Supporting Information

Unsymmetrical unsaturated cycloakyl-based NHC ligands : flexibility and dissymetry in ruthenium catalysed olefin metathesis

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General Information

All the reactions were carried out under inert atmosphere (argon). Dichloromethane was dried over calcium hydride overnight then distilled and degassed. Toluene and THF were distilled over sodium/benzophenone and degassed priori to use. All commercial chemicals were used as received unless otherwise noted.
^{1}H (400 MHz), ^{11}B (128 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer with complete proton decoupling for nucleus other than ^{1}H. ^{1}H and ^{13}C 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, ^{13}C : 53.8 ppm); ^{11}B chemical shifts are reported in parts per millions with $BF_3.Et_2O$ (δ = 0.0 ppm) as the internal standard; ^{19}F chemical shifts are reported in parts per millions with $CFCl_3$ (δ = 0.0 ppm) as the internal standard. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, sep = septet, m = multiplet, br = broad. Due to long relaxation time, carbon of C=Ru may not be visible in ^{13}C NMR spectra. High resolution mass spectroscopy analyses were performed at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1 and at the Service Central d'Analyse, CNRS, Villeurbane (France). Melting points were measured on a Stuart Melting Point Apparatus SMP3 and are uncorrected. Elementary analysis were performed at Institut de Recherche en Chimie Organique Fine – Chimie Organique, Bioorganique Recherche et Analyse (IRCOF-COBRA), Université de Rouen.

Experimental Procedure

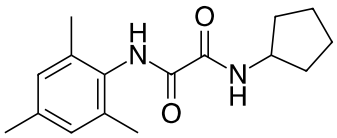
Synthesis of N-(2,4,6-trimethylphenyl)-oxalamic acid ethyl ester (15) :

Ethyloxalyl chloride **11** (2.681 mL, 24 mmol, 1.2 eq.) is added dropwise at 0 °C to a solution of 2,4,6-trimethylamine (2.817 mL, 20 mmol, 1 eq.) and triethylamine (1.940 mL, 24 mmol, 1.2 eq.) in dry dichloromethane (20 mL). The resulting solution is stirred overnight at room temperature. The reaction mixture is diluted with ethyl acetate, washed successively with 1 N HCl (3 times), saturated $NaHCO_3$ solution and brine. The organic layer is dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford the desired product as a white solid (4.564 g, 97% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.41 (s, 1H), 6.90 (s, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 2.19 (s, 6H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.8, 154.8, 137.6, 134.6, 129.4, 128.9, 63.4, 20.8, 18.1, 13.8. mp = 109 °C

General procedure for the synthesis oxalamide

Oxalamic acid ethyl ester **15** (1 eq.), cycloalkyl amine **16** (1.5 eq.) and toluene (0.5 mL/mmol) were added in a tube. The tube is closed and the reaction mixture is heated at 140 °C during 20 minutes (200 W). After cooling at room temperature, the solid is filtered off on a frit and washed with cyclohexane to afford the desired oxalamide **17a, 17b**.

N-(2,4,6-trimethylphenyl)-N'-cyclopentyl-oxalamide (17a)

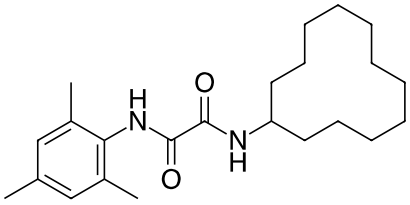


(17a)

Following the general procedure for the synthesis of oxalamide with cyclopentylamine (3 mmol, 297 µL) the desired product was obtained as a white solid (455 mg, 83% yield) after filtration.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.87 (s, 1H), 7.70 (bd, *J* = 7.6 Hz, 1H), 6.89 (s, 2H), 4.21 (sext, *J* = 7.6 Hz, 1H), 2.27 (s, 3H), 2.16 (s, 6H), 2.02-1.96 (m, 2H), 1.63-1.57 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.3, 158.4, 137.3, 134.7 (2C), 129.8, 128.7 (2C), 51.5 (1C), 32.6 (2C), 23.7 (2C), 20.8 (1C), 18.2 (2C). HRMS (ESI): m/z: [M+Na]+ ($C_{16}H_{22}N_2O_2Na$) calc. : 297.15790 ; found : 297.1578 (0 ppm). mp = 219 °C

N-(2,4,6-trimethylphenyl)-N'-cyclododecyl-oxalamide (17b)



(17b)

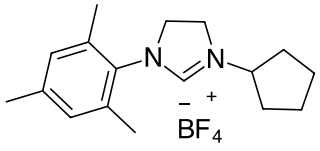
Following the general procedure for the synthesis of oxalamide with cyclododecylamine (15 mmol, 2.75 g) the desired product was isolated as a white solid (2.941 g, 79% yield) after filtration.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (s, 1H), 7.42 (bd, *J* = 8.7 Hz, 1H), 6.90 (s, 2H), 4.07 (m, 1H), 2.28 (s, 3H), 2.18 (s, 6H), 1.74-1.66 (m, 2H), 1.40 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.2, 158.4, 137.4, 134.7 (2C), 129.9, 129.0 (2C), 46.9, 30.1 (2C), 23.7 (2C), 23.6, 23.5 (2C), 23.4 (2C), 21.6 (2C), 20.9, 18.3 (2C). HRMS (ESI): m/z : [M+Na]+ ($C_{23}H_{36}N_2O_2Na$) calc. : 395.26745 ; found : 395.2673 (0 ppm). mp = 248°C

General procedure for the synthesis of imidazolium salts:

To a suspension of lithium aluminium hydride (4 eq.) in dry THF (5 mL/mmol) at 0 °C is added the oxalamide. The reaction mixture is refluxed during 24 h. After cooling down to 0 °C, water (60 µL/ mmol of $LiAlH_4$) and aqueous solution of 15% NaOH (60 µL/ mmol of $LiAlH_4$) are added dropwise. The crude product is purified on a plug of silica to give the corresponding diamine wich was used without characterization. Then, the diamine (1 eq.), NH_4BF_4 (1 eq.) and triethylorthoformate (1 mL/mmol of diamine) are heated at 120 °C during 2 h under an argon atmosphere. The volatiles were removed under vaccum and the corresponding imidazolium salt is purified by precipitation with diethyl ether of by flash chromatography (dichloromethane/acetone 8/2).

1H-2-(2,4,6-trimethylphenyl)-3,4-dihydro-5-cyclopentyl-imidazolin-1-ium tetrafluoroborate (18a)

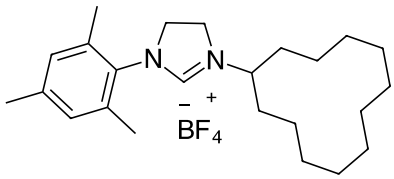


(18a)

Following the general procedure for the synthesis of imidazolium salts with **17a** (1.097 g, 4 mmol) the desired product was obtained as a white solid (505 mg, 36% yield) after precipitation.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96 (s, 1H), 6.89 (s, 2H), 4.30 (m, 1H), 4.17 (m, 4H), 2.26 (s, 3H), 2.22 (s, 6H), 2.09-2.07 (m, 2H), 1.78-1.65 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.9, 140.1, 135.4 (2C), 130.6, 129.8 (2C), 59.7, 50.6, 46.6, 30.0 (2C), 23.4 (2C), 20.9, 17.4 (2C). ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -152.6 (4F). ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) -1.11 (1B). HRMS (ESI): m/z: C+ ($C_{17}H_{25}N_2$) calc. : 257.20177 ; found : 257.2018 (0 ppm). mp = 171 °C

1H-2-(2,4,6-trimethylphenyl)-3,4-dihydro-5-cyclododecyl-imidazolin-1-ium tetrafluoroborate (18b)



(18b)

Following the general procedure for the synthesis of imidazolium salts with **17b** (1.863 g, 5 mmol) the desired product was obtained as a white solid (1.019 g, 46% yield) after precipitation.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (s, 1H), 6.87 (s, 2H), 4.16 (m, 4H), 3.96 (m, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 1.80 (m, 2H), 1.64 (m, 2H), 1.34 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.9, 140.1, 135.4 (2C), 130.7, 129.8 (2C), 67.9, 56.5, 50.5, 46.5 (2C), 27.4 (2C), 23.5, 23.4 (2C), 23.3 (2C), 21.3 (2C), 21.0, 17.5 (2C).

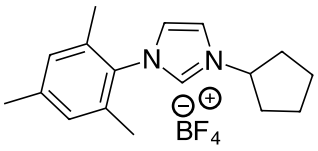
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -152.4 (4F). ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) -1.14 (1B). mp = 220 °C. HRMS (ESI): m/z: C+ ($C_{24}H_{39}N_2$) calc.: 355.31132; found: 355.3114 (0 ppm).

General procedure for the synthesis of imidazolium salts :

The methodology used has been recently published in *Angew. Chem. Int. Ed.*, DOI: anie.201308873

In a round-bottomed flask were placed 2,4,6-trimethylaniline (1.0 eq.), cycloalkylamine (1.0 eq.) and acetic acid (4.5 eq.) then the mixture was heated at 80 °C for 5-10 min (mixture A). In another round-bottomed flask were placed gloxal (1.0 eq., 40 % wt in aqueous solution), formaldehyde (1.0 eq., 37 % wt in aqueous solution) and acetic acid (4.5 eq.) then the mixture was heated at 80 °C for 5-10 min (mixture B). At 80 °C mixture B was added to the mixture A and the resulting mixture was stirred at 80 °C overnight. Dichloromethane and water were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (twice). The combined organic phases were dried over magnesium sulfate, filtered and the volatiles were removed under reduced pressure. The crude mixture was dissolved in dichloromethane and potassium tetrafluoroborate (1.0 eq.) was added then the mixture was stirred at room temperature for 2 h. The organic phase was washed with water (twice), dried over magnesium sulfate, filtered and the volatiles were removed under reduced pressure. The desired dissymmetric imidazolium salt was finally isolated by precipitation in ethyl acetate.

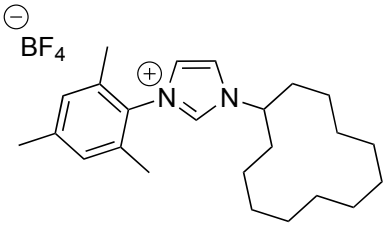
2-mesityl-5-cyclopentyl-imidazolium tetrafluoroborate 9a



(9a)

Following the general procedure with cyclopentylamine (3.41 g, 40 mmol, 1 eq.), 2,4,6-trimethylaniline (5.6 mL, 40 mmol, 1 eq.), gloxal (4.6 mL, 40 mmol, 1 eq., 40 % wt in aqueous solution), formaldehyde (3.0 mL, 40 mmol, 1 eq., 37 % wt in aqueous solution), acetic acid (20.6 mL, 360 mmol, 9 eq.) then potassium tetrafluoroborate (5.0 g, 40 mmol, 1 eq.). **7a** was obtained as a pale white solid (4.80 g, 35 %,). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.82 (t, *J* = 1.7 Hz, 1H), 7.70 (t, *J* = 1.7 Hz, 1H), 7.24 (t, *J* = 1.7 Hz, 1H), 6.97 (s, 2H), 5.03 (quint, *J* = 7.5 Hz, 1H), 2.46-2.35 (m, 2H), 2.32 (s, 3H), 2.00 (s, 6H), 1.97-1.87 (m, 4H), 1.83-1.71 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 141.3, 136.6, 134.4 (2C), 130.8, 129.9 (2C), 124.3, 121.4, 62.0, 35.6 (2C), 24.0 (2C), 21.2, 17.3 (2C); ^{11}B-NMR (128 MHz, $CDCl_3$): δ (ppm) -1.03; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -152.1; mp = 96 °C; HRMS calcd for $C_{17}H_{23}N_2^+$ $[M]^+$: m/z 255.1861, found: m/z 255.1861 (0 ppm)

2-mesityl-5-cyclododecyl-imidazolium tetrafluoroborate 9b



(9b)

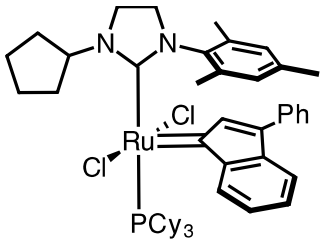
Following the general procedure with cyclododecylamine (7.32 g, 40 mmol, 1 eq.), 2,4,6-trimethylaniline (5.6 mL, 40 mmol, 1 eq.), gloxal (4.6 mL, 40 mmol, 1 eq., 40 % wt in aqueous solution), formaldehyde (3.0 mL, 40 mmol, 1 eq., 37 % wt in aqueous solution), acetic acid (20.6 mL, 360 mmol) then potassium tetrafluoroborate (5.04 g, 40 mmol, 1 eq.). **7b** was obtained as a pale white solid (10.90 g, 62 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (t, *J* = 1.8 Hz, 1H), 7.73 (t, *J* = 1.8 Hz, 1H), 7.27 (t, *J* = 1.8 Hz, 1H), 6.96 (s, 2H), 4.79-4.69 (m**,** 1H), 2.31 (s, 3H), 2.17-2.07 (m, 2H), 2.00 (s, 6H), 1.87-1.76 (m, 2H), 1.54-1.22 (m, 18H);

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 141.1, 135.9, 134.4 (2C), 130.9, 129.8 (2C), 124.2, 121.9, 59.4, 30.2 (2C), 23.7, 23.4 (2C), 23.35 (2C), 23.3 (2C), 21.4 (2C), 21.2, 17.2 (2C). ^{11}B-NMR (128 MHz, $CDCl_3$): δ (ppm) -1.03. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -151.5; mp = 177 °C; HRMS calcd for $C_{24}H_{37}N_2^+$ $[M]^+$: m/z 353.2957, found: m/z 353.2956 (0 ppm)

General procedure for the synthesis of second generation catalyst (8a, 8b)

In the glovebox, to a suspension of imidazolium salt (2 eq.) in toluene (1 mL/mmol of Ru) was added a solution of potassium bis(trimethylsilyl)amide in toluene (1.95 eq.). After 15 min of strirring, dichloro-(3-phenyl-1H-inden-1 ylidene)bis(tricyclohexylphosphine)ruthenium(II) or M1 **10** (1 eq.) was added and the mixture was heated at 60 °C outside of the glovebox during 3 h. The crude mixture is purified by flash chromatography using a mixture of pentane/ether solvent.

Dichloro-(2-mesityl-5-cyclopentyl-3,4-dihydroimidazol-1-ylidene)-(3-phenyl-1H-inden-1-ylidene)tricyclohexylphosphine ruthenium(II) 8a



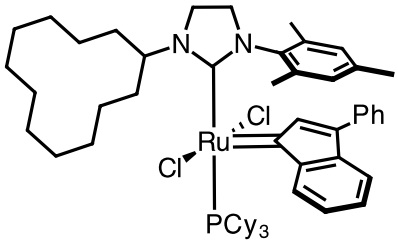
(8a)

Following the general procedure for the synthesis of second generation catalyst with **18a** (63 mg, 0.2 mmol, 2 eq.), KHMDS (390 µL, 0.195 mmol, 1.95 eq.) and M1 (92 mg, 0.1 mmol, 1 eq.) the desired product **8a** was isolated as a red solid (21 mg, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.35 (d, *J* = 7.6 Hz, 1H), 7.66-7.60 (m, 2H), 7.53-7.36 (m, 4H), 7.36-7.26 (m, 2H), 7.13 (td, *J* = 7.3, 1.1 Hz, 1H), 7.07 (td, *J* = 7.4, 1.2 Hz, 1H), 7.06 (s, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.31 (s, 1H), 5.89 (s, 1H), 5.66 (q, *J* = 7.7 Hz, 1H), 3.89-3.74 (m, 2H), 3.73-3.55 (m, 2H), 2.43-2.29 (m, 2H), 2.30-2.13 (m, 3H), 2.02 (s, 3H), 1.88 (s, 3H), 1.78 (s, 3H), 1.72-1.43 (m, 20H), 1.42-1.14 (m, 20H), 1.04 (m, 10H). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.91.^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 293.0, 213.6, 212.9, 144.3, 140.9, 137.5, 137.4, 137.4, 137.2, 137.0, 136.2, 129.1, 128.9, 128.8, 128.7, 128.4, 128.2, 127.6, 127.1, 126.5, 116.1, 62.0, 51.4, 51.37, 43.3, 43.27, 33.2, 33.1, 29.7, 29.6, 29.6, 29.2, 27.9, 27.8, 27.8, 27.7, 27.12, 27.11, 27.04, 27.0, 26.7, 26.5, 26.45, 25.2, 25.1, 21.1, 18.6, 18.6.

