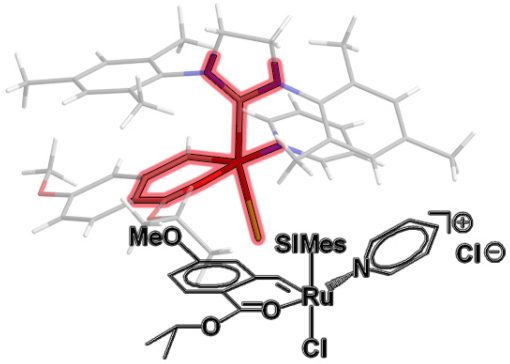
Pyridine as trigger for chloride isomerisation in chelated ruthenium benzylidene complexes: implications for olefin metathesis.

Michaela Zirngast, Eva Pump, Anita Leitgeb, Jörg H. Albering and Christian Slugovc*

Graz University of Technology,
Institute for Chemistry and Technology of Materials,
Stremayrgasse 9, A 8010 Graz, Austria

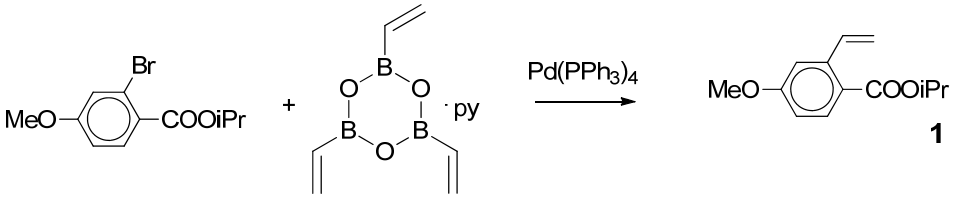
ELECTRONIC SUPPORTING INFORMATION



General information

Unless otherwise noted, all reactions were carried out under argon in pre-dried glassware using Schlenk techniques. Materials were obtained from commercial sources (Aldrich, Fluka or Alfa Aesar) and were used without further purification. The monomers dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**5**) [1] was prepared according to literature. CH_2Cl_2 was dried over CaH_2 and degassed with argon. NMR (^1H, ^{13}C) spectra were recorded on a Bruker Avanze 300MHz or a INOVA 500 MHz spectrometer, respectively. Chemical shifts are given in ppm relative to a $SiMe_4$ standard. The solvent peak of $CDCl_3$ was used for referencing the NMR spectra to 7.26 (^1H) and 77.16 ppm (^{13}C), respectively. Gel permeation chromatography (GPC) was used to determine molecular weights and the polydispersity index (PDI). Measurements were carried out in THF with the following arrangement: a Merck Hitachi L6000 pump, separation columns of Polymer Standards Service (5 µm grade size) and a refractive-index detector from Wyatt Technology. For calibration Polystyrene Standards purchased from Polymer Standard Service were used. X-Ray measurements were performed on a Bruker AXS Kappa APEX II diffractometer using Mo Kα radiation. The structures were solved by direct methods using SHELXS and refined with SHELXL. The absorption correction was performed using the program SADABS.

Preparation of **4-Methoxy-2-vinyl benzoic acid *iso*-propyl ester** (**1**)



2-Bromo-4-methoxy benzoic acid *iso*-propyl ester (3.00 mmol, 1 eq.), vinylboronic anhydride pyridine complex (3.59 mmol, 1.2 eq.) and K_2CO_3 (5.99 mmol, 2 eq) were dissolved in 20 mL degassed DME/H_2O (3:1). $Pd(PPh_3)_4$ (0.104 g, 0.090 mmol, 0.03 eq.) was added and the reaction mixture was heated to 90°C and stirred for 18 hours. The reaction mixture was extracted with water, Et_2O, 10% HCl- and saturated $NaHCO_3$ solution. The organic layer was dried with Na_2SO_4, filtered and evaporated. The orange, oily residue was purified by column chromatography, using cyclohexane : ethyl acetate = 5:1 (v:v). Yield: 0.561 g (85%), yellowish oil.

Anal. calcd. for $C_{13}H_{16}O_3$ (220.26 g/mol): C, 70.89; H, 7.32; found: C, 70.96; H, 7.46. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 7.89 (d, 1H, $^3J_{HH}$ = 8.7 Hz , ph^6), 7.54 (q, 1H, $^3J_{HH}$ = 11.1 Hz, $CHCH_2$), 7.03 (d, 1H, $^4J_{HH}$ = 2.6 Hz, ph^3), 6.82 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.6 Hz, , ph^5), 5.61 (dd, 1H, $^3J_{HH}$ = 17.2 Hz, $^4J_{HH}$ = 1.2 Hz, $CHCH_2$), 5.34 (dd, 1H, $^3J_{HH}$ = 10.9 Hz, $^4J_{HH}$ = 1.2 Hz, $CHCH_2$), 5.21 (m, 1H, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$), 3.87 (s, 3H, OCH_3), 1.35 (d, 6H, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 166.38 (1C, COO^iPr), 162.26 (1C, ph^4), 142.15 (1C, ph^2), 136.48 (1C, $CHCH_2$), 132.54 (1C, ph^{3,5,6}), 121.63 (1C, ph^1), 116.11 (1C, CH_2CH), 112.75, 112.31 (2C, ph^{3,5,6}), 68.06 (1C, $CH(CH_3)_2$), 55.37 (1C, OCH_3), 21.97 (2C, $CH(CH_3)_2$).

