H	5.765000	2.616000	10.111000
C	5.688000	4.794000	9.921000
C	5.484000	4.874000	8.550000
H	5.428000	3.969000	7.953000
C	5.347000	6.131000	7.949000
H	5.189000	6.204000	6.878000
C	5.404000	7.287000	8.725000
H	5.284000	8.261000	8.264000
C	5.610000	7.204000	10.108000
H	5.601000	8.121000	10.690000
C	5.770000	5.959000	10.702000
C	6.005000	5.636000	12.178000
C	7.292000	4.778000	12.243000
C	8.418000	4.991000	13.024000
H	8.507000	5.880000	13.636000
C	9.465000	4.060000	12.973000
H	10.355000	4.227000	13.570000
C	9.376000	2.937000	12.153000
H	10.196000	2.227000	12.114000
C	8.228000	2.717000	11.379000
H	8.148000	1.837000	10.749000
C	7.186000	3.631000	11.438000
H	7.731000	9.835000	14.769000

3.7 **SynAS-4d**

Ru	3.279000	14.448000	4.215000
Cl	2.491000	13.549000	2.153000
Cl	4.982000	15.745000	5.261000
C	1.806000	15.346000	4.760000
H	1.113000	15.026000	5.541000
C	3.079000	12.963000	5.424000
N	3.946000	11.938000	5.453000
C	5.093000	11.880000	4.576000
C	6.315000	12.450000	4.994000
C	7.404000	12.389000	4.118000
H	8.343000	12.838000	4.430000
C	7.314000	11.789000	2.861000
C	6.092000	11.231000	2.481000
H	5.998000	10.767000	1.503000
C	4.969000	11.262000	3.313000
C	6.517000	13.113000	6.330000
H	7.061000	12.451000	7.014000
H	5.578000	13.404000	6.799000
H	7.100000	14.028000	6.206000
C	8.490000	11.782000	1.923000
H	8.469000	10.912000	1.260000
H	9.438000	11.772000	2.470000
H	8.486000	12.678000	1.290000
C	3.699000	10.627000	2.813000
H	3.755000	9.534000	2.887000

H	3.541000	10.889000	1.765000
H	2.818000	10.969000	3.355000
C	3.666000	10.836000	6.458000
C	4.807000	10.703000	7.471000
H	4.944000	11.626000	8.036000
H	5.743000	10.439000	6.968000
H	4.555000	9.904000	8.175000
C	3.437000	9.492000	5.759000
H	3.232000	8.735000	6.522000
H	4.328000	9.189000	5.201000
H	2.581000	9.537000	5.085000
C	2.413000	11.358000	7.092000
C	1.614000	10.901000	8.055000
H	1.744000	9.976000	8.605000
C	0.436000	11.840000	8.336000
H	-0.227000	11.478000	9.123000
C	1.048000	13.196000	8.663000
C	0.840000	13.925000	9.826000
H	0.161000	13.553000	10.588000
C	1.525000	15.133000	10.011000
H	1.371000	15.706000	10.920000
C	2.412000	15.588000	9.039000
H	2.957000	16.514000	9.189000
C	2.617000	14.860000	7.858000
H	3.321000	15.224000	7.118000
C	1.917000	13.674000	7.665000
C	2.004000	12.701000	6.470000
C	0.560000	12.478000	5.973000
C	0.068000	12.614000	4.679000
H	0.710000	12.925000	3.864000
C	-1.283000	12.331000	4.431000
H	-1.667000	12.439000	3.422000
C	-2.124000	11.915000	5.460000
H	-3.169000	11.703000	5.257000
C	-1.620000	11.755000	6.757000
H	-2.265000	11.412000	7.561000
C	-0.281000	12.024000	7.004000
H	1.580000	16.302000	4.266000

3.8 **AntiAS-4d**

Ru	4.093000	14.448000	4.443000
Cl	4.713000	13.248000	2.495000
Cl	5.055000	15.897000	6.069000
C	2.610000	15.321000	3.889000
H	1.582000	15.126000	4.183000
C	3.325000	13.092000	5.586000
N	2.363000	13.172000	6.522000
C	1.455000	14.280000	6.706000
C	0.268000	14.314000	5.941000
C	-0.635000	15.360000	6.154000
H	-1.546000	15.389000	5.561000
C	-0.393000	16.367000	7.091000
C	0.794000	16.310000	7.822000
H	1.013000	17.092000	8.544000
C	1.732000	15.285000	7.652000
C	-0.063000	13.298000	4.876000
H	-0.847000	12.611000	5.214000
H	0.799000	12.698000	4.584000
H	-0.441000	13.799000	3.978000
C	-1.363000	17.502000	7.276000
H	-1.335000	17.890000	8.299000
H	-2.389000	17.192000	7.057000
H	-1.121000	18.335000	6.603000
C	2.982000	15.334000	8.487000
H	2.758000	15.111000	9.537000
H	3.421000	16.333000	8.439000
H	3.747000	14.646000	8.134000
C	2.194000	11.944000	7.416000
C	0.806000	11.318000	7.221000
H	0.669000	10.986000	6.190000
H	0.017000	12.026000	7.492000
H	0.727000	10.442000	7.872000
C	2.408000	12.281000	8.892000
H	2.301000	11.357000	9.469000
H	1.658000	12.995000	9.246000
H	3.407000	12.680000	9.069000
C	3.261000	11.049000	6.869000
C	3.633000	9.799000	7.142000
H	3.256000	9.184000	7.951000
C	4.594000	9.235000	6.089000
H	4.892000	8.204000	6.284000
C	3.854000	9.394000	4.761000
C	3.526000	8.369000	3.885000
H	3.847000	7.353000	4.091000
C	2.761000	8.658000	2.747000
H	2.496000	7.862000	2.059000
C	2.336000	9.962000	2.503000
H	1.745000	10.185000	1.622000
C	2.683000	11.001000	3.378000
H	2.389000	12.018000	3.154000
C	3.454000	10.716000	4.496000
C	3.898000	11.679000	5.628000
C	5.414000	11.517000	5.771000
C	6.389000	12.505000	5.720000
H	6.140000	13.555000	5.605000
C	7.736000	12.152000	5.873000
H	8.495000	12.926000	5.826000
C	8.100000	10.825000	6.087000

H	9.146000	10.559000	6.201000	C	5.781000	10.183000	6.013000
C	7.116000	9.832000	6.165000	H	2.777000	16.148000	3.182000
H	7.390000	8.797000	6.345000				

4 Topological Steric Maps

Topological steric maps analyzed in this study were performed using SambVca 2.1 program developed by Cavallo *et al*.[17]. Using the directions provided by these authors on their website,[18] topological steric maps were obtained using the xyz coordinates generated through computation (see section 3 of this ESI).

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