HRMS (ESI): m/z : $M^{+\cdot}$ $C_{50}H_{67}Cl_2N_2PRu$ calc : 899.3465; found : 899.3430 (3 ppm)

Dichloro-(2-mesityl-5-cyclododecyl-3,4-dihydroimidazol-1-ylidene)-(3-phenyl-1H-inden-1-ylidene)tricyclohexylphosphine ruthenium(II) 8b



(8b)

Following the general procedure for the synthesis of second generation catalyst with **18b** (495 mg, 1.12 mmol, 1.65 eq.), KHMDS (2.17 mL, 1.09 mmol, 1.6 eq.) and M1 **16** (626 mg, 0.68 mmol, 1 eq.) the desired product **8b** was isolated as a red solid (439 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.43 (d, *J* = 7.4 Hz, 1H), 7.71-7.69 (m, 2H), 7.52-7.47 (m, 1H), 7.42-7.37 (m, 2H), 7.19 (td, *J* = 7.4, 1.3 Hz, 1H), 7.15 (td, *J* = 7.5, 1.3 Hz, 1H), 7.12

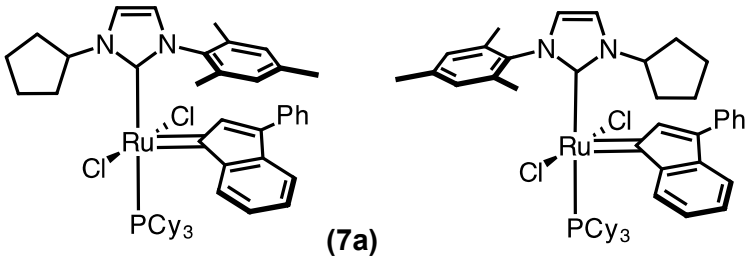
(s, 1H), 7.03-7.00 (d, *J* = 7.2, 1H), 6.37 (s, 1H), 5.95 (s, 1H), 5.43-5.30 (m, 1H), 3.87-3.73 (m, 2H), 3.60-3.36 (m, 2H), 2.25-2.02 (m, 6H), 2.09 (s, 3H), 1.94 (s, 3H), 1.84 (s, 3H), 1.65-1.36 (m, 22H), 1.36-1.06 (m, 26H), 1.17-1.05 (m, 10H). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.11. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) : 217.4, 172.7, 150.9, 148.7, 141.2, 139.9, 136.2, 130.1, 129.7, 128.8, 127.9, 127.4, 126.8, 126.0, 125.1, 124.5, 123.7, 117.3, 28.9, 28.7, 27.2, 27.1, 22.9, 22.6.
HRMS (ESI) : m/z : M+ ($C_{57}H_{81}N_2{}^{35}Cl_2PO_2Ru$) calc. : 996.45579 ; found : 996.4570 (1 ppm) ;[M-Cl]+ ($C_{57}H_{81}N_2{}^{35}ClPO_2Ru$) calc. : 961.48694 ; found : 961.4890 (2 ppm).

General procedure for the synthesis of second generation catalyst (7a, 7b)

In the glovebox, to a suspension of imidazolium salt (1.3 eq.) in toluene (6.5 mL/mmol of Ru) was added a solution of potassium *tert*-amylate in toluene (1.25 eq.). After 30 min of strirring, dichloro-(3-phenyl-1H-inden-1 ylidene)bis(tricyclohexylphosphine)ruthenium(II) or M1 **16** (1 eq.) was added and the mixture was heated at 80 °C outside of the glovebox during 2 h. The crude mixture is purified by flash chromatography using a mixture of pentane/ether solvent.

Dichloro-(2-mesityl-5-cyclopentyl-imidazo-1-ylidene)-(3-phenyl-1H-inden-1-ylidene) tricyclohexylphospine ruthenium (II) (7a)

Determination of the major isomer: Single crystals of **8b** have been dissolved in $CDCl_3$, and a chemical shift of δ = 27.11 ppm have been recorded in ^{31}P NMR spectroscopy. When catalyst **7a** was analyzed in the same condition, two signals are observed at δ = 30.06 ppm and δ = 16.85 ppm, allowing us to suggest that the major conformer have mesityl substituent pointing toward indenylidene (π-π interaction).



Major Isomer **(7a)** **Minor Isomer**

Following the general procedure for the synthesis of second generation catalyst with **9a** (487 mg, 1.42 mmol, 1.3 eq.), potassium *tert*-amylate (0.82 mL, 1.39 mmol, 1.25 eq.) and M1 **16** (1.03g, 1.11 mmol, 1 eq.), the desired product was isolated as a red solid (435 mg, 43% yield).

The compound was obtained as a mixture of two conformers in a 87:17 ratio, the most abundant is described:

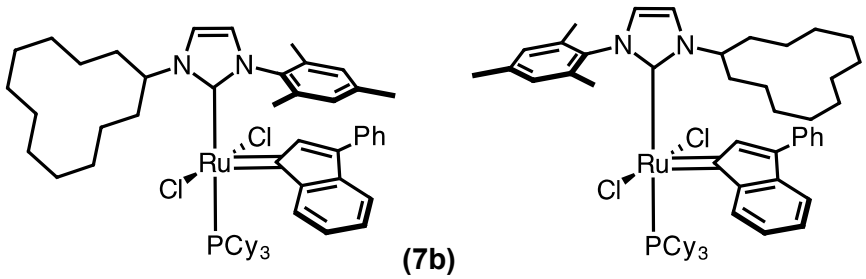
^{1}H (400MHz, $CDCl_3$): δ (ppm) 8.35 (d, *J* = 7Hz, 1H), 7.73 (d, *J* = 4Hz, 2H), 7.57-7.50 (m, 1H), 7.40-7.27 (m, 2H), 7.22-7.21 (m, 2H), 7.17-7.15 (m, 2H), 7.07-7.06 (m, 1H), 6.76 (d, *J* = 2Hz, 1H), 6.44 (s, 1H), 6.09-6.03 (m, 2H), 2.76-2.65 (m, 2H), 2.37-2.34 (m, 3H), 2.03-1.90 (m, 4H), 1.89 (m, 9H), 1.77-1.11 (m, 33H). ^{31}P (162 MHz, $CDCl_3$): δ (ppm) 30.06 (major isomer), 16.85 (minor isomer). ^{13}C (100 MHz, $CDCl_3$): δ (ppm) 292.8, 183.0, 182.2, 176.7, 175.7, 144.2, 140.9, 138.1, 137.7, 137.6, 137.5, 137.0, 136.5, 136.3, 135.9, 129.3, 128.5, 128.4,

128.3, 128.1, 127.7, 127.5, 127.1, 126.4, 126.2, 125.0, 118.0, 116.2, 63.04, 59.9, 34.6, 34.5, 33.3, 33.1, 30.0, 29.8, 29.5, 27.9, 27.8, 27.7, 26.7, 25.3, 22.8; 22.4; 21.0; 20.6; 20.5; 18.5; 18.4.

HRMS (ESI) m/z : $M^{+\cdot}$ calculated for $C_{50}H_{65}Cl_2N_2PRu$ 896.3308 found : 896.3282 (2 ppm)

Dichloro-(2-mesityl-5-cyclododecyl-imidazo-1-ylidene)-(3-phenyl-1H-inden-1-ylidene) (tricyclohexylphospine) ruthenium (II) (7b)

Determination of the major isomer: Single crystals of **8b** have been dissolved in $CDCl_3$, and a chemical shift of δ = 27.11 ppm have been recorded in ^{31}P NMR spectroscopy. When catalyst **7b** was analyzed in the same condition, two signals are observed at δ = 29.06 ppm and δ = 17.05 ppm, allowing us to suggest that the major conformer have mesityl substituent pointing toward indenylidene (π-π interaction).



(7b)

Major Isomer **Minor Isomer**

Following the general procedure for the synthesis of second generation catalyst with **9b** (1.227g, 2.79 mmol, 1.28 eq.), potassium *tert*-amylate (1.65 mL, 2.80 mmol, 1.28 eq.) and M1 **16** (2.02 g, 2.17 mmol, 1 eq.), the desired product was isolated as a red solid (1.352 g, 62% yield).
The compound was obtained as a mixture of two conformers in a 93:7 ratio, the most abundant is described:

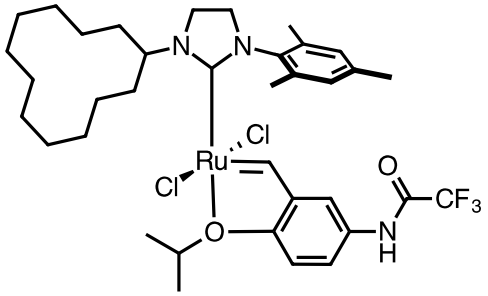
^1H (400MHz, $CDCl_3$): δ (ppm) 8.36 (d, *J* = 7.5Hz), 7.72 (m, 2Har); 7.50 (m, 1Har) ; 7.40 (m, 2Har) ; 7.23 (m, 3Har) ; 7.15 (m, 2Har) ; 7.06 (m, 1Har); 6.7 (d, *J*=2Hz, 1H); 6.44 (s, 1H) ; 6.01 (s, 1H) ; 5.88 (m; $1H_{C12}$) ; 2,50-1.12 (m, 64H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 293.0, 213.6, 212.9, 144.3, 140.9, 137.5, 137.4, 137.35, 137.2, 137.0, 136.2, 129.1, 128.9, 128.8, 128.7, 128.4, 128.2, 127.6, 127.1, 126.5, 116.1, 62.0, 51.4, 51.37, 43.3, 43.27, 33.2, 33.1, 29.7, 29.6, 29.56, 29.2, 27.9, 27.81, 27.79, 27.69, 27.12, 27.11, 27.04, 27.0, 26.66, 26.48, 26.45, 25.2, 25.1, 21.1, 18.6, 18.6. ^{31}P (162 MHz, $CDCl_3$): δ (ppm) 29.06 (major isomer), 17.05 (minor isomer).
HRMS (ESI) : m/z $M^{+\cdot}$: calculated for $C_{57}H_{79}{}^{35}Cl_2N_2PRu$: 994.4405, found 994.4376 (2 ppm).

General procedure for the synthesis of Hoveyda type ruthenium complexes

To a solution of second generation ruthenium catalyst in DCM (10 mL / mmol) was added styrenylether (1.1 eq.) and copper chloride (1.1 eq.). The mixture was refluxed under argon till reaction was completed, then concentrated under reduced pressure. The residue was dissolved in a minimal amount of acetone, filtrate trough a celite plug, and then concentrated

under reduced pressure. The crude was purified by flash chromatography on silica gel with pentane acetone mixture to afforded the desired ruthenium complexes.

Dichloro-(2-mesityl-5-cyclododecyl-3,4-dihydroimidazol-1-ylidene)-(2-isopropoxy-5-trifluoroacetamido)-benzylidene) ruthenium(II) 8c



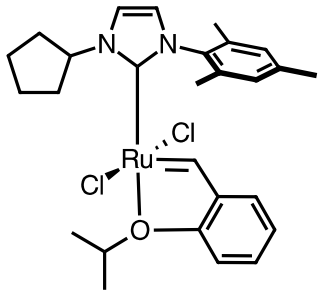
(8c)

Following the general procedure for the synthesis of Hoveyda type ruthenium catalyst with **8b** (228 mg, 0.23 mmol, 1 eq.), CuCl (25 mg, 0.25 mmol, 1.1 eq.) and aminocarbonyl ligand (69 mg, 0.25 mmol, 1.1 eq.) for 15 minutes at 60 °C, the desired product **8c** was isolated as a green solid (114 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 16.23 (s, 1H), 7.81 (bs, 1H), 7.60 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.29 (d, *J* = 2.6 Hz,1H), 7.08 (s, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.26-5.18 (m, 1H), 5.11 (sept, *J* = 6.1 Hz, 1H), 4.00-3.88 (m, 4H), 2.49 (s, 3H), 2.22 (s, 6H), 2.17-2.07 (m, 2H), 2.07-1.98 (m, 2H), 1.74 (d, *J* = 6.1 Hz, 6H), 1.71-1.62 (m, 4H), 1.52-1.43 (m, 14H). ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -75.6 (3F). ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 241.2, 150.1, 144.4, 139.3, 138.3, 138.0, 131.2, 130.2, 129.8, 127.1, 125.8, 125.2, 120.8, 114.7, 113.2, 75.6, 60.1, 51.7, 45.75, 28.8, 26.2, 25.4, 23.1, 22.3, 22.2, 22.0, 21.3, 18.3.

HRMS (APCI) : m/z : $M^{+\cdot}$ ($C_{36}H_{50}{}^{35}Cl_2F_3N_3O_2Ru$) calc : 785.2274, found : 785.2268 (0.3 ppm).

Dichloro-(2-mesityl-5-cyclopentyl-imidazol-1-ylidene)-(2-isopropoxybenzylidene) ruthenium(II) 7e



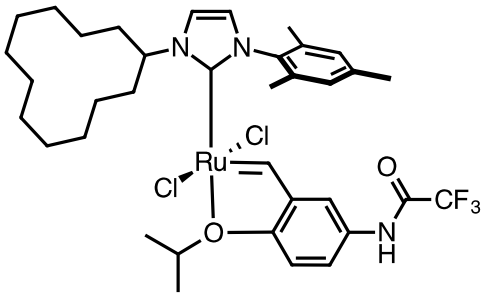
(7e)

Following the general procedure for the synthesis of Hoveyda type ruthenium complexe with **7a** (309 mg, 0.344 mmol, 1 eq.), CuCl (37 mg, 0.37 mmol, 1.1 eq.) and isopropoxyphenyl-2-propenyl (36.8 mg, 0.37 mmol, 1.1 eq.) for 4 h, the desired product **7e** was isolated as a brownish solid (89 mg, 45% yield).

^{1}H (400MHz, $CDCl_3$): δ (ppm) 16.42 (s, 1H); 7.50 (m, 1H); 7.27 (m, 1H); 7.10 (s, 2H); 7.01 (m, 1H); 6.95 (m, 2H); 6.88 (d, J = 2Hz, 1H); 5.96, (q, J = 7.5Hz, 1H); 5.18 (sept., J = 6.21 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$): δ (ppm) 172.2; 152.7; 144.5; 139.6; 137.6; 137.4; 129.3; 129.0; 125.0; 122.7; 122.4; 118.5; 113.0; 75.1; 64.2; 34.4; 24.7; 22.0; 21.4; 18.2

HRMS : (APCI) : m/z :$M^{+\cdot}$ ($C_{27}H_{34}{}^{35}Cl_2N_2ORu$) calc : 574.1087, found : 574.1112 (4 ppm).

Dichloro-(2-mesityl-5-cyclododecyl-imidazol-1-ylidene)-(2-isopropoxy-5-trifluoroacetamido)-benzylidene) ruthenium(II) 7d

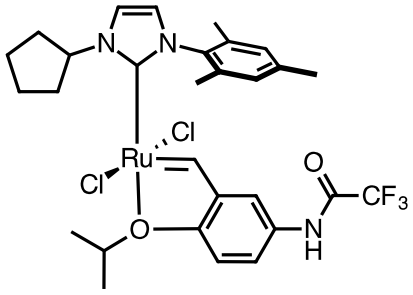


(7d)

Following the general procedure for the synthesis of Hoveyda type ruthenium complexes with **7b** (243 mg, 0.24 mmol, 1 eq.), CuCl (38 mg, 0.38 mmol, 1.1 eq.) and aminocarbonyl ligand (122 mg, 0.42 mmol, 1.75 eq.) for 4 hours, the desired product **7d** was isolated as a brownish solid (146 mg, 76% yield).

^{1}H (400MHz, $CDCl_3$): δ (ppm) 16.34 (s, 1H) ; 7.89 (s, 1H) ; 7.54 (dd, *J* = 2.5 Hz , *J* = 8.8 Hz, 1H) ; 7.43 (d, *J* = 2.5Hz, 1H) ; 7.28 (d, *J* = 2.2 Hz) ; 7.13 (s, 2H) ; 6.88 (m, 2H) ; 5.61 (sept., *J* = 3.3 Hz, 1H) ; 5.12 (sept., *J* = 6.2 Hz, 1H) ; 2.55 (s, 3H) ; 2.23 (m, 4H) ; 2.01 (s, 6H) ; 1.78 (d, *J* = 6.2 Hz, 6H) ; 1.69 (m, 4H) ; 1.46 (m, 14H). ^{13}C (100 MHz, $CDCl_3$): δ (ppm) 286.5, 169.4, 154.8, 154.4, 150.1, 144.5, 140.0, 137.4, 137.2, 130.3, 129.2, 124.3, 120.0 (2C), 114.2, 113.1, 75.6, 60.9, 30.5, 25.4, 24.9, 23.0, 22.9, 22.0, 21.5, 21.2, 18.0. ^{19}F (376 MHz, $CDCl_3$): δ (ppm) -75.5.
HRMS (APCI) m/z $M^{+\cdot}$ ($C_{36}H_{48}{}^{35}Cl_2F_3N_3O_2Ru$) calc : 783?2117, found : 783.2127 (1 ppm).

Dichloro-(2-mesityl-5-cyclopentyl-imidazol-1-ylidene)-(2-isopropoxy-5-trifluoroacetamido)-benzylidene) ruthenium(II) 7c



(7c)

Following the general procedure for the synthesis of Hoveyda type ruthenium complexes with **7a** (308 mg, 0.34 mmol, 1 eq.), CuCl (37 mg, 0.37 mmol, 1.1 eq.) and aminocarbonyl ligand (127 mg, 0.44 mmol, 1.3 eq.) for 6 hours, the desired product **7c** was isolated as a brownish solid (99 mg, 42 % yield).