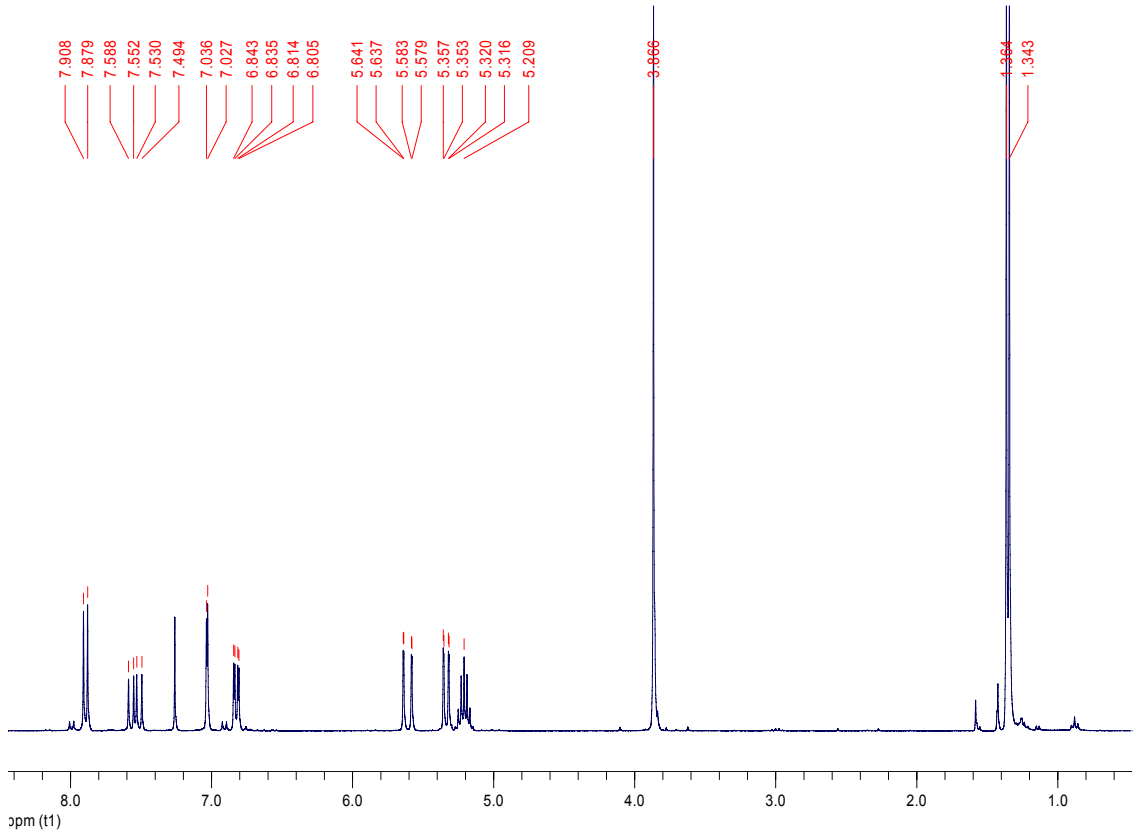
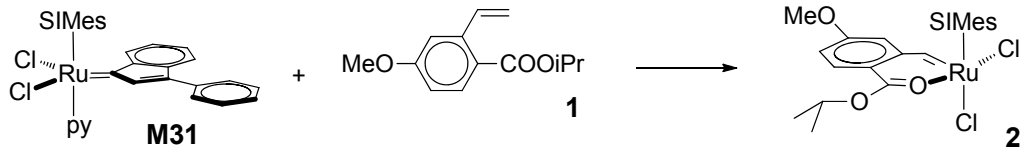


Figure S1. ^{1}H-NMR (300MHz, $CDCl_3$) of **1**.

Preparation of **(SPY-5-34)-dichloro-(κ^2(C,O)-(2-iso-propyl ester-5-methoxy benzylidene)-(1,3-bis(2,4,6- trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)-ruthenium** (**2**)



In a Schlenk flask, **M31** (165 mg; 0.221 mmol; 1.0 eq.) was dissolved in degassed, dry CH_2Cl_2 (5 mL). **1** (56.2 mg; 0.255 mmol; 1.2 eq.) was added. The reaction mixture was stirred in a Schlenk flask under argon atmosphere for 20 h. The colour turned from deep red to deep green. The solvent was reduced to 1 to 2 mL and the complex was then precipitated with *n*-pentane. The dark green precipitate was filtered, washed with *n*-pentane and dried in vacuo. Separation of two main products was done by column chromatography on silica gel using CH_2Cl_2/MeOH 20:1 (v:v) as eluent sampling a green band. A turquoise band was eluated using CH_2Cl_2/MeOH 5:1 (v:v) (5% yield, *cf*. next preparation). Upon drying in vacuum, **2** was obtained as dark green powder (60.2 mg, 34 %) yield.

Anal. calcd. for $C_{33}H_{40}Cl_2N_2O_3Ru$ (684.66 g/mol): C, 57.89; H, 5.89; N, 4.09; found: C, 57.78; H, 6.07; N, 3.94. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 18.91 (s, 1H, Ru=CH), 7.99 (d, 1H, $^3J_{HH}$ = 8.7 Hz, ph^3), 7.14 - 7.08 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz, ph^4), 7.20, 7.17, 6.92, 6.02 (s, 4H, mes), 6.74 (d, 1H, $^4J_{HH}$ = 2.5 Hz, ph^6), 5.25 (m, 1H, $^3J_{HH}$ = 6.2 Hz, C*H*$(CH_3)_2$), 4.34-4.19 (m, 1H, H_2Im), 4.13-3.93 (m, 2H, H_2Im), 3.90 (s, 3H, OCH_3), 3.80-3.66 (m, 1H, H_2Im), 2.67, 2.55, 2.46, 2.40, 2.10, 1.40 (s, 18H, mes-CH_3), 1.49, 1.40 (d, 6H, $^3J_{HH}$ = 6.1 Hz, CH(C*H*$_3)_2$). ^{13}C-NMR (δ, 20°C, CD_2Cl_2, 75 MHz): Ru=CH (not observed), 217.7 (1C, C_q, CNN), 175.3 (1C, C_q, $COOCH_3$), 166.0 (1C, C_q, ph^5), 144.7 (1C, C_q, ph^1), 140.0, 139.6, 138.4, 137.9, 136.3, 135.1 (6C, C_q, mes-C), 135.6 (1C, C_q, mes-N), 133.2 (1C, ph^{3,4,6}), 132.4 (1C, C_q, mes-N), 131.0, 129.6, 129.5, 128.4 (1C, mes), 113.9 (1C, C_q, ph^2), 113.7, 111.9 (2C, ph^{3,4,6}), 72.1 (1C, *C*H$(CH_3)_2$), 55.7 (1C, OCH_3), 51.1, 50.95 (2C, H_2Im), 22.0, 21.8 (2C, CH(*C*H$_3)_2$), 21.4, 20.7, 20.1, 18.3, 18.2, 16.3 (6C, mes-CH_3).

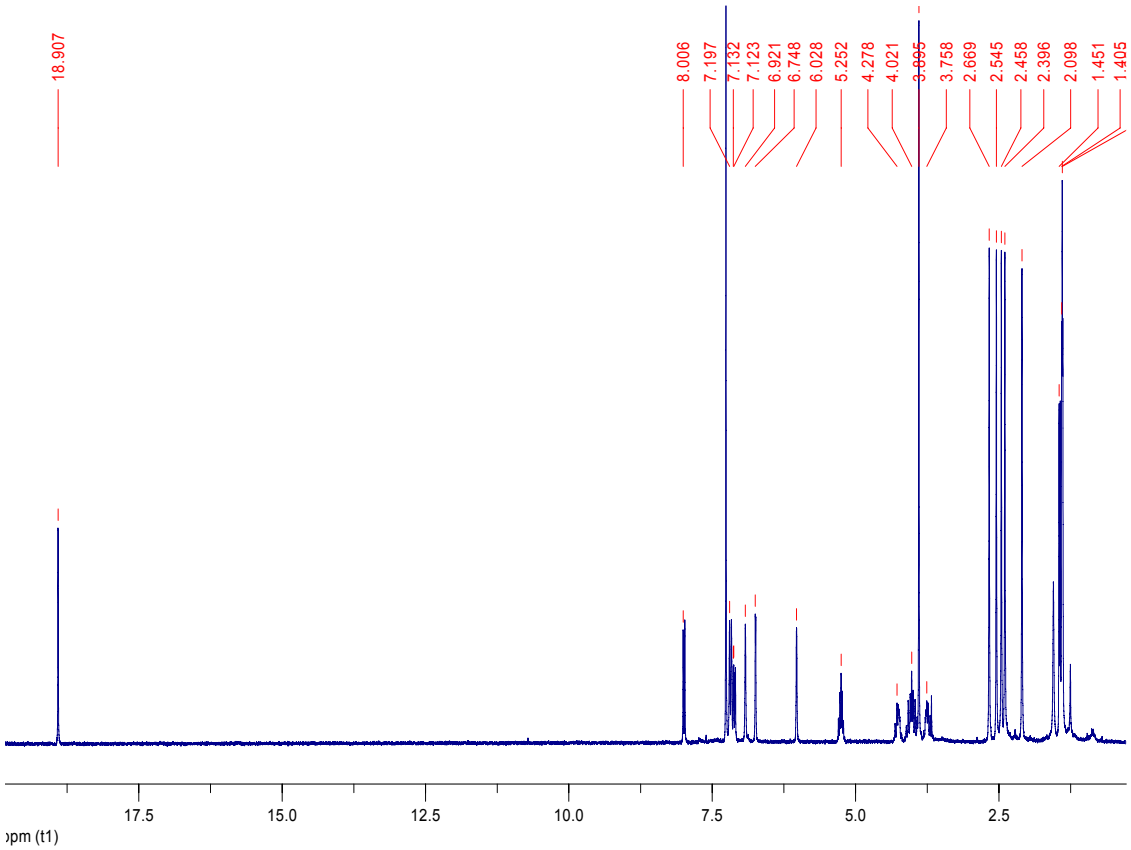
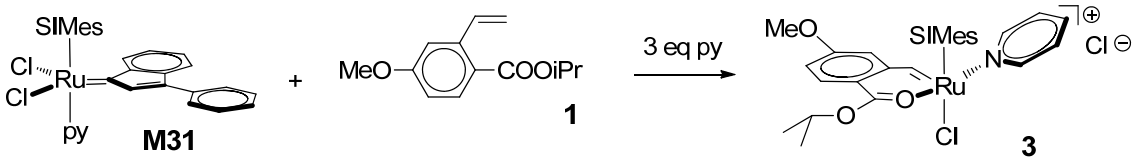


Figure S2. ^{1}H-NMR (300MHz, $CDCl_3$) of complex **2**

Preparation of **[(SPY-5-43)-(chloro)(κ²(C,O)-(2-iso-propyl ester-5-methoxy benzylidene) (pyridine)(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)-ruthenium] chloride** (**3**)



M31 (284.2 mg; 0.379 mmol; 1.0 eq.) was dissolved in 5 mL degassed CH_2Cl_2. **1** (99.7 mg; 0.453 mmol; 1.2 eq.) and pyridine (89.9 mg, 1.13 mmol, 3.0 eq.) were added. The reaction mixture was stirred in a Schlenk flask under argon atmosphere for 18 h. The colour turned from deep red to deep green. From integration of the ^{1}H-NMR the crude product was identified as a mixture of **2** (47%) and **3** (45%). **2** and **3** were separated and isolated as described above. Yield: 78.1 mg of **2** (29%) and 106.7 mg of **3** (37 %).

Anal. calcd. for $C_{38}H_{45}Cl_2N_3O_3Ru$ (763.76 g/mol): C, 59.76; H, 5.94; N, 5.50; found: C, 59.92; H, 6.09; N, 5.35. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 17.92 (s, 1H, Ru=CH), 8.51 (d, 2H, $^3J_{HH}$ = 5.3 Hz, py^{7,11}), 8.04 (d, 1H, $^3J_{HH}$ = 8.8 Hz, ph^3), 7.77 (t, 1H, $^3J_{HH}$ = 7.2 Hz, py^9), 7.33 (t, 2H, $^3J_{HH}$ = 6.6 Hz, py^{8,10}), 7.31 (d, 1H, $^4J_{HH}$ = 2.1 Hz, ph^6), 7.20 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.1 Hz, ph^4), 7.07, 6.40 (s, 4H, mes), 5.29 (m, 1H, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$), 4.17 (s, 4H, H_2Im), 4.01 (s, 3H, OCH_3), 2.65, 2.16, 1.63 (s, 18H, mes-CH_3), 1.56, 1.52 (d, 6H, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$). ^{13}C-NMR (δ, 20°C, CD_2Cl_2, 75 MHz): 298.3 (1C, Ru=CH), 208.2 (1C, C_q, CNN), 175.4 (1C, C_q, COO^{i}Pr), 166.1 (1C, C_q, ph^5), 155.2 (2C, py^{7,11}), 145.9 (1C, C_q, ph^1), 139.5, 136.6, 136.0 (6C, C_q, mes-C), 137.4 (1C, py^9), 133.6 (1C, ph^{3,4,6}), 133.4 (2C, C_q, mes-N), 130.4, 129.7 (4C, mes), 125.1 (2C, py^{8,10}), 115.7 (1C, ph^{3,4,6}), 114.5 (1C, C_q, ph^2), 113.3 (1C, ph^{3,4,6}), 73.6 (1C, *C*H$(CH_3)_2$), 56.7 (1C, OCH_3), 52.3 (2C, H_2Im), 21.9, 21.6 (2C, CH(*C*$H_3)_2$), 20.8, 18.2, 17.2 (6C, mes-*C*H_3).