^{1}H (400MHz, CD_2Cl_2): δ (ppm) 16.21 (s, 1H), 8.02 (s, 1H), 7.67 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.15 (s, 2H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 5.86 (p, *J* = 7.8, 7.1 Hz, 1H), 5.16 (hept., *J* = 6.0 Hz, 1H), 2.70 – 2.58 (m, 2H), 2.58 – 2.52 (m, 3H), 2.10 – 1.99 (m, 3H), 1.98 (s, 7H), 1.95 – 1.80 (m, 6H), 1.74 (d, *J* = 6.1 Hz, 6H), 1.54 (s, 7H). ^{19}F (376 MHZ, CD_2Cl_2): -76.06
^{13}C (400 MHz, CD_2Cl_2): δ (ppm) 170.8, 150.6, 144.8, 140.7, 137.9, 137.6, 131.0, 129.7, 125.62, 120.8, 119.1, 114.3, 113.8, 76.4, 64.7, 34.7, 25.1, 22.2, 18.2.

HRMS (APCI) m/z : ($C_{29}H_{34}{}^{35}Cl_2F_3N_3O_2Ru$) calc : 685.1020, found : 685.1034 (2 ppm).

Evaluation of ruthenium complexes in RCM of allylmetallyldiethylmalonate **18**

To a solution of diethylallylmetallylmalonate **18** (0.4 mmol, 1 eq.) and mesitylene (17 mg) in DCM (4 mL), was added a solution of ruthenium catalyst in DCM (0.004 mmol, 1 mol%), and the mixture was heated at 30 °C. Aliquot were taken and analyzed by 1H NMR to determine the conversion.

Indenylidene type ruthenium complexes :

Catalyst	Time (h)	Conversion (%)	Catalyst	Time (h)	Conversion (%)
2	0	0	**3**	0	0
	1	15		1	9
	2	30		2	23
	3	47		3	40
	5	75		5	60
	6	85		7	65
	19	99		23	91
7a	0	0	**7b**	0	0
	1	59		1	33
	2	81		2	47
	3	92		3	66
	5	96		4	72
	6	98		5	78
	19	97		7	84
				23	87
8a	0	0	**8b**	0	0
	1	26		1	10
	2	44		2	22
	4	60		5	45
	6	67		6	55
	8	70		8	60
	9	71		24	82
	23	76		31	83
	31	76			

Hoveyda type ruthenium complexes:

Catalyst	Time (h)	Conversion (%)	Catalyst	Time (h)	Conversion (%)
4a	0	0	**4b**	0	0
	0,1	7		0,025	4
	0,4	40		0,05	11
	0,6	65		0,13	37
	0,9	81		0,19	52
	1,1	84		0,28	66
	1,5	92		0,39	78
	2	94		0,62	89
	3	96		0,78	91
	5	98		0,955	94
	7	100		1,08	95
				1,5	100
4c	0	0	**4c**	0,67	76
	0,035	1		0,80	78
	0,07	10		0,86	79
	0,11	20		0,995	84
	0,17	37		2	89
	0,24	50		4	90
	0,32	60		6	90
	0,465	70		24	90
7c	0	0	**7d**	0	0
	1	51		0,67	40
	2	65		1	48
	3	74		1,33	53
	5	80		2	57
	6	80		5	66
	7	80		7	70
	30	80		17	86
				19	87
				36	87
7e	0	0	**8c**	0	0
	0,5	44		1	5
	1	56		2	14
	2	67		5	26
	3	73		6	30
	4	78		8	35
	5	82		24	58
	6	84		31	64
	7	85			
	23,5	93			

Thermal stability of ruthenium complexes

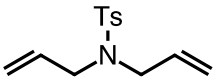
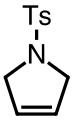
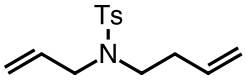
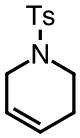
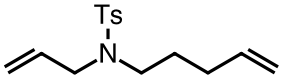
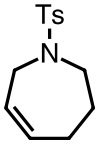
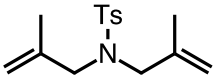
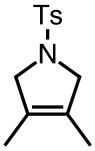
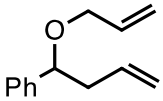
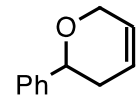
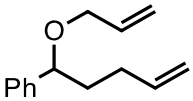
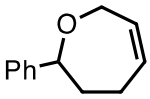
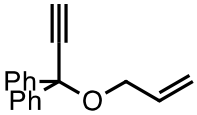
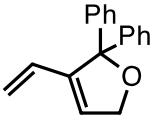
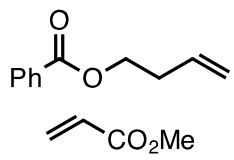
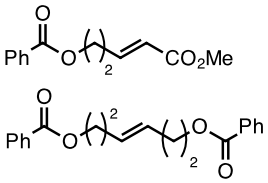
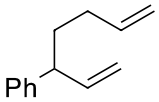
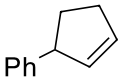
In a flame dried NMR tube were placed catalyst (0,005 mmol, 1 eq.) and anthracene (2 mg) in Toluene d_8 (0.5 mL, [C = 10 mM]), and the mixture was then heated at 60 °C until complete decomposition of the catalyst. ^{1}H NMR spectra were recorded for determining the amount of remaining catalyst.

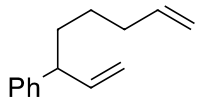
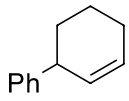
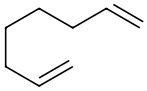
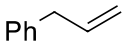
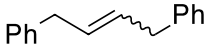
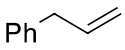
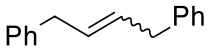
Catalyst	Time (h)	Remaining catalyst (%)	Catalyst	Time (h)	Conversion (%)
2	0	100	**3**	0	100
	1	71		1	92
	2	54		2	84
	3	37		3	76
	5	9		5	56
	18	0		18	20
				20	0
4b	0	100	**4c**	0	100
	6	96		5	97
	30	74		7	93
	108	42		21	83
	132	33		35	72
	156	24		83	47
	240	0		131	13
				151	4
7a	0	100	**7b**	0	100
	1	63		1	73
	2	43		2	52
	3	30		3	36
	5	0		4	19
				5	10
				6	0
7c	0	100	**7d**	0	100
	4	99		1	100
	6	98		2	98
	30	70		49	41
	108	12		120	6
	132	0		144	0
7e	0	100	**8a**	0	100
	15	44		1	71
	20	30		2	53
	24	25		3	35
	40	7		4	19
	44	4		5	0
	48	2			
	63	0	**8b**	0	100
				0,5	33
				1	0
8c	0	100	**8c**	21	71
	0,5	100		29	64
	2	95		52	46
	4	91		123	17
	5,5	90		192	0

Scope of transformation with Dichloro-(2-mesityl-5-cyclopentyl-imidazo-1-ylidene)-(3-phenyl-1H-inden-1-ylidene) (tricyclohexylphospine) ruthenium (II) ***8c***

All metathesis substrates were prepared following the procedures described in the literature and purified by flash chromatography on silica gel with ethylacetate/pentane or diethyl ether/pentane.

All reactions have been carried out using 1 mol% of catalyst in CD_2Cl_2 at 30 °C. Conversion are determined by ^1H NMR, and yield are determined using mesitylene as internal standard. In a NMR tube were placed substrate (0.05 mmol, 1eq.) and mesitylene (5 μL, 0.036 mmol, 0.72 eq.) in CD_2Cl_2 (0.45 mL), then a stock solution of catalyst (0.1 M, 0.05 mL, 1 mol%) was added and tubes were placed at 30°C for the expected time. The conversion was determined by ^1H NMR.

Entry	Substrate	Product	Time	Conv. (%)[a]	Isolated Yield
1			2h	100	92%
2			5h	60	45%
3			2h	88	75%
4			3h	54	50%
5			2h	100	95%
6			5h	30	29%
7			30min	100	97%
8			5h	55 Cross : 28 % Self : 27 %	Cross : E:Z 100:0 27% Self : E:Z 80:20 27%
9			1h	82%	70%

10			1,5h	98%	87%
11			1,5h	93%[b]	/
12			5h	65% 84:16	/
13			5 min [(d)]	82 %	75 %

(a) Determined by 1H NMR with mesitylene as internal standard
(b) 500 ppm of 7a were used instead of 1 mol%
(c) Reaction performed at 80°C in neat conditions

For isolated yield, reactions were carried out on 0.2 mmole. Substrates were dissolved in in freshly distillated and degased CH_2Cl_2, and stock solution of catalyst was added. Aliquot were taken and analyzed by ^1H NMR to check reaction conversion.
When reaction were completed, the mixture was evaporated and purified by SIO_2 gel chromatography using pentane / diethyl ether mixture.

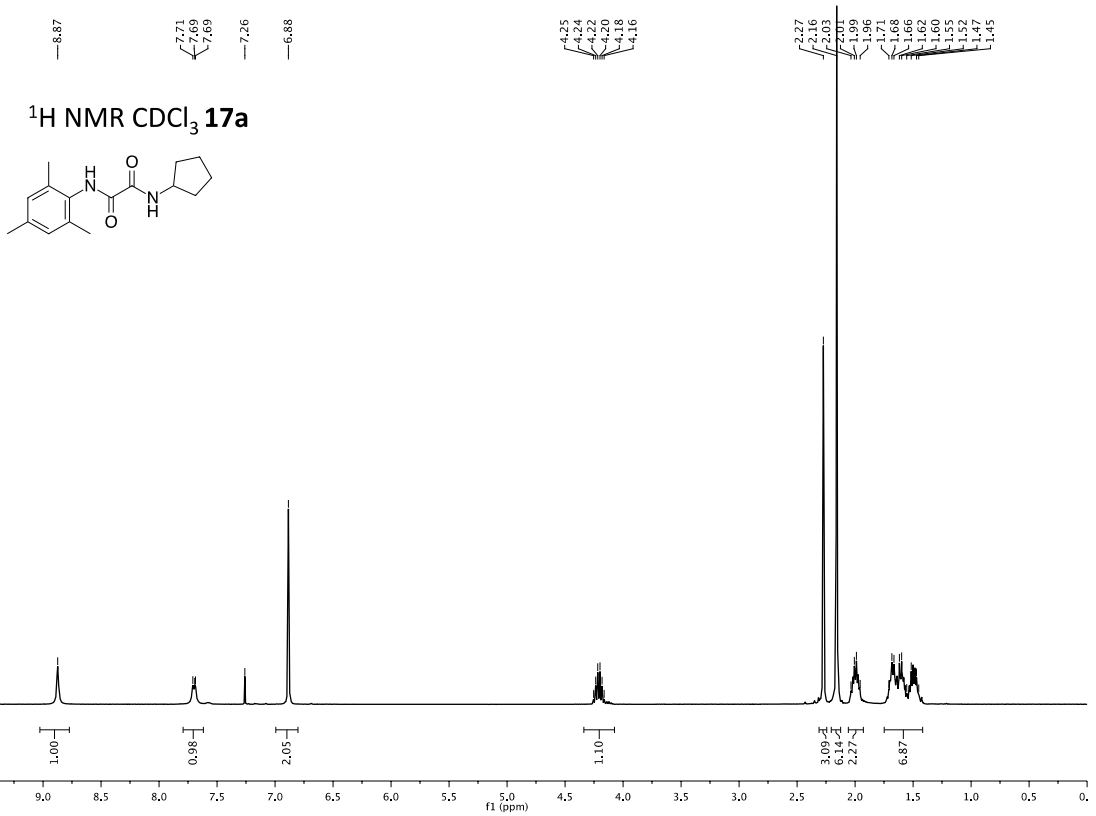
Entry	Mass of substrate	Mass of product	Yield
1	50.1 mg	40.8 mg	92 %
2	55.6 mg	21.4 mg	45 %
3	57.1 mg	38.4 mg	75 %
4	55.2 mg	25.3 mg	50 %
5	38.0 mg	31.4 mg	95 %
6	40.7 mg	10.2 mg	29 %
7	41.7 mg	40.6 mg	97 %
8	35.7 mg	Self: 17.8 mg Cross: 13.0 mg	27 % 27 %
9	31.3 mg	24.1 mg	70%
10	38.0 mg	28.3 mg	87%
11	45.0 mg		/
12	237.1 mg	155.3 mg	75 %

DFT calculations

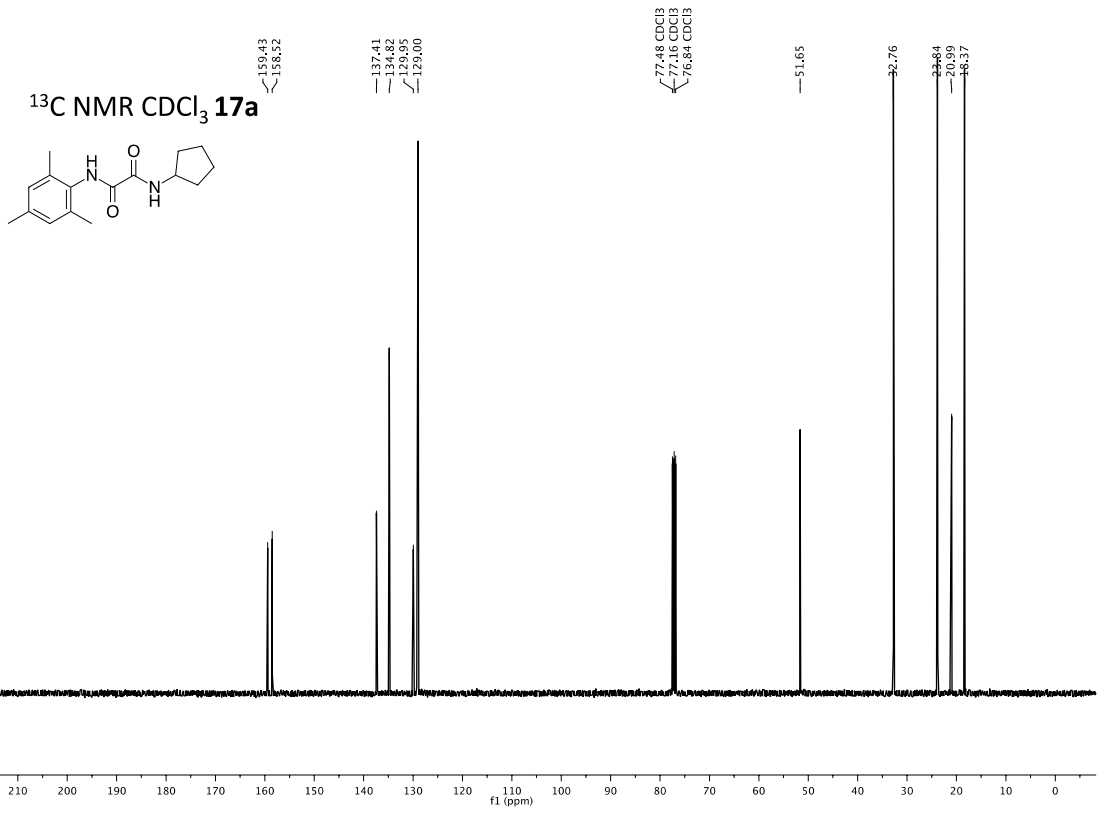
All the geometry optimizations were performed with the Gaussian09 package using the BP86 functional in connection with the SDD electrons core potential, and the associated valence basis set for Ru, and the TZVP basis set on all main group atoms.