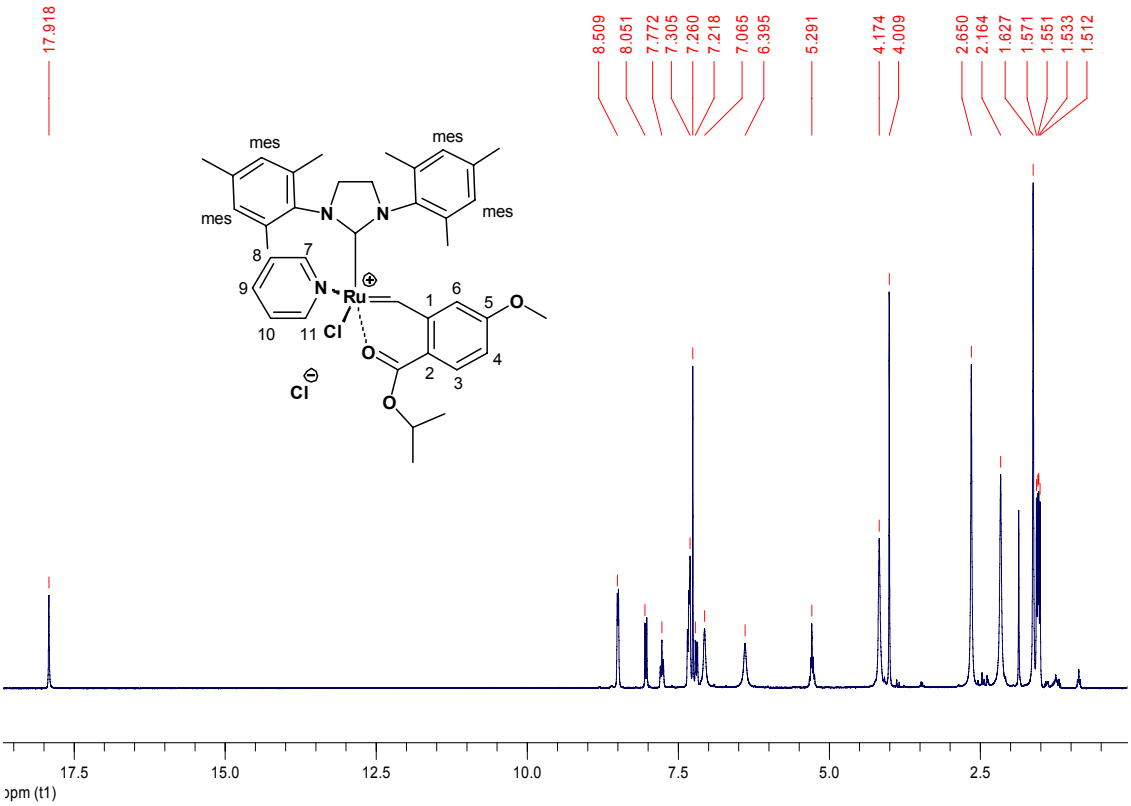


Figure S3. ^{1}H-NMR (300MHz, $CDCl_3$) of complex **3**

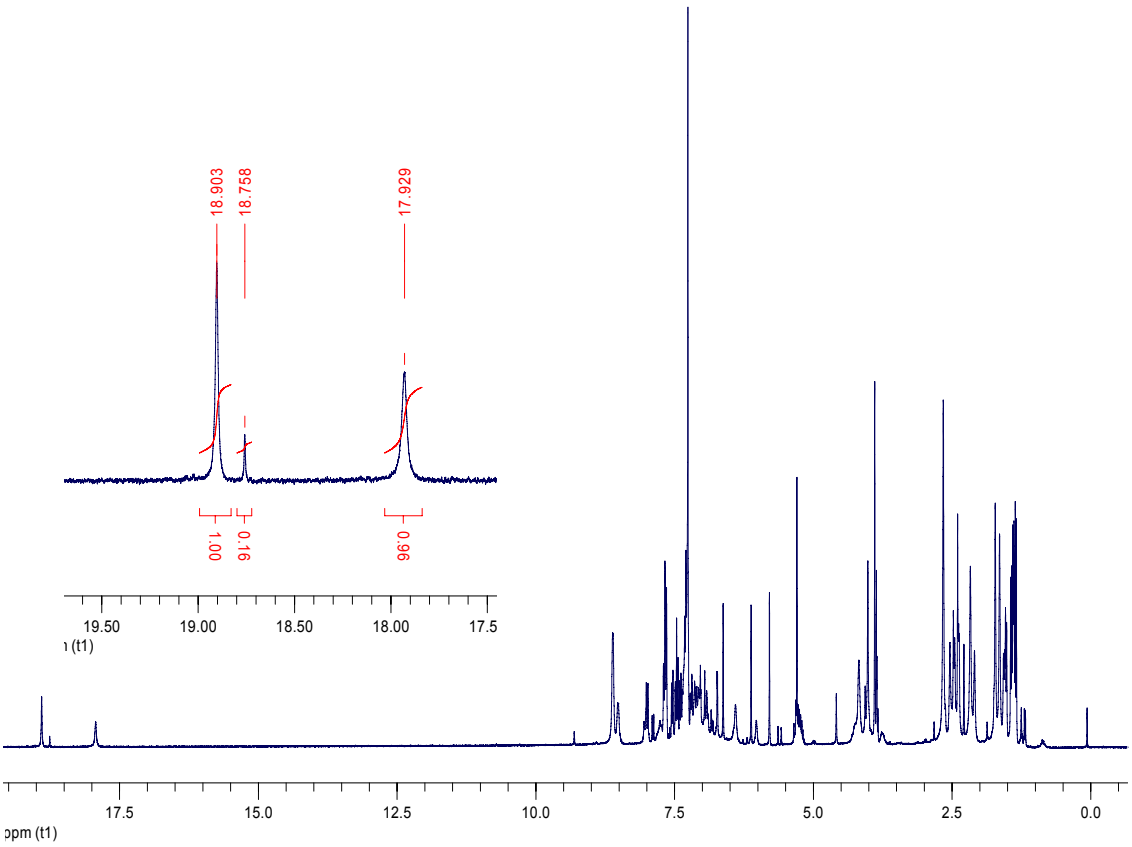
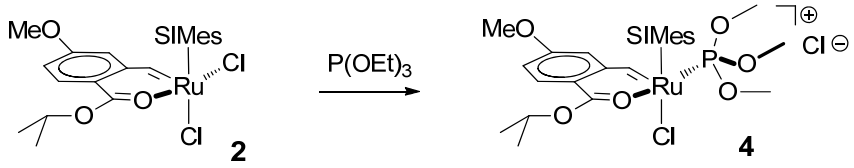


Figure S4. ^{1}H-NMR (300MHz, $CDCl_3$) of raw product (mixture of **2** and **3**), carbene region zoomed in.