NMR Spectra IMIDAZOLI(-DI)-NIUM SALTS & PRECURSORS

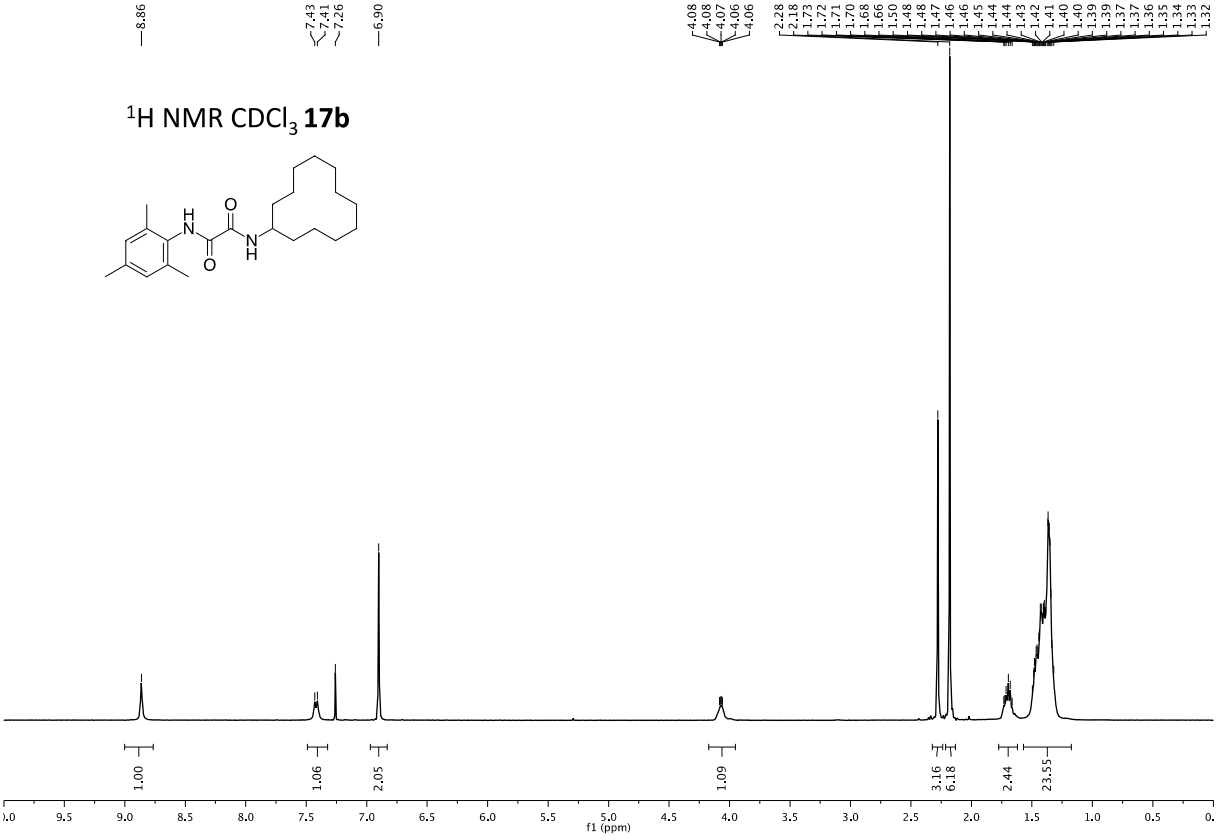
^{1}H NMR $CDCl_3$ **17a**



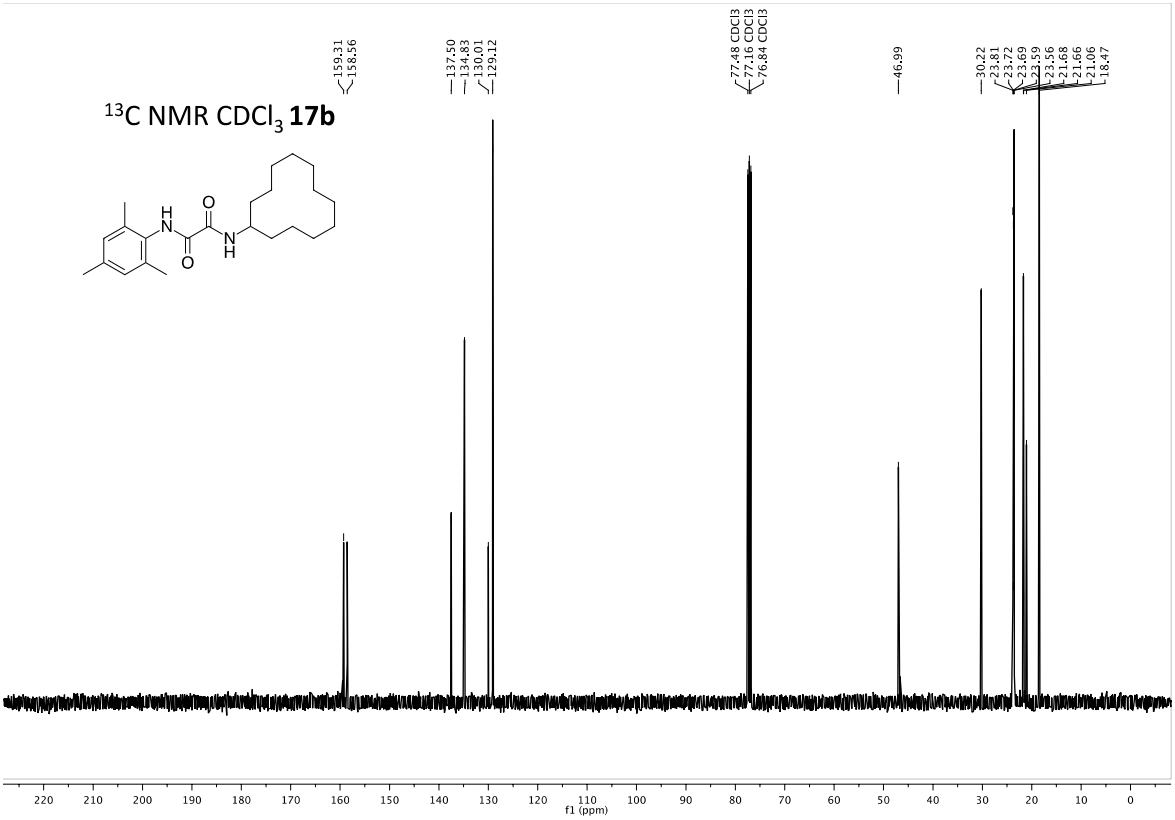
^{13}C NMR $CDCl_3$ **17a**



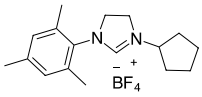
^{1}H NMR $CDCl_3$ **17b**



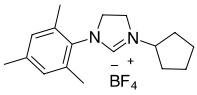
^{13}C NMR $CDCl_3$ **17b**



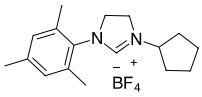
^{1}H NMR $CDCl_3$ **18a**



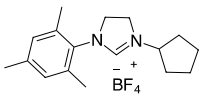
^{13}C NMR $CDCl_3$ **18a**



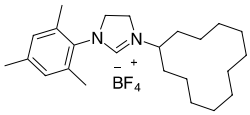
^{19}F NMR $CDCl_3$ **18a**



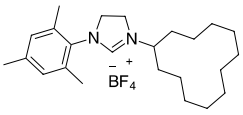
^{11}B NMR $CDCl_3$ **18a**



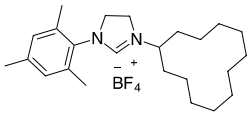
^{1}H NMR $CDCl_3$ **18b**



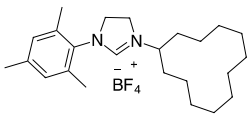
^{13}C NMR $CDCl_3$ **18b**



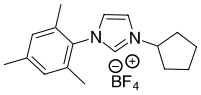
^{19}F NMR $CDCl_3$ **18b**



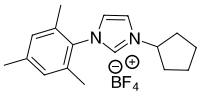
^{11}B NMR $CDCl_3$ **18b**



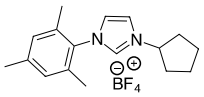
^{1}H NMR $CDCl_3$ **9a**



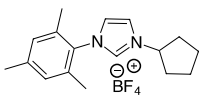
^{13}C NMR $CDCl_3$ **9a**



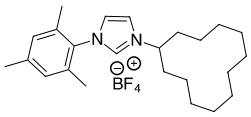
^{19}F NMR $CDCl_3$ **9a**



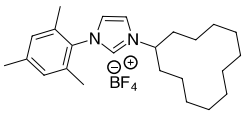
^{11}B NMR $CDCl_3$ **9a**



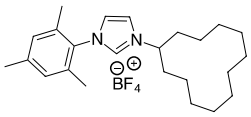
^{1}H NMR $CDCl_3$ **9b**



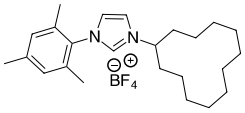
^{13}C NMR $CDCl_3$ **9b**



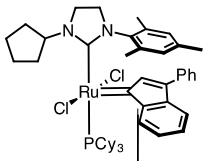
^{19}F NMR $CDCl_3$ **9b**



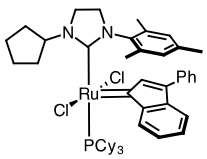
^{11}B NMR $CDCl_3$ **9b**



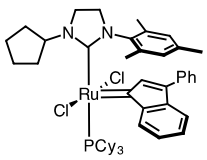
^{1}H NMR $CDCl_3$ **8a**

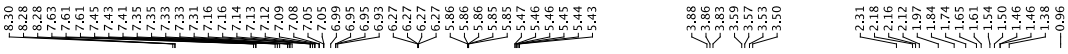


^{31}P NMR $CDCl_3$ **8a**

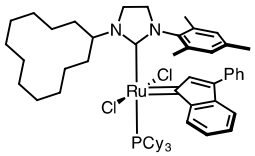


^{13}C NMR $CDCl_3$ **8a**

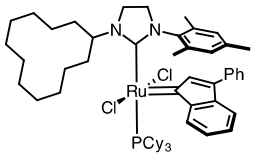




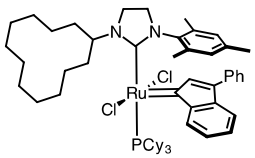
^{1}H NMR $CDCl_3$ **8b**



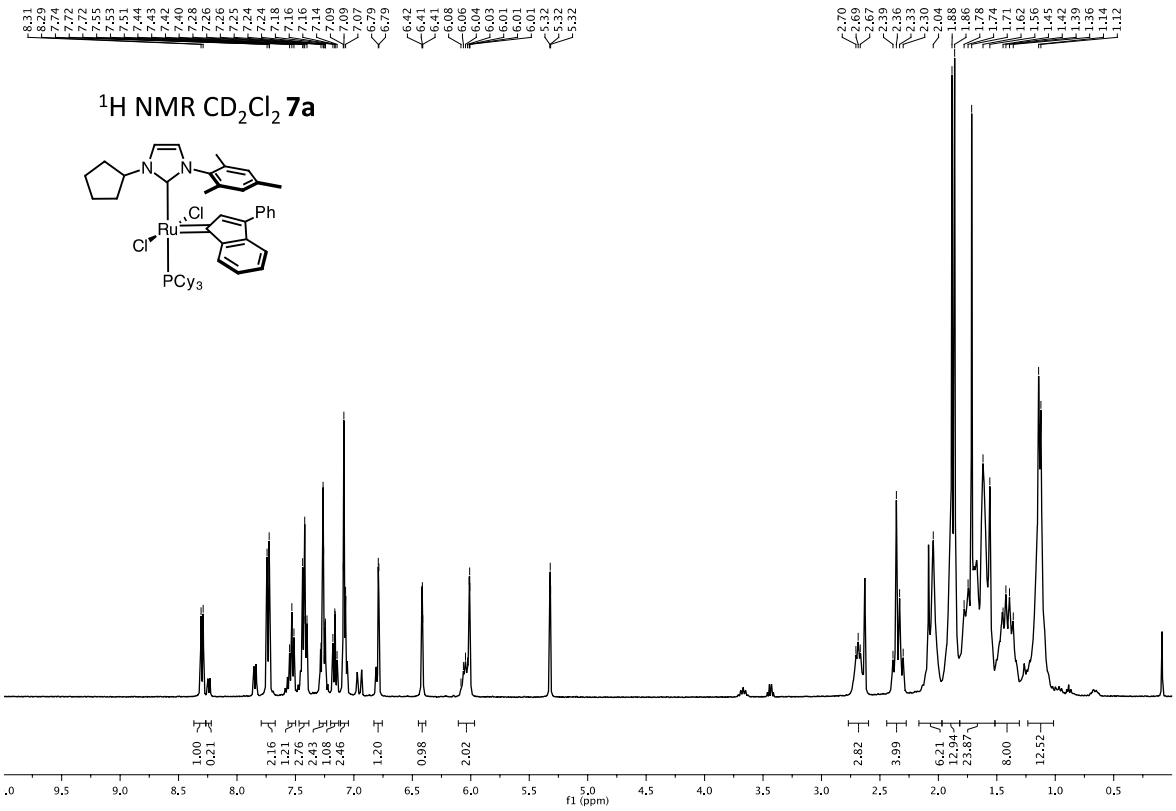
^{31}P NMR $CDCl_3$ **8b**



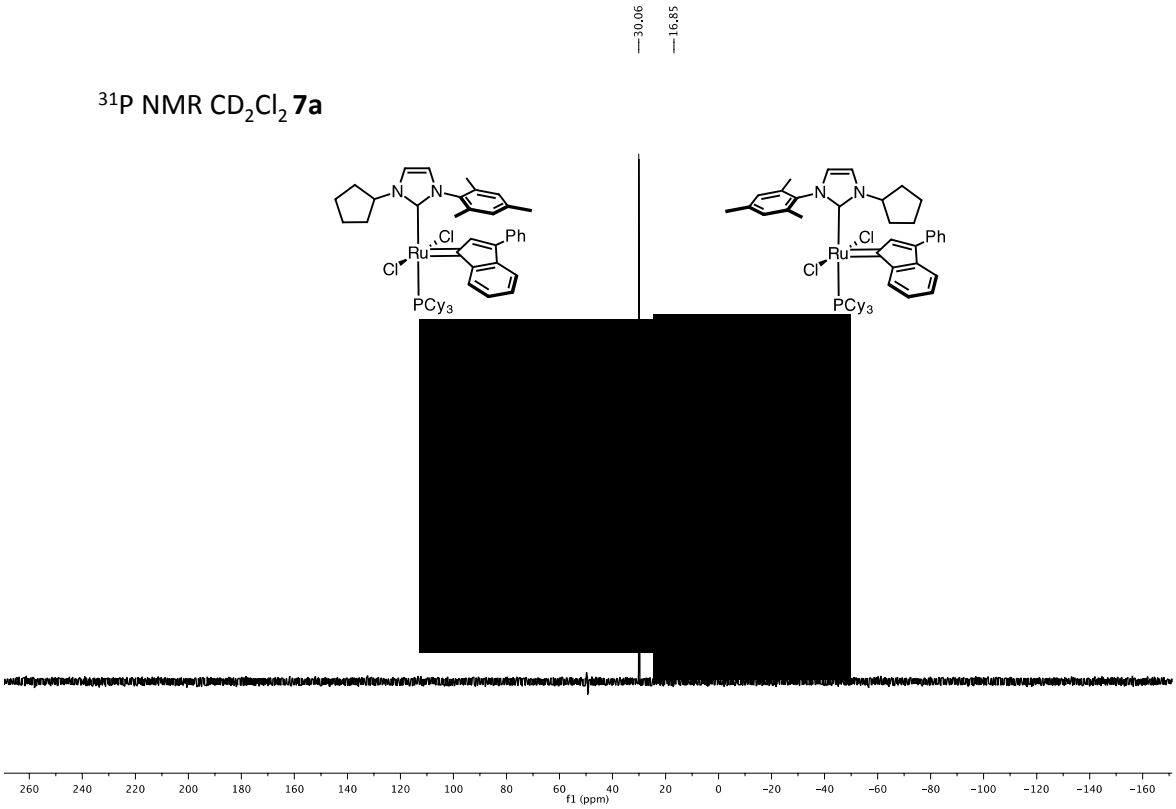
^{13}C NMR $CDCl_3$ **8b**



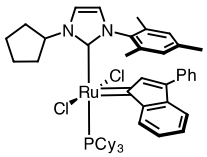
^{1}H NMR CD_2Cl_2 **7a**



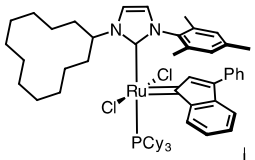
^{31}P NMR CD_2Cl_2 **7a**



^{13}C NMR CD_2Cl_2 **7a**

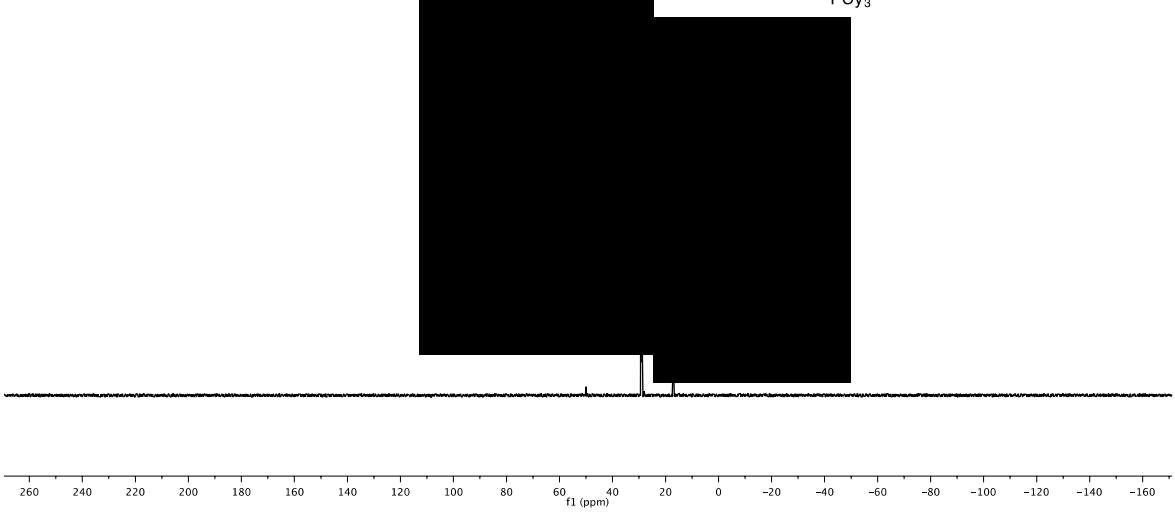


^{1}H NMR $CDCl_3$ **7b**



29.10
29.07
29.04
17.05

^{31}P NMR $CDCl_3$ **7b**



292.81
292.74

182.39
181.62
144.22
140.83
137.64
137.60
137.22
137.03
136.51
136.27
136.03
132.95
129.03
128.97
128.51
128.31
128.23
128.05
127.59
127.48
127.02
126.36
126.33
123.92
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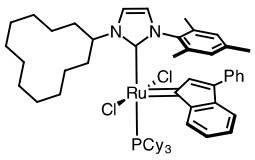
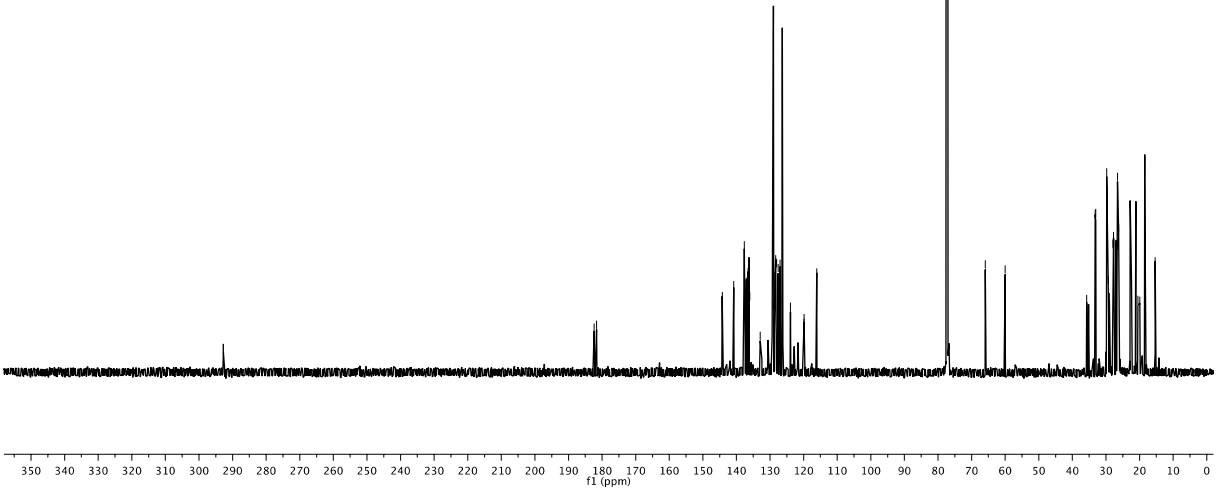
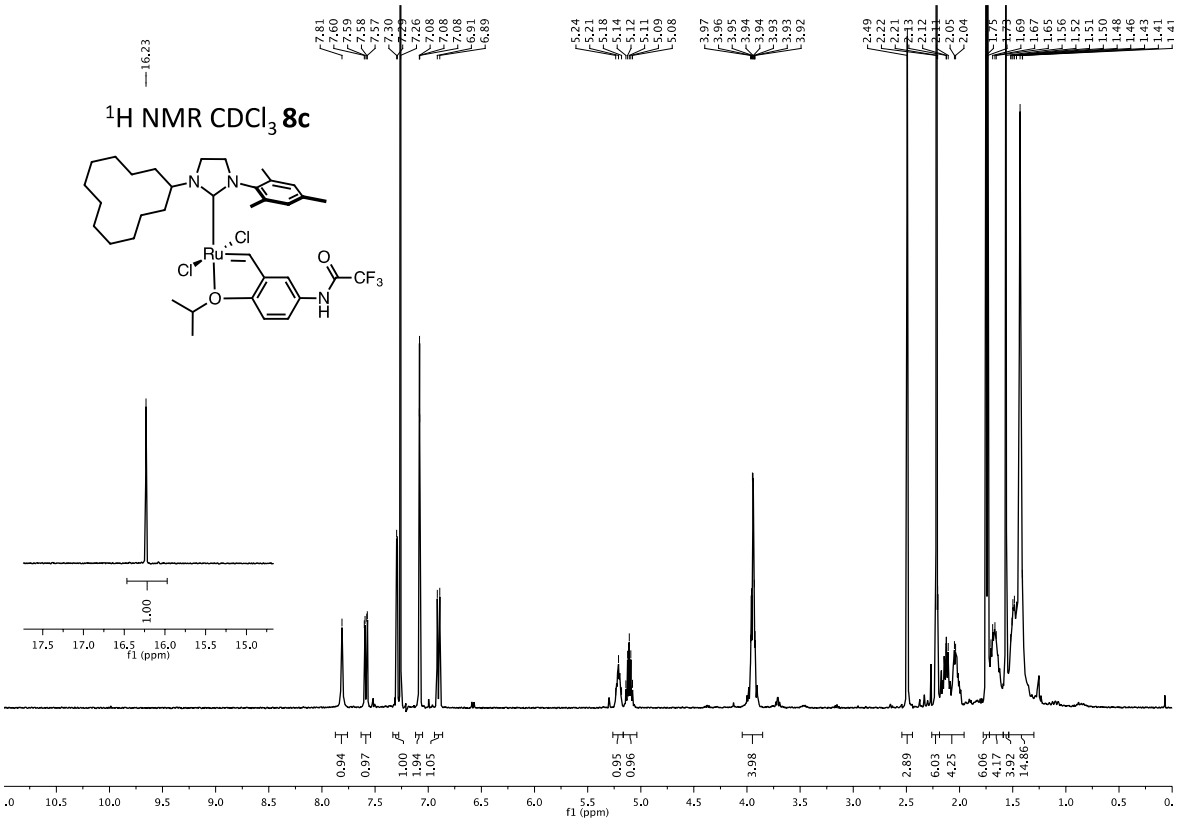
119.84
116.10
65.93
59.99
35.77
35.16
33.19
33.04
29.77
29.66
29.32
29.01
27.91
27.81
27.76
27.66
27.08
26.96
26.66
26.59
26.45
26.43
26.24
22.77
22.46
22.40
21.13
20.48
19.93
18.46
15.37

^{13}C NMR $CDCl_3$ **7b**

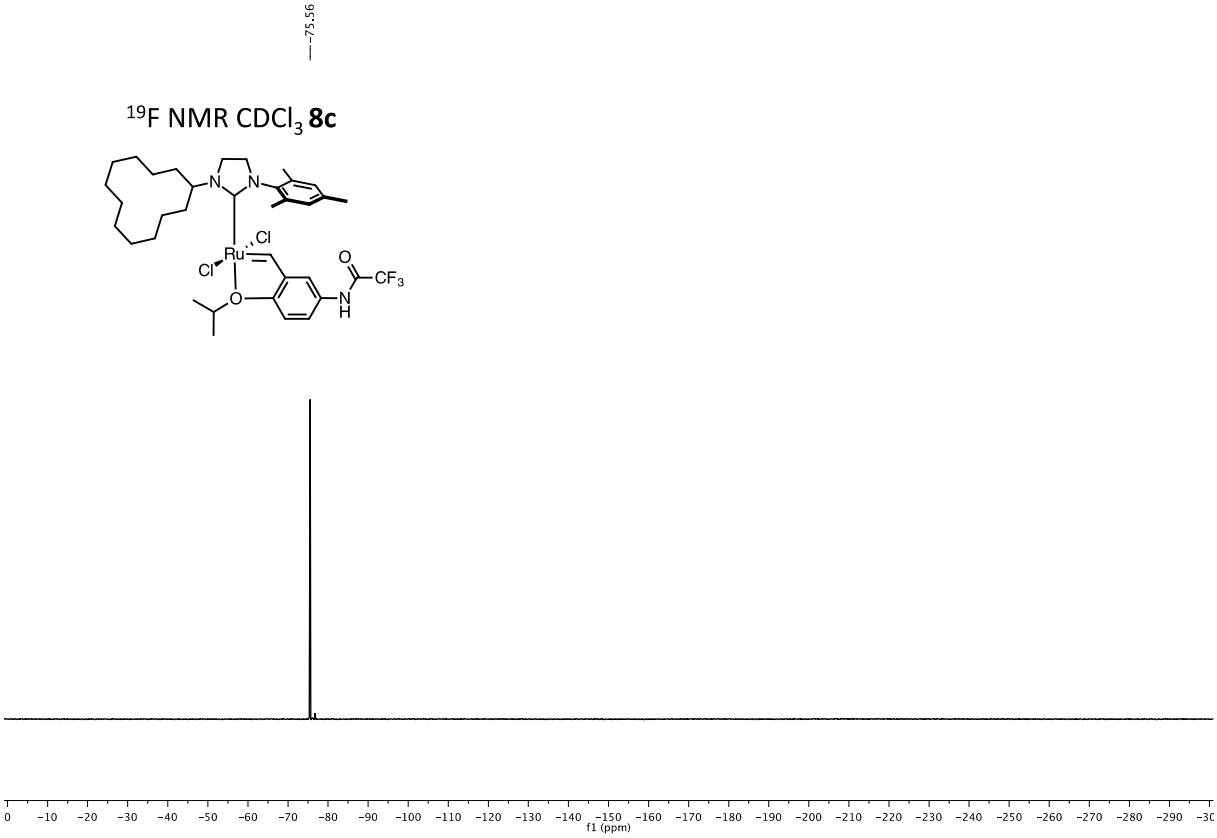


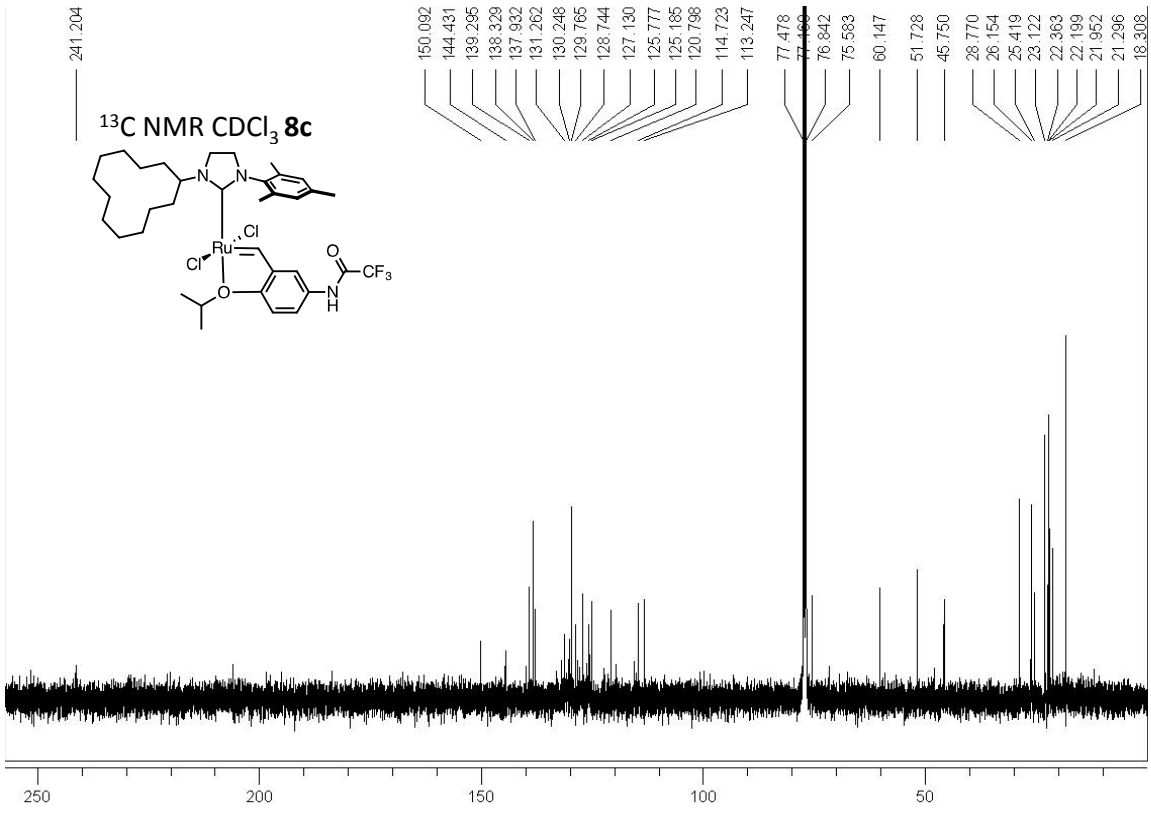


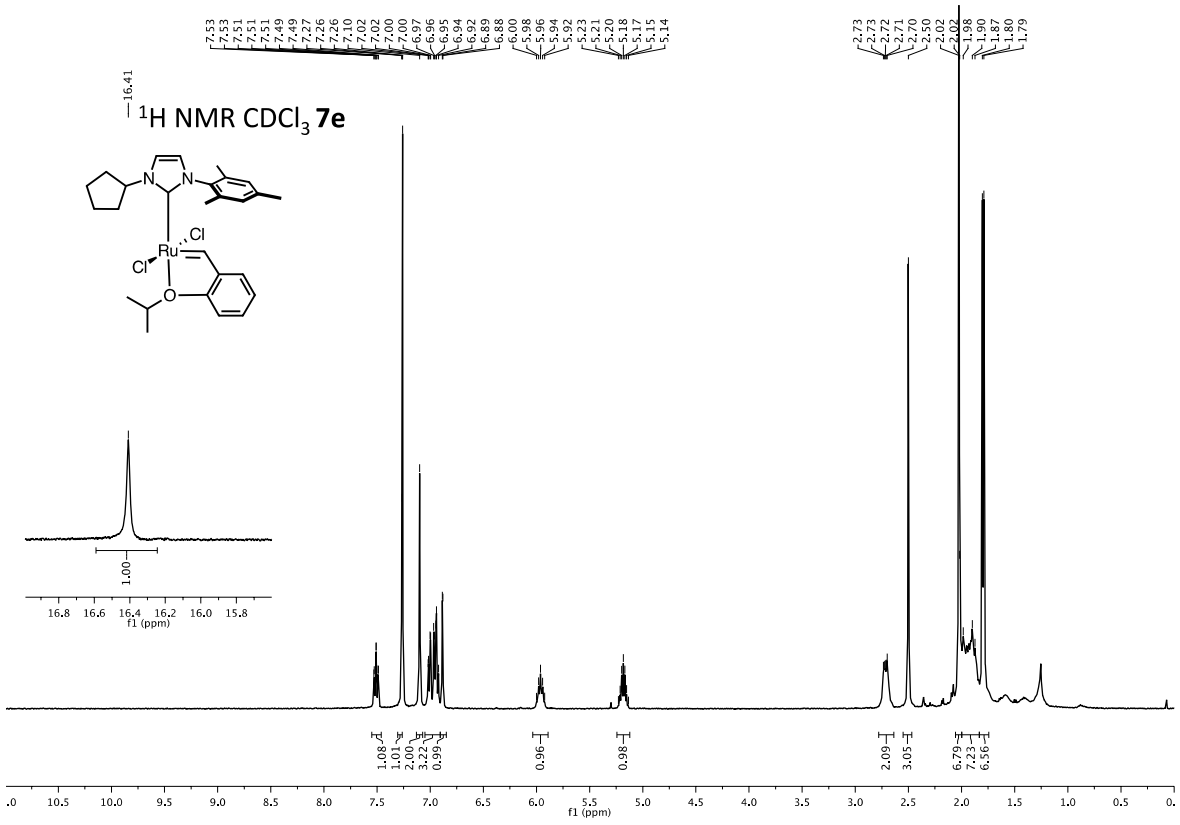
^{1}H NMR $CDCl_3$ **8c**



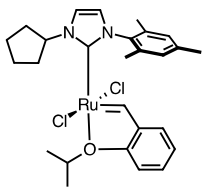
^{19}F NMR $CDCl_3$ **8c**



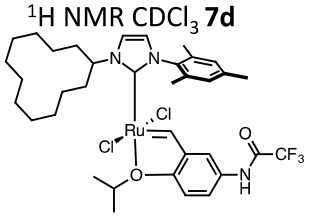

^{13}C NMR $CDCl_3$ **8c**
241.204
150.092
144.431
139.295
138.329
137.932
131.262
130.248
129.765
128.744
127.130
125.777
125.185
120.798
114.723
113.247
77.478
77.160
76.842
75.583
60.147
51.728
45.750
28.770
26.154
25.419
23.122
22.363
22.199
21.952
21.296
18.308
250
200
150
100
50