Preparation of **[(SPY-5-34)-(chloro)(κ^2(C,O)-(2-iso-propyl ester-5-methoxy benz-ylidene)(triethyl phosphite)(1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene)-ruthenium] chloride** (**4**)



Compound **2** (30 mg, 0.0438 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (2 mL) and triethyl phosphite (8.8 mg; 0.0526 mmol; 1.2 eq.) was added. The reaction mixture was stirred under argon atmosphere for 1h. . **4** was obtained by slow diffusion of diethyl ether to a saturated solution of **4** in CH_2Cl_2, followed by separation, washing and drying of the solids in vacuo. Yield: 29 mg (78 %).

Anal. calcd. for $C_{39}H_{55}Cl_2N_2O_6PRu$ (850.81 g/mol): C, 55.06; H, 6.52; N, 3.29; found: C, 54.89; H, 6.77; N, 3.03. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 18.58 (s, 1H, Ru=CH), 8.20 (d, 1H, $^3J_{HH}$ = 8.8 Hz, ph^4), 7.56 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz, ph^3), 7.21-6.74 (m, 4H, mes), 6.70 (d, 1H, $^4J_{HH}$ = 2.2 Hz, ph^2), 5.20 (m, 1H, $^3J_{HH}$ = 6.2 Hz, C*H*$(CH_3)_2$), 4.30-3.29 (bs, 4H, H_2Im), 4.02 (s, 3H, OCH_3), 3.40 (m, 6H, $^3J_{HH}$ = 7.1 Hz, O*C*H_2CH$_3$), 2.72-1.49 (bs, 18H, mes-C*H*$_3$), 1.48, 1.41 (d, 6H, $^3J_{HH}$ = 6.2 H, CH(C*H*$_3$)$_2$), 0.89 (t, 9H, $^3J_{HH}$ = 7.1 Hz, OCH_2C*H*$_3$). ^{31}P-NMR (δ, 20°C, $CDCl_3$, 120Hz): 121.8 ppm.

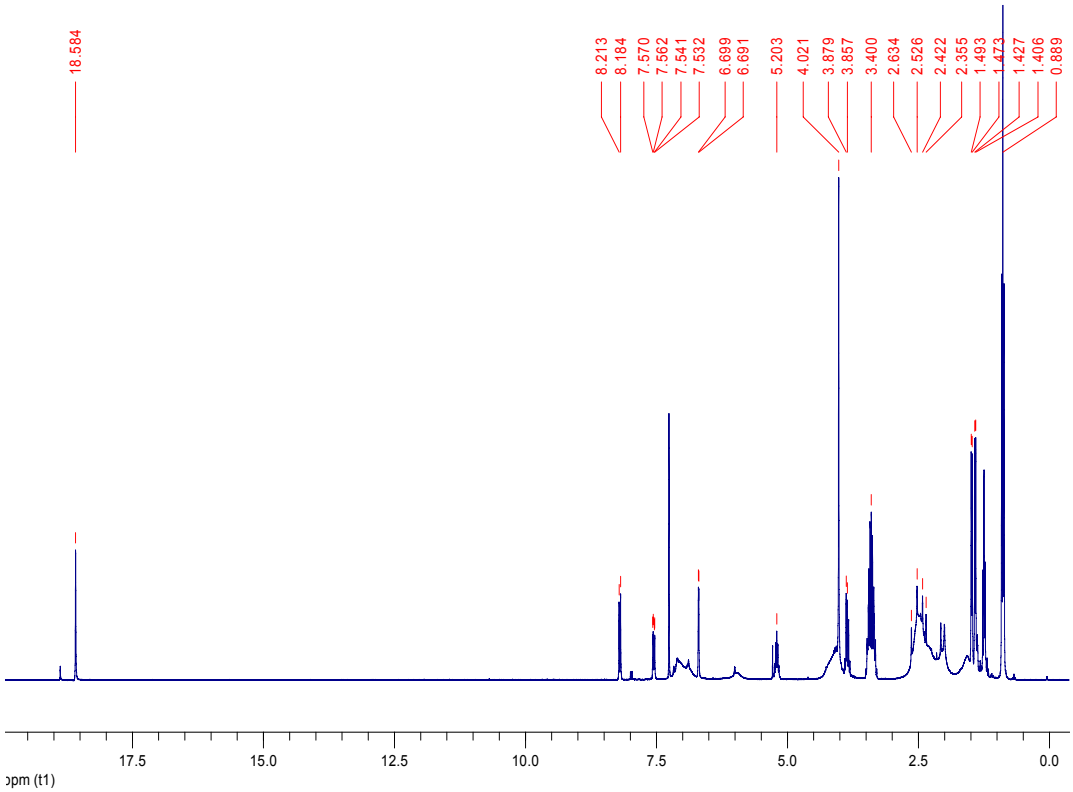
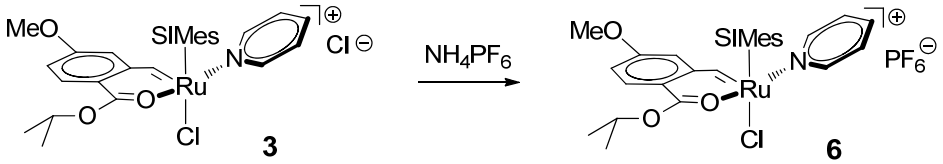


Figure S5. ^{1}H-NMR (300MHz, $CDCl_3$) of complex **4**

Preparation of **[(SPY-5-43)-(chloro)(κ²(C,O)-(2-iso-propyl ester-5-methoxy benz-ylidene)(pyridine)(1,3-bis(2,4,6- trimethylphenyl)4,5-dihydroimidazol-2-ylidene)-ruthenium] hexafluorophosphate** (**6**)



Compound **3** (17.3 mg, 0.0226 mmol, 1.0 eq.) was dissolved in 2 mL degassed methanol and ammonium hexafluorophosphate (8.8 mg, 0.0539 mmol, 1.1 eq.) was added. The reaction mixture was stirred under argon atmosphere for 30 min. The bluish precipitate was filtered, washed with methanol and eluted with dichloromethane. After evaporation of the solvent and drying the solids in vacuo, the product was isolated as blue crystals. Yield: 12.9 mg (65%).

Anal. calcd. for $C_{38}H_{45}ClF_6N_3O_3PRu$ (873.27 g/mol): C, 52.26; H, 5.19; N, 4.81; found: C, 52.29; H, 5.36; N, 5.03. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 17.87 (s, Ru=CH), 8.43 (d, 2H, $^3J_{HH}$ = 5.6 Hz, py^{5,9}), 8.04 (d, 1H, $^3J_{HH}$ = 8.8 Hz, ph^3), 7.72 (t, 1H, $^3J_{HH}$ = 7.5 Hz, py^7), 7.33 (bs, 1H, mes), 7.26 (t, 2H, $^3J_{HH}$ = 6.9 Hz, py^{6,8}), 7.20 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz, ph^3), 7.12 (d, 1H, $^4J_{HH}$ = 2.5 Hz, ph^6), 6.84, 6.70, 6.10 (bs, 3H, mes), 5.30 (m, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*$(CH_3)_2$), 4.18 (s, 1H, H_2Im), 4.05 (t, 2H, $^3J_{HH}$ = 6.8 Hz, , H_2Im), 3.99 (s, 3H, OCH_3), 3.83 (s, 1H, H_2Im), 2.83, 2.40, 1.96, 1.68, 1.52 (bs, 18H, mes-C*H*$_3$), 1.57, 1.53 (d, 6H, $^3J_{HH}$ = 6.1 Hz, CH$(CH_3)_2$). ^{1}H-NMR (δ, 20°C, CD_2Cl_2, 300 MHz): 17.70 (s, Ru=CH), 8.39 (d, 2H, $^3J_{HH}$ = 5.4 Hz, py^{5,9}), 8.12 (d, 1H, $^3J_{HH}$ = 8.8 Hz, ph^4), 7.80 (t, 1H, $^3J_{HH}$ = 7.6 Hz, py^7), 7.26 (t, 2H, $^3J_{HH}$ = 6.7 Hz, py^{6,8}), 7.26 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.8 Hz, ph^2), 6.96 (s, 1H, $^3J_{HH}$ = 2.5 Hz, ph^1), 7.08, 6.46 (bs, mes, 4H), 5.30 (m, 1H, $^3J_{HH}$ = 6.2 Hz, C*H*$(CH_3)_2$), 4.03 (bs, H_2Im, 4H), 3.95 (s, 3H, OCH_3), 2.57, 2.18, 1.53 (bs, 18H, mes-C*H*$_3$), 1.54, 1.52 (d, 6H, $^3J_{HH}$ = 7.0, 5.6 Hz, CH$(CH_3)_2$)**.** ^{13}C-NMR (δ, 20°C, CD_2Cl_2, 75 MHz): Ru=CH not observed, 208.3 (1C, C_q, CNN), 175.3 (1C, C_q, COO^{i}Pr), 166.0 (1C, C_q, ph^5), 154.7 (2C, py^{7,11}), 145.7 (1C, C_q, ph^1), 140.3, 137.3, 135.7 (6C, C_q, mes-C), 137.5 (1C, py^9), 133.8 (1C, ph^{3,4,6}), 133.5 (2C, mes-N), 129.7 (4C, mes), 124.9 (2C, py^{8,10}), 115.6 (1C, ph^{3,4,6}), 114.5 (1C, C_q, ph^2), 112.8 (1C, ph^{3,4,6}), 73.7 (1C, CH$(CH_3)_2$), 56.2 (1C, OCH_3), 51.6 (2C, H_2Im), 21.5, 21.3 (2C, CH$(CH_3)_2$), 20.6, 17.6, 16.7 (6C, mes-*C*H$_3$).