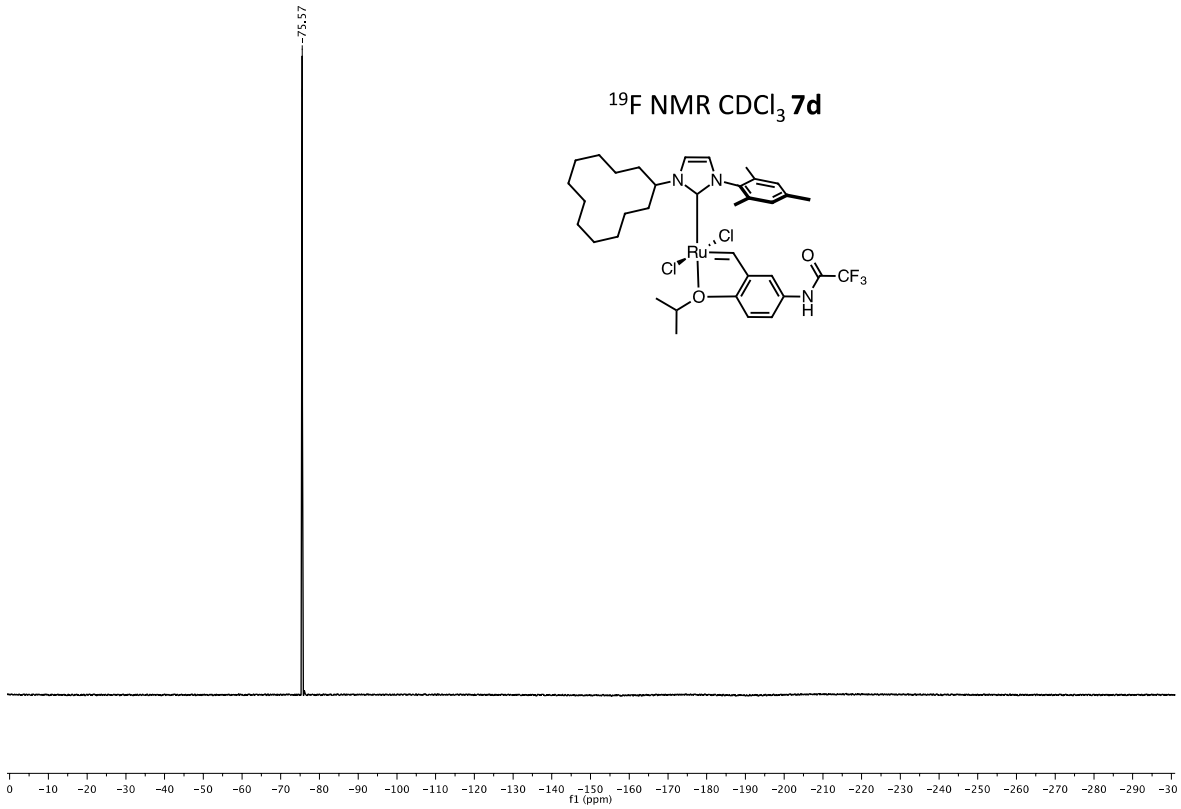

^{1}H NMR $CDCl_3$ **7e**
16.41
7.53
7.53
7.51
7.51
7.51
7.49
7.49
7.27
7.26
7.26
7.10
7.02
7.02
7.00
7.00
6.97
6.96
6.95
6.94
6.92
6.89
6.88
6.00
5.98
5.96
5.94
5.92
5.23
5.21
5.20
5.18
5.17
5.15
5.14
2.73
2.73
2.72
2.71
2.70
2.50
2.02
2.02
1.98
1.90
1.87
1.80
1.79
1.00
16.8 16.6 16.4 16.2 16.0 15.8
f1 (ppm)
1.08
1.01
2.00
3.22
0.99
0.96
0.98
2.09
3.05
6.79
7.23
6.56
f1 (ppm)

^{13}C NMR $CDCl_3$ **7e**

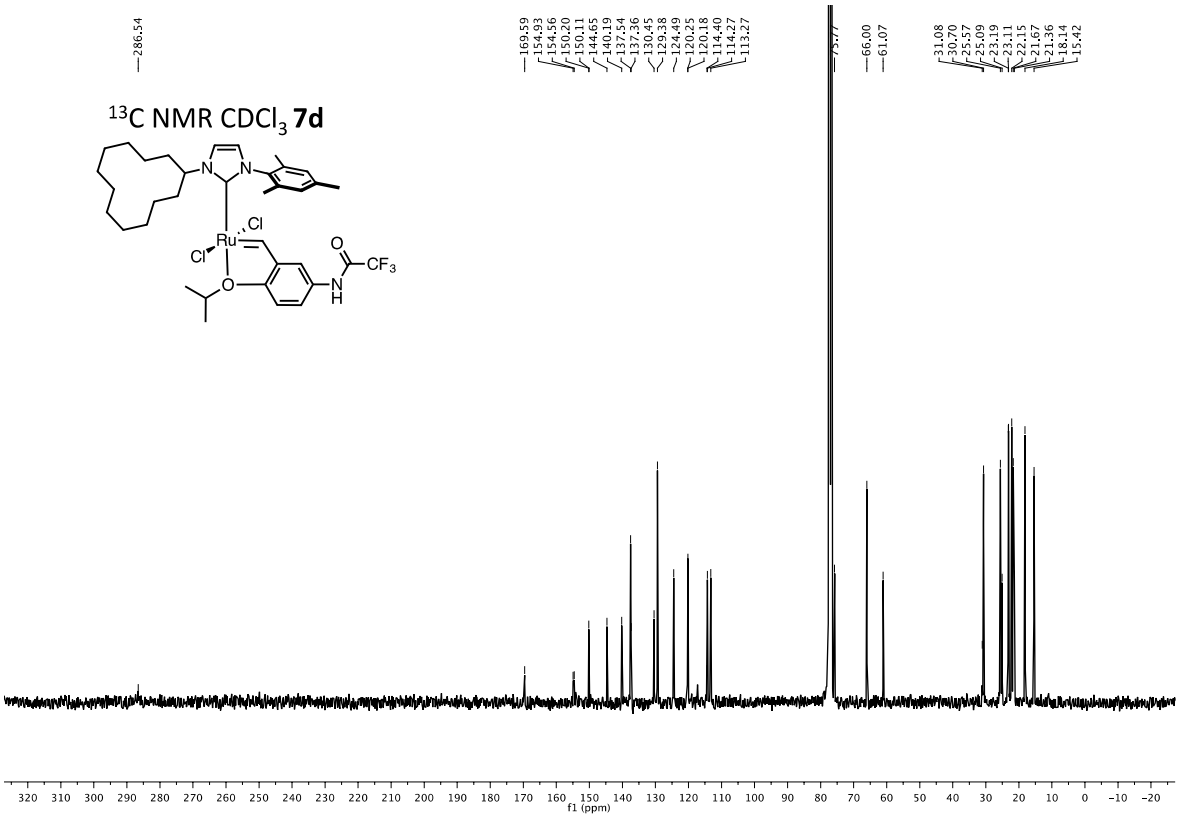


^{1}H NMR $CDCl_3$ **7d**

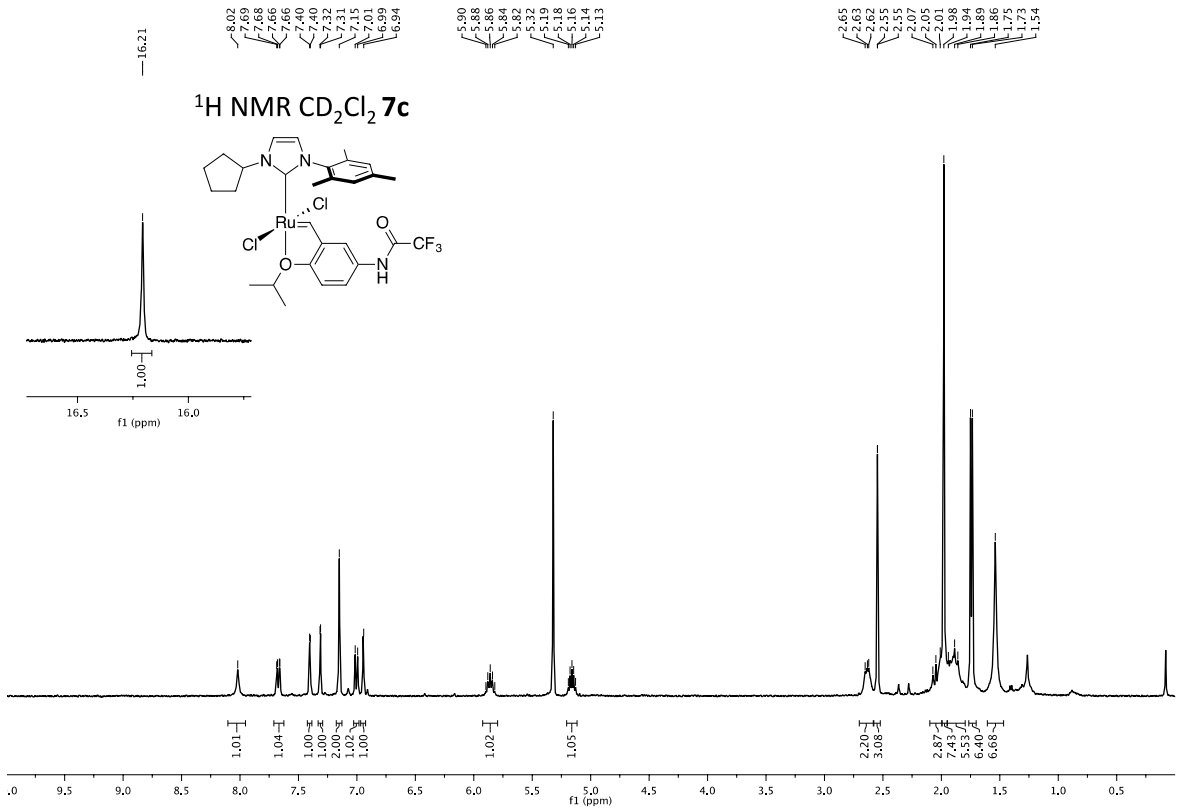




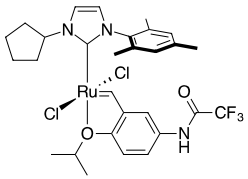
^{19}F NMR $CDCl_3$ **7d**



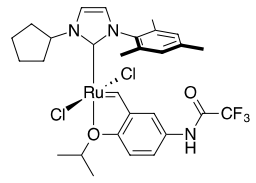
^{13}C NMR $CDCl_3$ **7d**

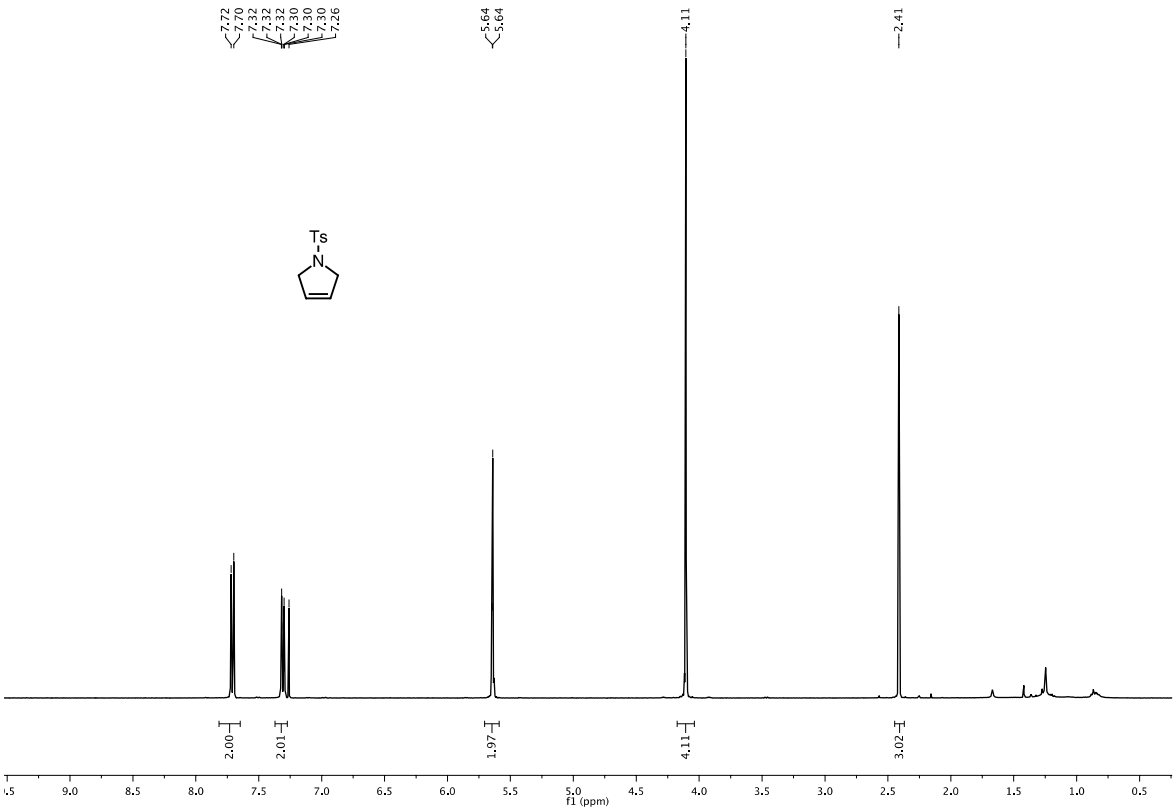

16.21
8.02
7.69
7.68
7.66
7.66
7.40
7.40
7.32
7.31
7.15
7.01
6.99
6.94
5.90
5.88
5.86
5.84
5.82
5.32
5.19
5.18
5.16
5.14
5.13
2.65
2.63
2.62
2.55
2.55
2.07
2.05
2.01
1.98
1.94
1.89
1.86
1.75
1.73
1.54
1H NMR CD2Cl2 7c
Cl
Ru
Cl
O
CF3
N
H
O
N
N
1.00
16.5
16.0
f1 (ppm)
1.01
1.04
1.00
2.00
1.02
1.00
1.02
1.05
2.20
3.08
2.87
7.43
5.53
6.40
6.68
f1 (ppm)

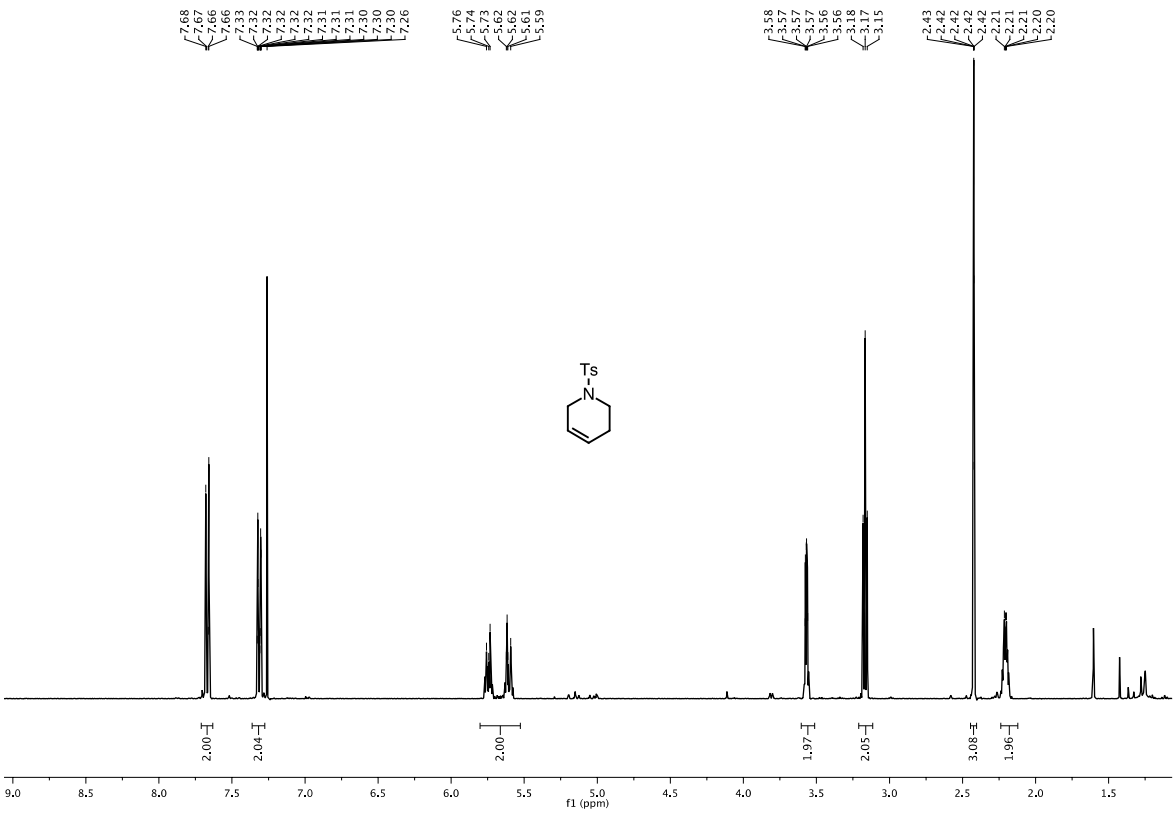
^{19}F NMR CD_2Cl_2 **7c**

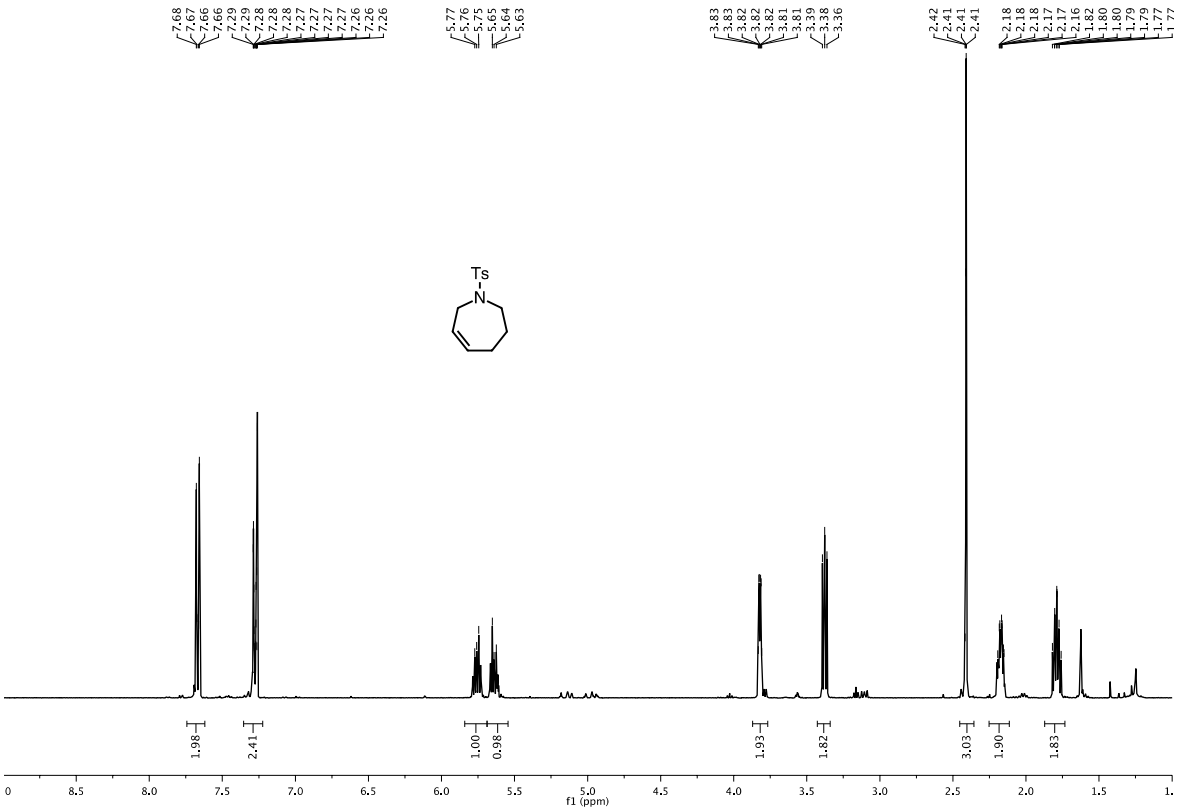


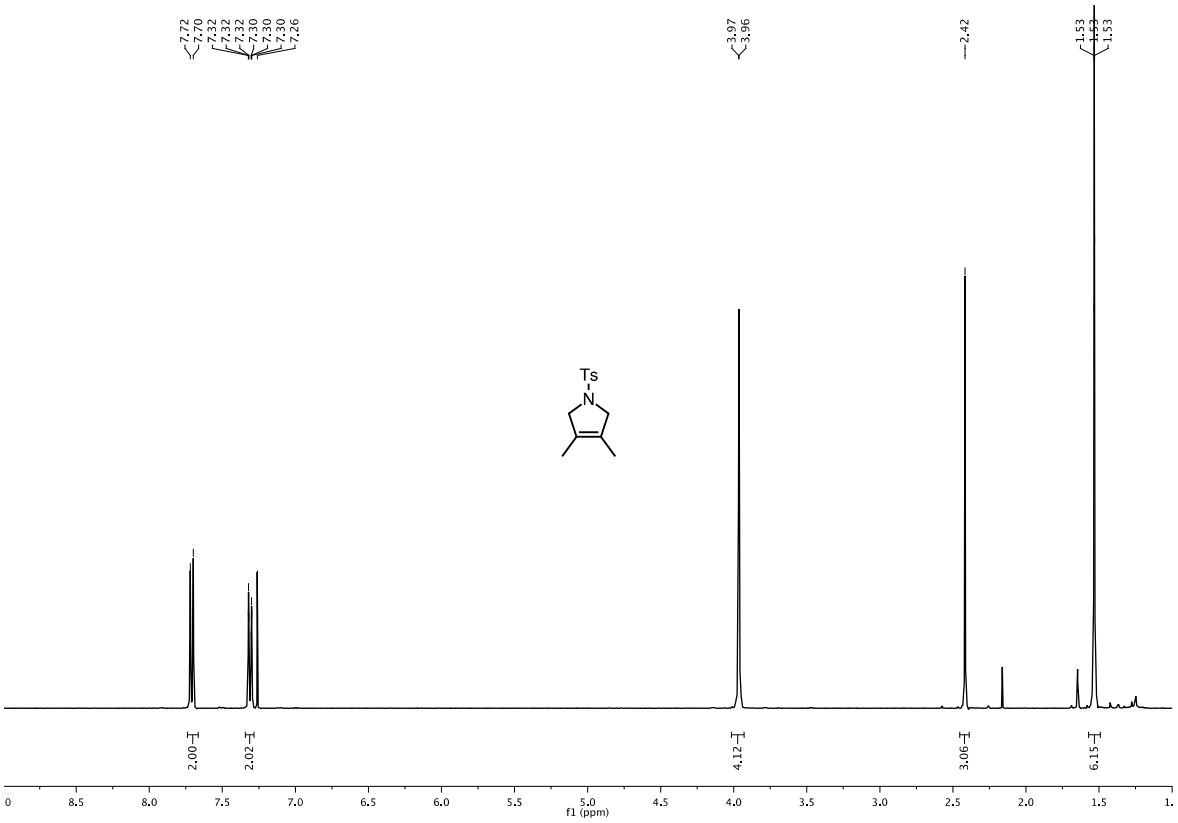
^{13}C NMR CD_2Cl_2 **7c**

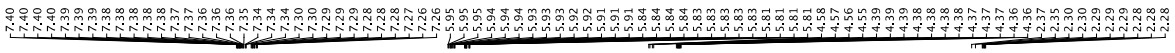


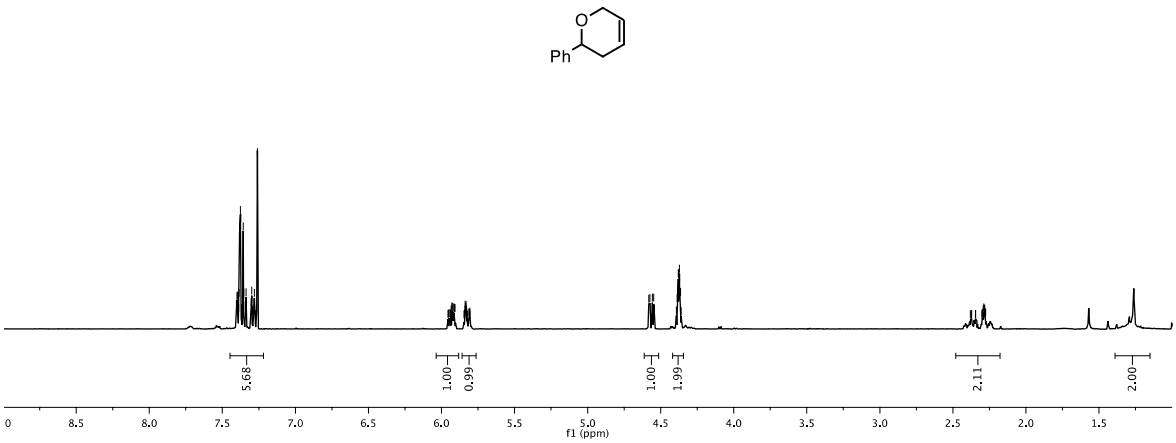

7.72
7.70
7.32
7.32
7.32
7.30
7.30
7.30
7.26
5.64
5.64
4.11
2.41
Ts
N
2.00
2.01
1.97
4.11
3.02
f1 (ppm)

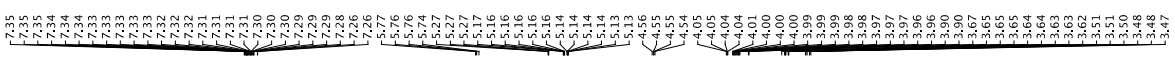

7.68
7.67
7.66
7.66
7.33
7.32
7.32
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.30
7.26
5.76
5.74
5.73
5.62
5.62
5.61
5.59
3.58
3.57
3.57
3.57
3.56
3.56
3.18
3.17
3.15
2.43
2.42
2.42
2.42
2.42
2.21
2.21
2.21
2.20
2.20
Ts
N
2.00
2.04
2.00
1.97
2.05
3.08
1.96
f1 (ppm)

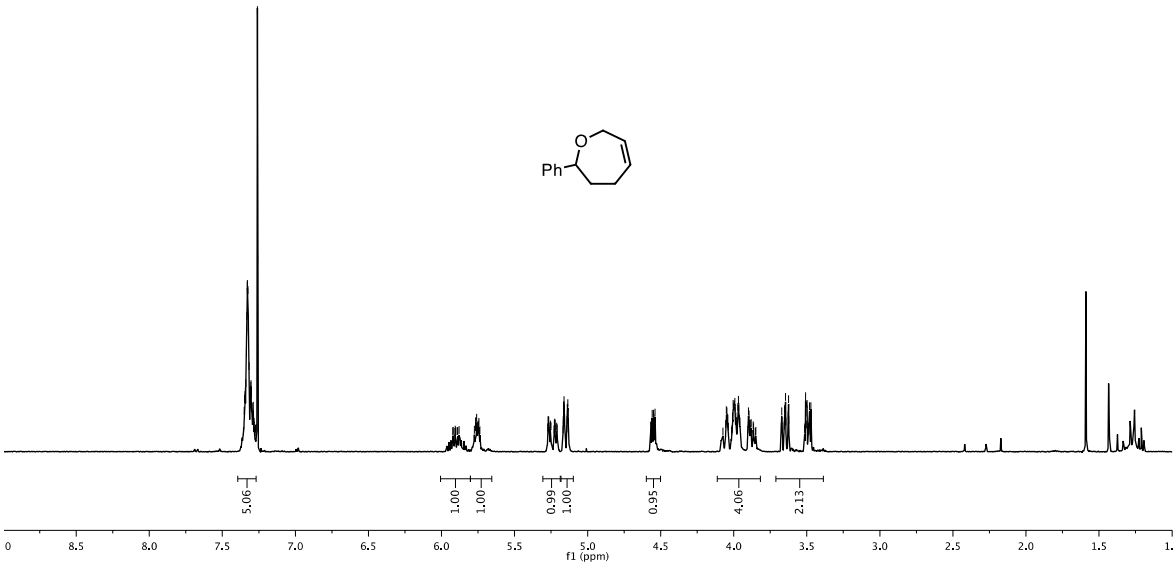

7.68
7.67
7.66
7.66
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.27
7.27
7.26
7.26
7.26
5.77
5.76
5.75
5.65
5.64
5.63
3.83
3.83
3.82
3.82
3.82
3.81
3.81
3.39
3.38
3.36
2.42
2.41
2.41
2.41
2.18
2.18
2.18
2.17
2.17
2.16
1.82
1.80
1.80
1.79
1.79
1.77
1.77
Ts
N
1.98
2.41
1.00
0.98
1.93
1.82
3.03
1.90
1.83
f1 (ppm)

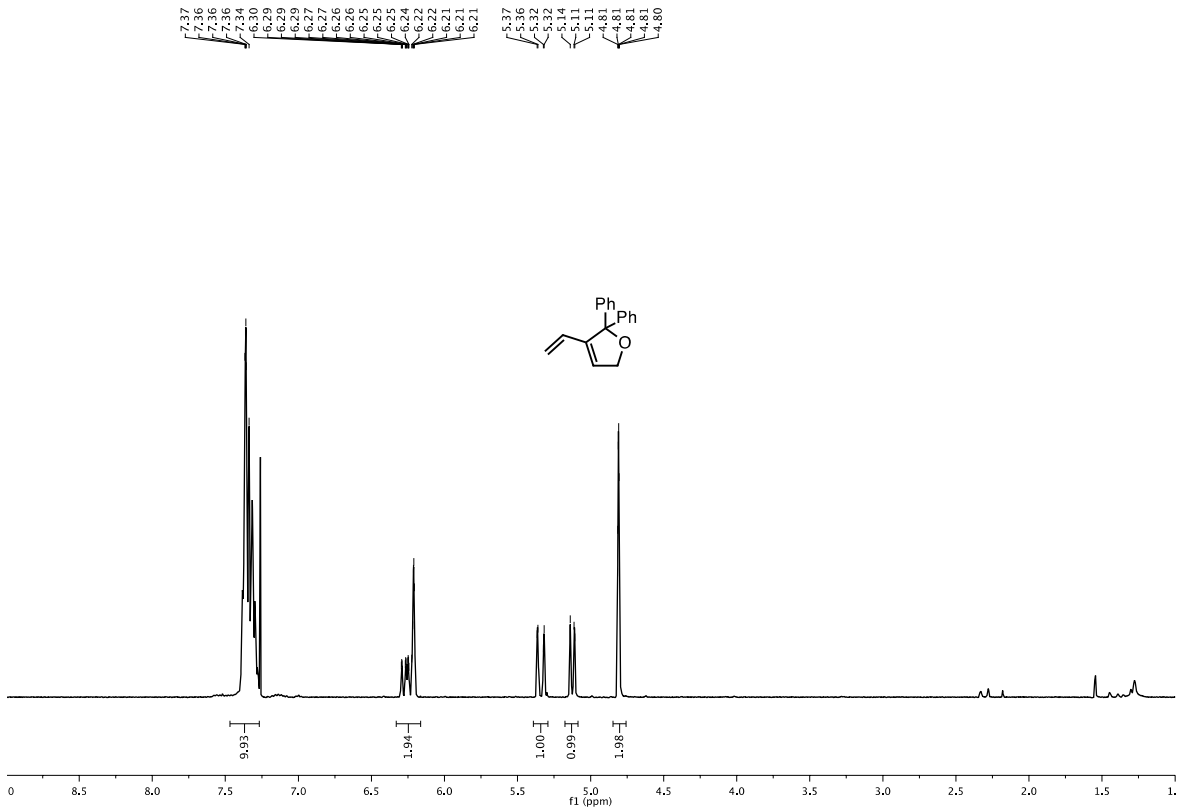

7.72
7.70
7.32
7.32
7.32
7.30
7.30
7.30
7.26
3.97
3.96
2.42
1.53
1.53
1.53
Ts
N
2.00
2.02
4.12
3.06
6.15
f1 (ppm)