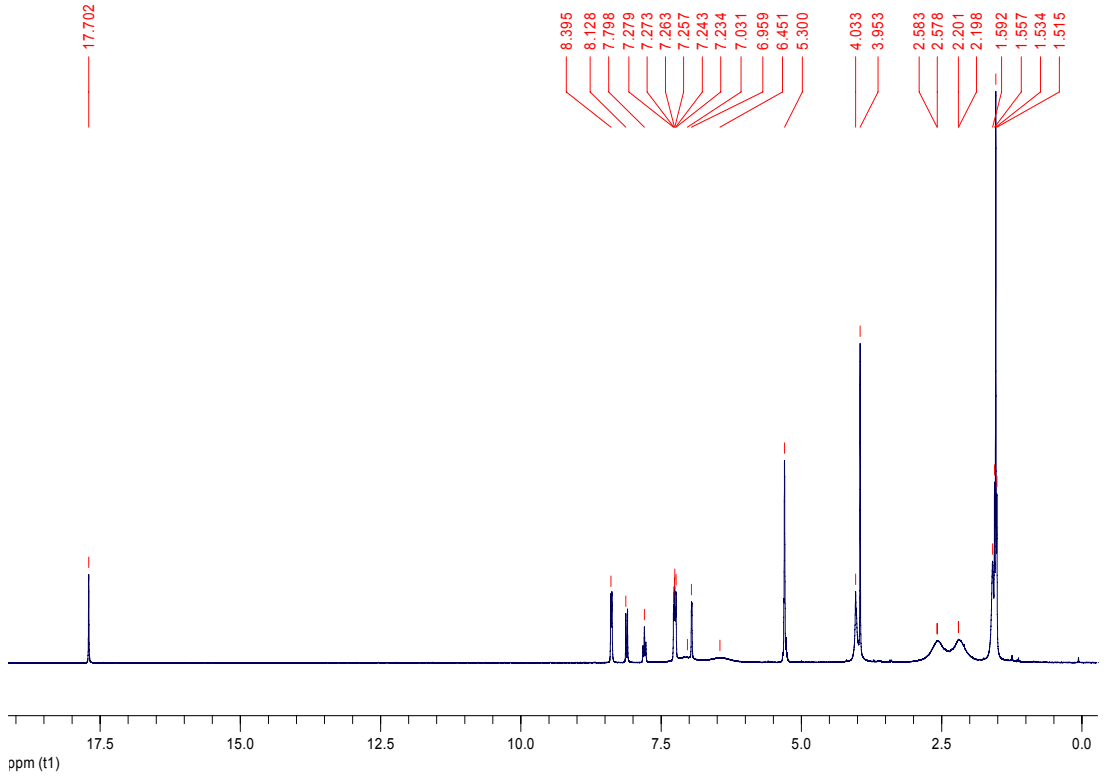


Figure S6. ^{1}H-NMR (300MHz, CD_2Cl_2) of complex **6**

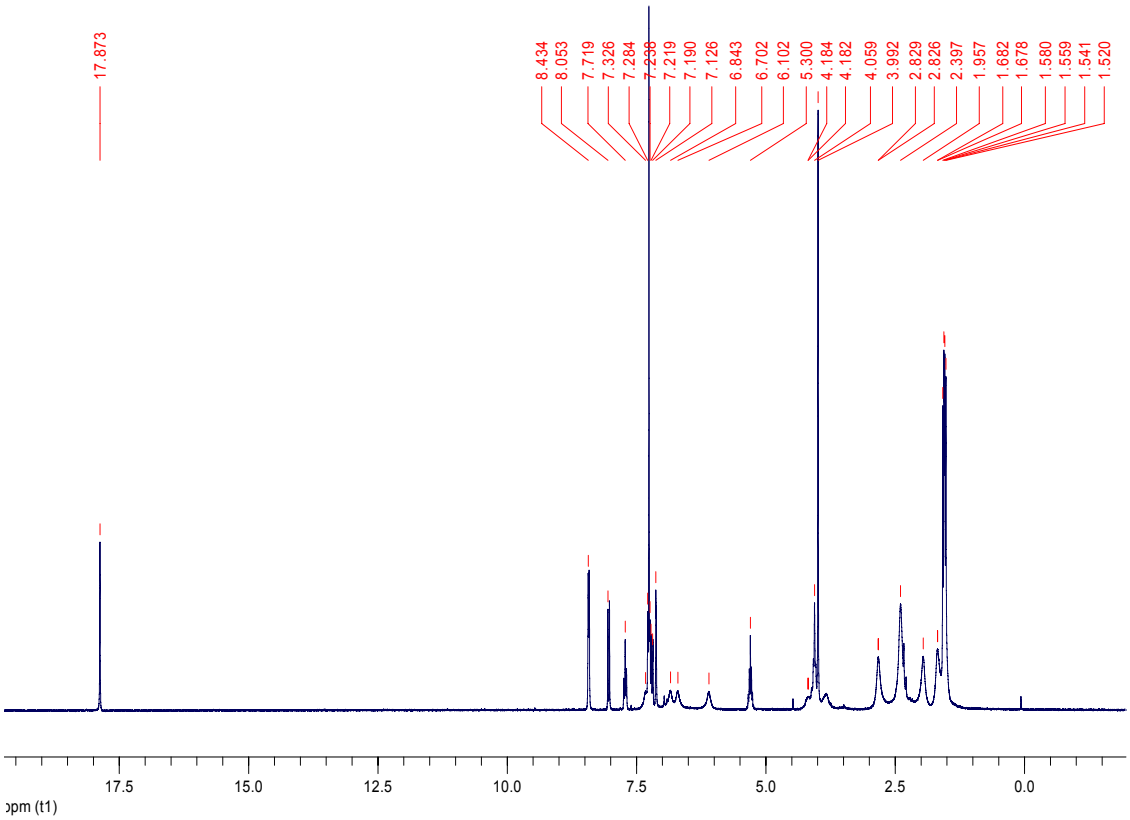
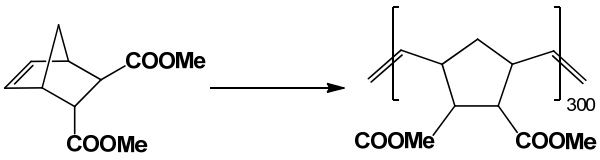


Figure S7. ^{1}H-NMR (300MHz, $CDCl_3$) of complex **6**

Polymerisation procedure



For a typical polymerisation procedure a concentration of 0.1 M in respect to the monomer was used. In a Schlenk flask 1 eq. initiator was dissolved in the appropriate amount of degassed, dry dichloromethane. The mixture was heated to 40°C, then monomer **5** (300 eq.) was added. The reaction was monitored until full conversion by TLC using cyclohexane/ethyl acetate, 3:1 (v:v) and $KMnO_4$ solution for staining. The reaction was quenched with 200µL ethyl vinyl ether and stirred for 15 minutes. Further, the solvent was evaporated to a volume of 2-3 mL and the polymer was precipitated in cold stirred methanol. The same procedure was used for 80°C in toluene as the solvent.

Polymerisation with M31, 2, 3 and 4

Monomer **5** was polymerised as described in the abovementioned procedure. The polymers were then characterized regarding their molecular weight distribution by means of GPC, relative to polystyrene standards in THF. Results are subsumed in Figure S8.

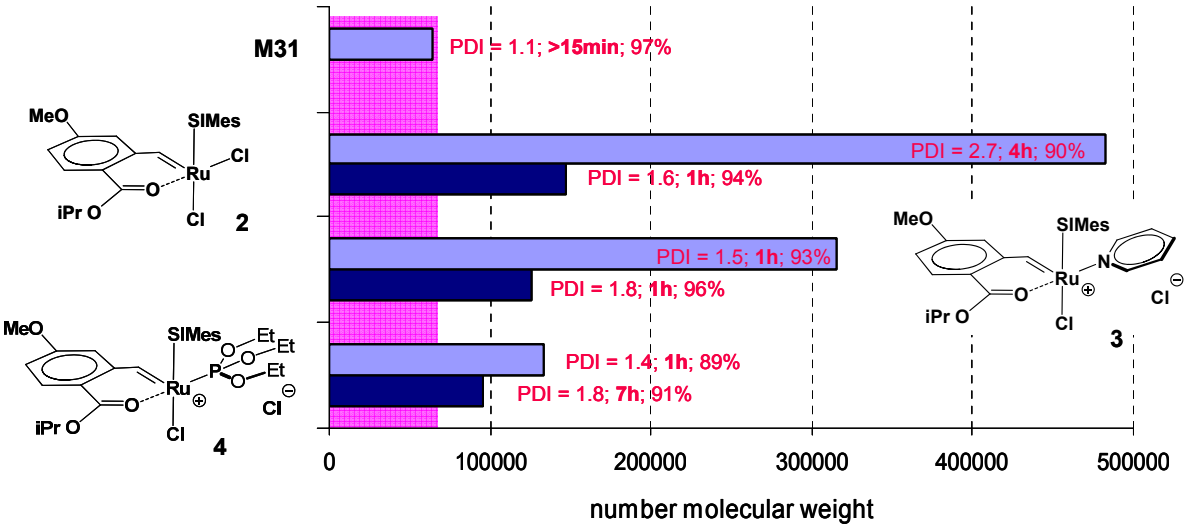


Figure S8. Results of polymerisations of **5** with initiators **M31**, **2, 3** and **4**. Reaction conditions: [**5**]:Initiator = 300:1, [**5**] = 0.1 mol/L, 40°C in CH_2Cl_2 (light blue), 80°C in toluene (dark blue).

Polymerisation with 6

Monomer **5** was polymerised as described in the abovementioned procedure. After 19 h the solvent was evaporated and conversion was determined to be less than 10 % by ^{1}H-NMR (300MHz, $CDCl_3$). Further, no signs of any decomposition of initiator **6** could be detected after this time.