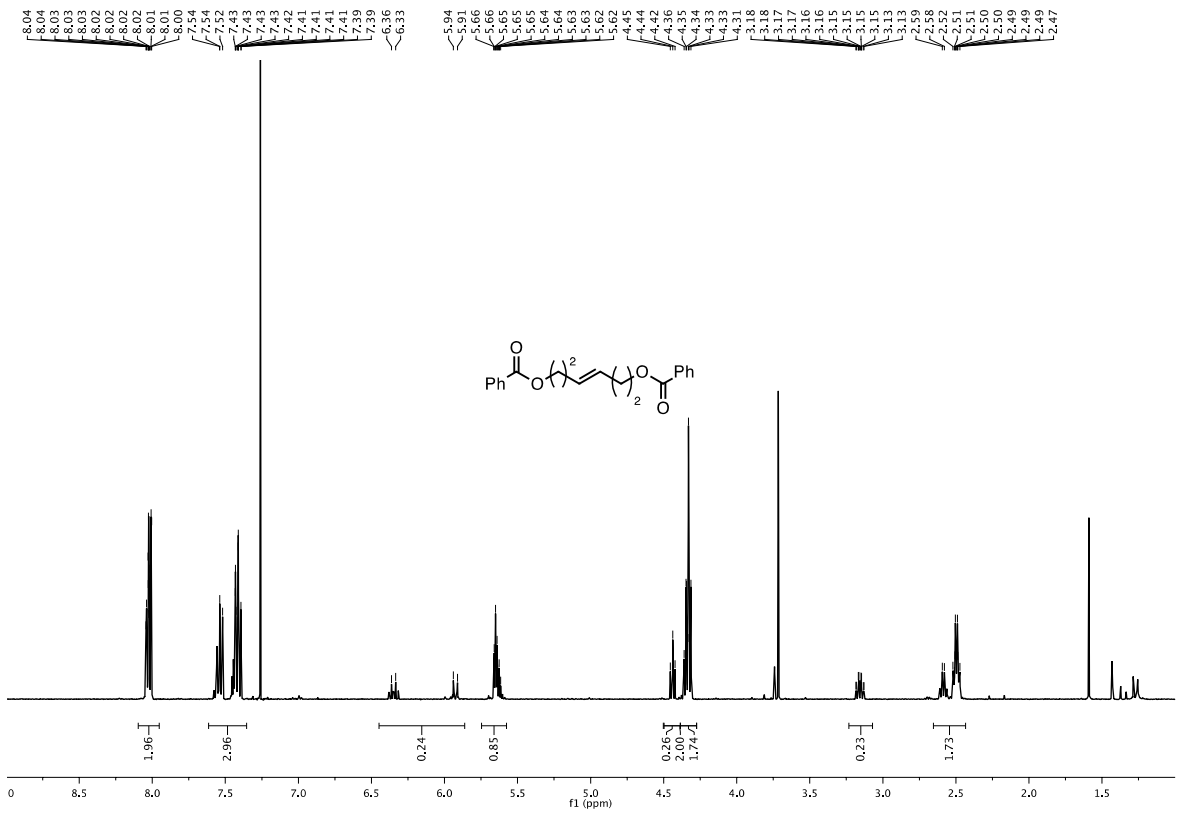


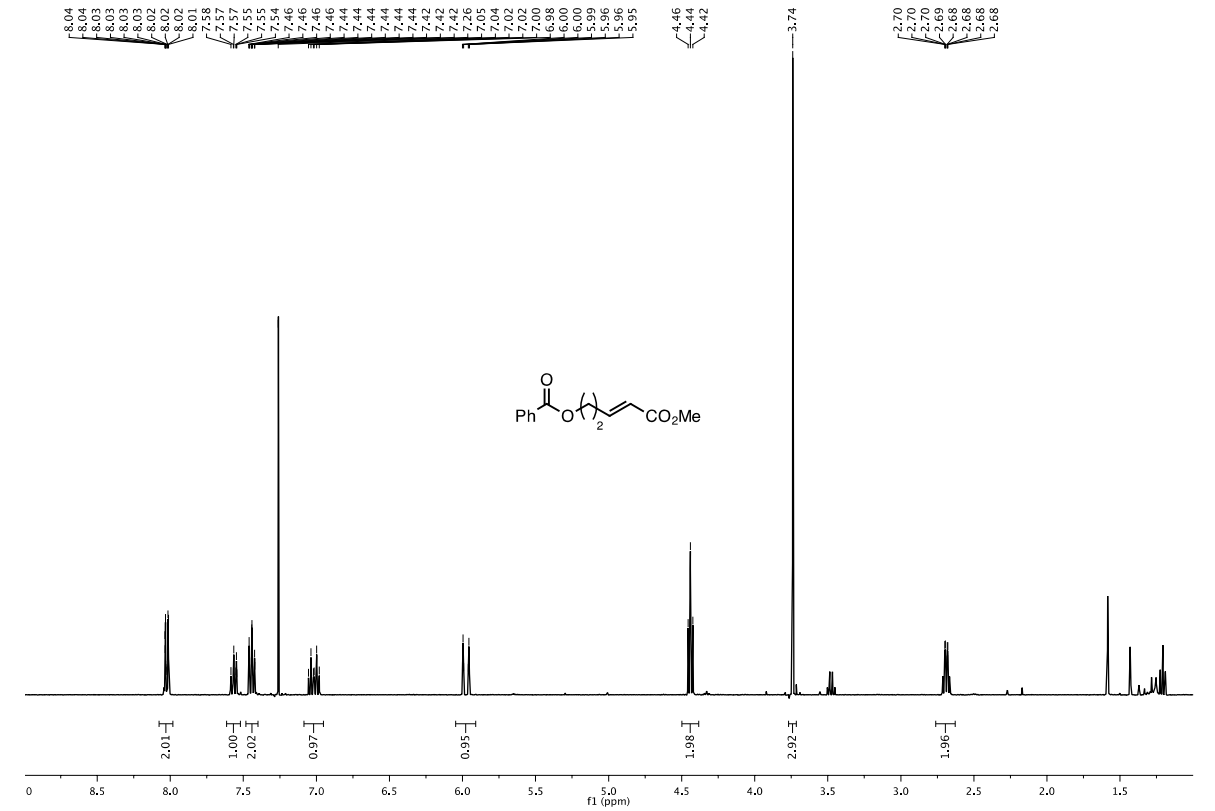

O
Ph
5.68
1.00
0.99
1.00
1.99
2.11
2.00
f1 (ppm)

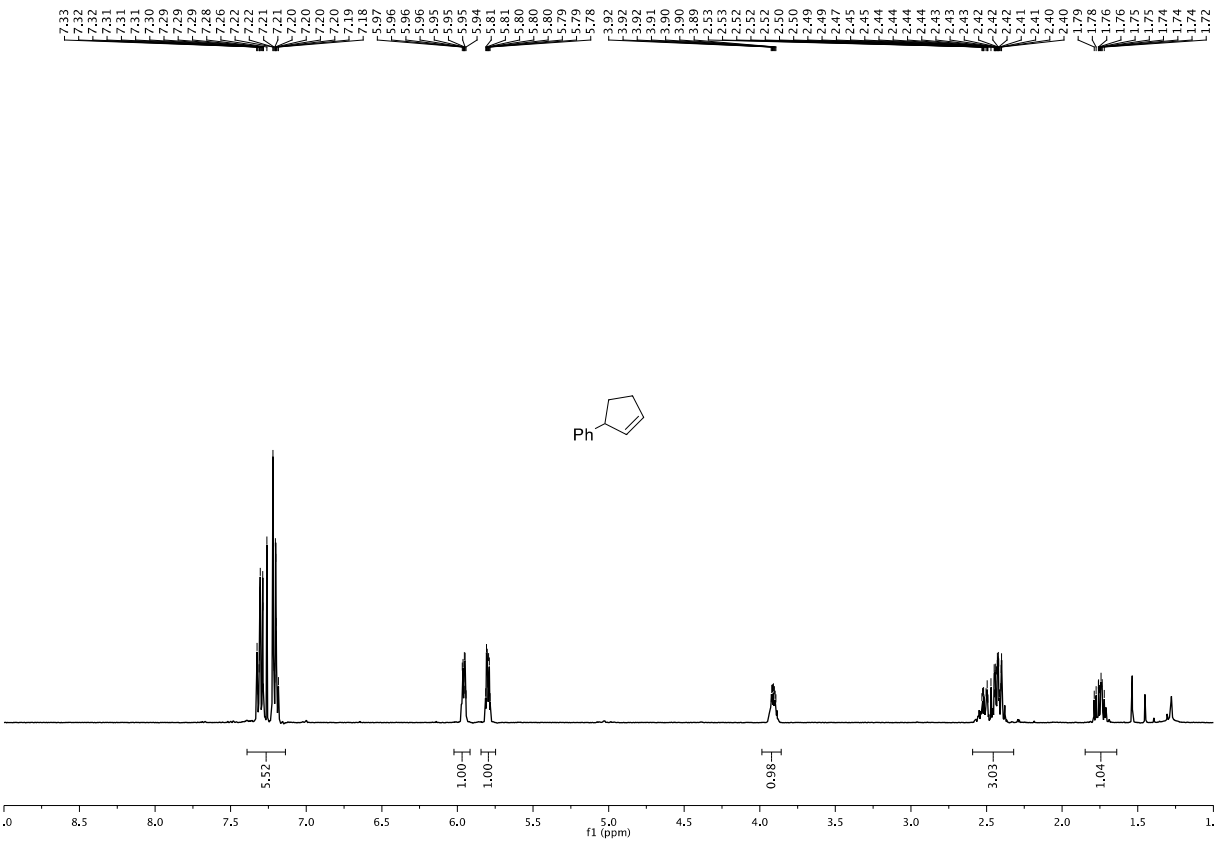


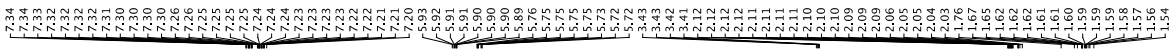

O
Ph
5.06
1.00
1.00
0.99
1.00
0.95
4.06
2.13
f1 (ppm)

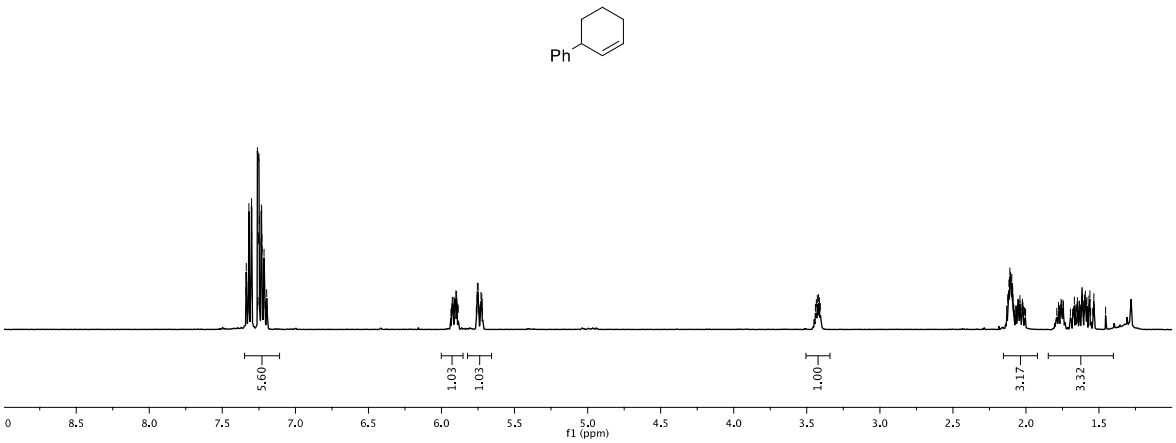

7.37
7.36
7.36
7.36
7.34
6.30
6.29
6.29
6.29
6.27
6.27
6.26
6.26
6.25
6.25
6.25
6.24
6.22
6.22
6.21
6.21
6.21
5.37
5.36
5.32
5.32
5.14
5.11
5.11
4.81
4.81
4.81
4.81
4.80
Ph
Ph
O
9.93
1.94
1.00
0.99
1.98
f1 (ppm)

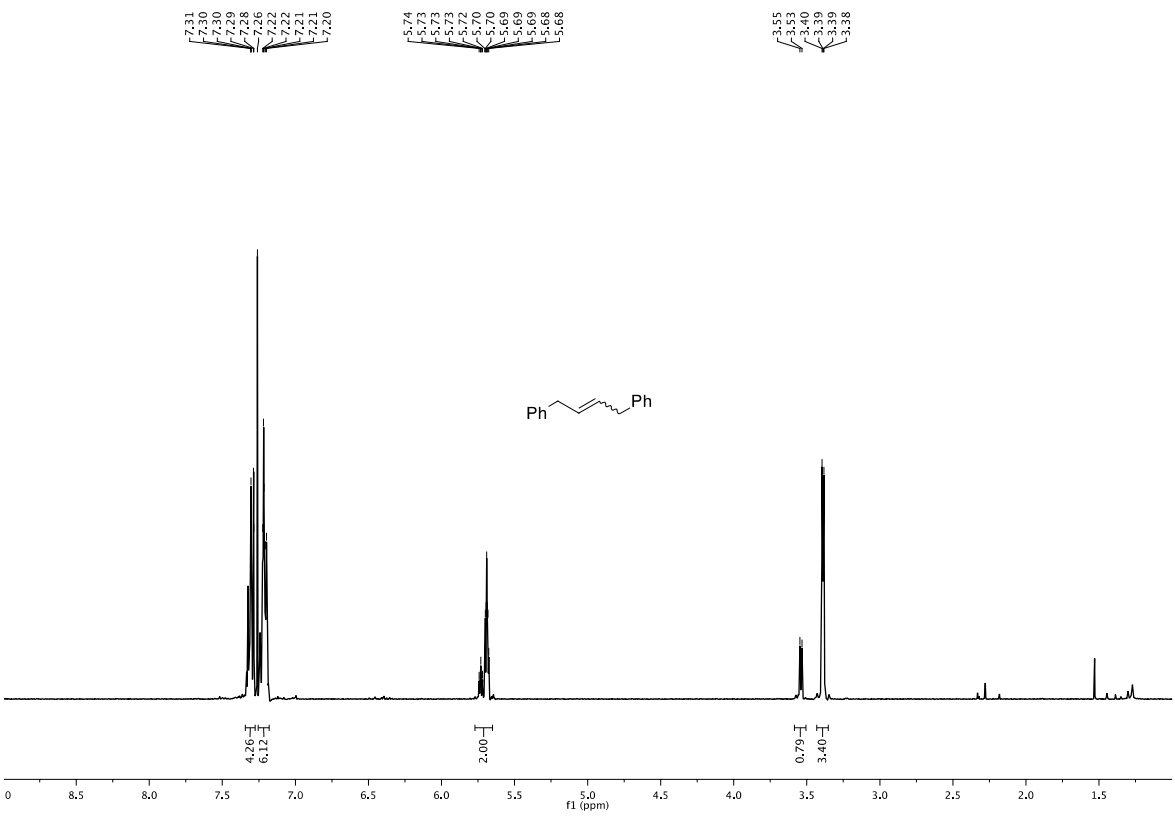

8.04
8.04
8.03
8.03
8.03
8.02
8.02
8.02
8.02
8.02
8.01
8.01
8.00
7.54
7.54
7.52
7.43
7.43
7.43
7.43
7.42
7.41
7.41
7.41
7.41
7.39
7.39
6.36
6.33
5.94
5.91
5.66
5.66
5.65
5.65
5.65
5.64
5.64
5.63
5.63
5.62
5.62
4.45
4.44
4.42
4.36
4.35
4.34
4.33
4.31
3.18
3.18
3.17
3.17
3.16
3.16
3.15
3.15
3.15
3.15
3.13
3.13
2.59
2.58
2.52
2.51
2.51
2.50
2.50
2.49
2.49
2.49
2.47
O
Ph
O
O
2
2
O
Ph
O
1.96
2.96
0.24
0.85
0.26
2.00
1.74
0.23
1.73
f1 (ppm)


8.04 8.04 8.03 8.03 8.03 8.03 8.02 8.02 8.02 8.01 7.58 7.57 7.57 7.55 7.55 7.54 7.46 7.46 7.46 7.46 7.44 7.44 7.44 7.44 7.44 7.42 7.42 7.42 7.26 7.05 7.04 7.02 7.02 7.00 6.98 6.00 6.00 5.99 5.96 5.96 5.95
4.46 4.44 4.42
3.74
2.70 2.70 2.70 2.69 2.68 2.68 2.68 2.68
Ph O O 2 CO2Me
2.01 1.00 2.02 0.97 0.95 1.98 2.92 1.96
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.26 7.22 7.21 7.21 7.20 7.20 7.20 7.20 7.19 7.18 5.97 5.96 5.96 5.95 5.95 5.95 5.94 5.81 5.81 5.80 5.80 5.80 5.79 5.79 5.78
3.92 3.92 3.92 3.91 3.90 3.90 3.89 2.53 2.52 2.52 2.52 2.50 2.50 2.49 2.49 2.47 2.45 2.45 2.44 2.44 2.44 2.43 2.43 2.42 2.42 2.42 2.41 2.41 2.40 2.40 1.79 1.78 1.76 1.76 1.75 1.75 1.74 1.74 1.74 1.72
Ph
5.52 1.00 1.00 0.98 3.03 1.04
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.
f1 (ppm)




Ph
5.60
1.03
1.03
1.00
3.17
3.32
f1 (ppm)


Ph
Ph
4.26
6.12
2.00
0.79
3.40
f1 (ppm)

X-ray crystal data

Ruthenium complexe 8b

CCDC : 843466

Empirical formula	C57 H81 Cl2 N2 P Ru
Formula weight	997.18
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 38.966(2) A alpha = 90 deg. b = 22.2805(9) A beta = 90 deg. c = 14.1432(4) A gamma = 90 deg.
Volume	12278.9(9) A^3
Z, Calculated density	8, 1.079 Mg/m^3
Absorption coefficient	0.401 mm^-1
F(000)	4240
Crystal size	0.342 x 0.322 x 0.035 mm
Theta range for data collection	2.78 to 27.00 deg.
Limiting indices	-49<=h<=40, -27<=k<=28, -18<=l<=18
Reflections collected / unique	96599 / 13375 [R(int) = 0.1017]
Completeness to theta = 27.00	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13375 / 0 / 550
Goodness-of-fit on F^2	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0824, wR2 = 0.1809
R indices (all data)	R1 = 0.1124, wR2 = 0.1924
Largest diff. peak and hole	1.193 and -2.645 e.A^-3

Ruthenium complexe 7d

CCDC : 890262

Empirical formula	C36 H48 Cl2 F3 N3 O2 Ru
Formula weight	783.74
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 18.7213(3) A alpha = 90 deg. b = 8.63550(10) A beta = 93.38(1) deg. c = 25.2389(3) A gamma = 90 deg.
Volume	4073.24(9) A^3
Z, Calculated density	4, 1.278 Mg/m^3
Absorption coefficient	0.562 mm^-1
F(000)	1624
Crystal size	0.343 x 0.278 x 0.102 mm
Theta range for data collection	2.60 to 27.00 deg.
Limiting indices	-23<=h<=23, -11<=k<=11, -32<=l<=32
Reflections collected / unique	56848 / 8874 [R(int) = 0.0549]
Completeness to theta = 27.00	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8874 / 0 / 424
Goodness-of-fit on F^2	0.952
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0943
R indices (all data)	R1 = 0.0661, wR2 = 0.1000
Largest diff. peak and hole	0.565 and -0.565 e.A^-3

Ruthenium complexe 7e

CCDC : 876822

Empirical formula	C27 H34 Cl2 N2 O Ru
Formula weight	574.53
Temperature	140(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/a
Unit cell dimensions	a = 13.6662(3) A alpha = 90 deg. b = 12.2444(2) A beta = 108.840(2) deg. c = 17.0887(4) A gamma = 90 deg.
Volume	2706.32(10) A^3
Z, Calculated density	4, 1.410 Mg/m^3
Absorption coefficient	0.798 mm^-1
F(000)	1184
Crystal size	0.28 x 0.22 x 0.09 mm
Theta range for data collection	2.85 to 27.00 deg.
Limiting indices	-17<=h<=17, -15<=k<=15, -21<=l<=20
Reflections collected / unique	20794 / 5897 [R(int) = 0.0401]
Completeness to theta = 27.00	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5897 / 0 / 298
Goodness-of-fit on F^2	0.932
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0702
R indices (all data)	R1 = 0.0487, wR2 = 0.0734
Largest diff. peak and hole	0.612 and -0.542 e.A^-3