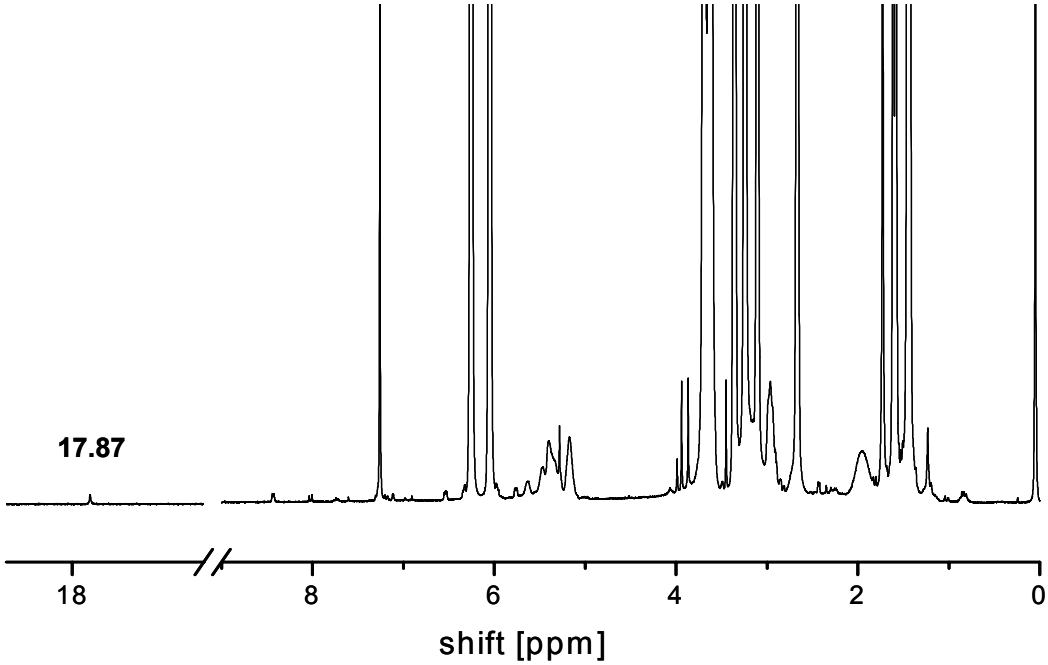


Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the polymerisation of **5** with initiator **6** after 19 h ([**5**]:[**6**] = 300:1, [**5**] = 0.1 mol/L, 40°C in CH_2Cl_2).

Polymerisation with 2, 3 and 6

Polymerisation of **5** with initiators **2, 3** and **6** was monitored by ^{1}H-NMR at 21°C in $CDCl_3$ with a ratio [**5**]:[I] = 5:1. A new carbene signal at 18.71 ppm that occurred during the course of polymerisation was tentatively assigned to active *trans*-dichloro species.

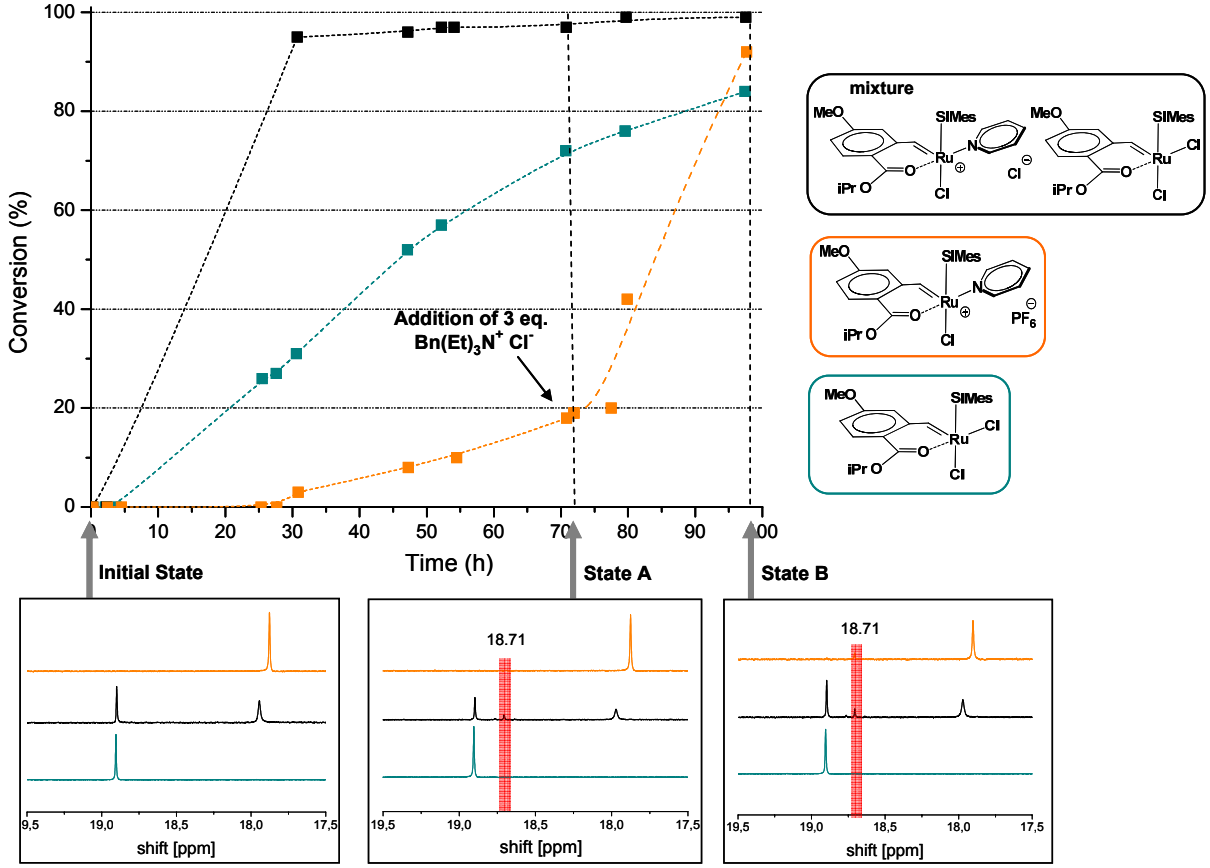


Figure S10. Monitoring polymerisation of monomer **5** with initiators **2**, **3** and **6** (M/I = 5) by ^{1}H-NMR (300 MHz, $CDCl_3$). New carbene signal at 18.71 ppm assigned to active *trans*-dichloro species.

References

[1] Devine, P. N.; Oh T. *J. Org. Chem*. **1992**, *57*, 397.