Electronic Supplementary Material (ESI) for Catalysis Science & Technology

A Highly Active Aqueous Olefin Metathesis Catalyst

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Contents

1. General

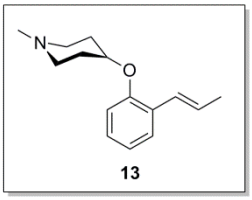
The solvents were dried by distillation over the following drying agents and were transferred under argon: toluene (Na), n-pentane, n-hexane, CH_2Cl_2 (CaH_2). MeOH was dried by stirring over MS 4A for 24h.

Column chromatography: Merck silica gel 60 (230–400 mesh), Aluminum oxide, activated, neutral, Brockman grade III alumina was generated by mixing 6% water (by mass) with neutral, Brockman grade I alumina (~150 mesh).
NMR: Spectra were recorded on Varian Unity Plus 200 MHz spectrometer, Varian Unity Plus 500 MHz spectrometer, Bruker Avance 300 MHz spectrometer and Bruker Avance II 600 MHz in $CDCl_3$, CD_2Cl_2, D_2O and MeOD; chemical shifts (δ) are given in parts per milion (ppm) downfield from tri-methylsilane as referenced to residual protio solvent peaks, coupling constants (*J*) in Hz.
MS (ESI): Micromass LCT mass spectrometer and LCT PremierXE Waters mass spectrometer. Indenylidene 1st generation catalyst (**Ind-I**)[1] and Indenylidene 2nd generation catalyst (**Ind-II**)[2] as well as benzylidene ligand **20**[3] were synthesized according to the literature method.

[1] E.A. Shaffer, Ch.-L. Chen, A.M. Beatty, E.J. Valente, H.-J. Schanz, *Journal of Organometallic Chemistry*, **2007**, *692*, 5221-5233.
[2] S. Monsaert, R. Drozdzak, V. Dragutan, I. Dragutan, F. Verpoort, *Eur. J. Inorg. Chem.*, **2008**, 432-440.
[3] R.L. Pederson, J.K. Woertink, Ch.M. Haar, D.E. Gindelberger, Y. Schrodi, *PCT Int. Appl.*(2003), WO 2003044060 A2 20030530.

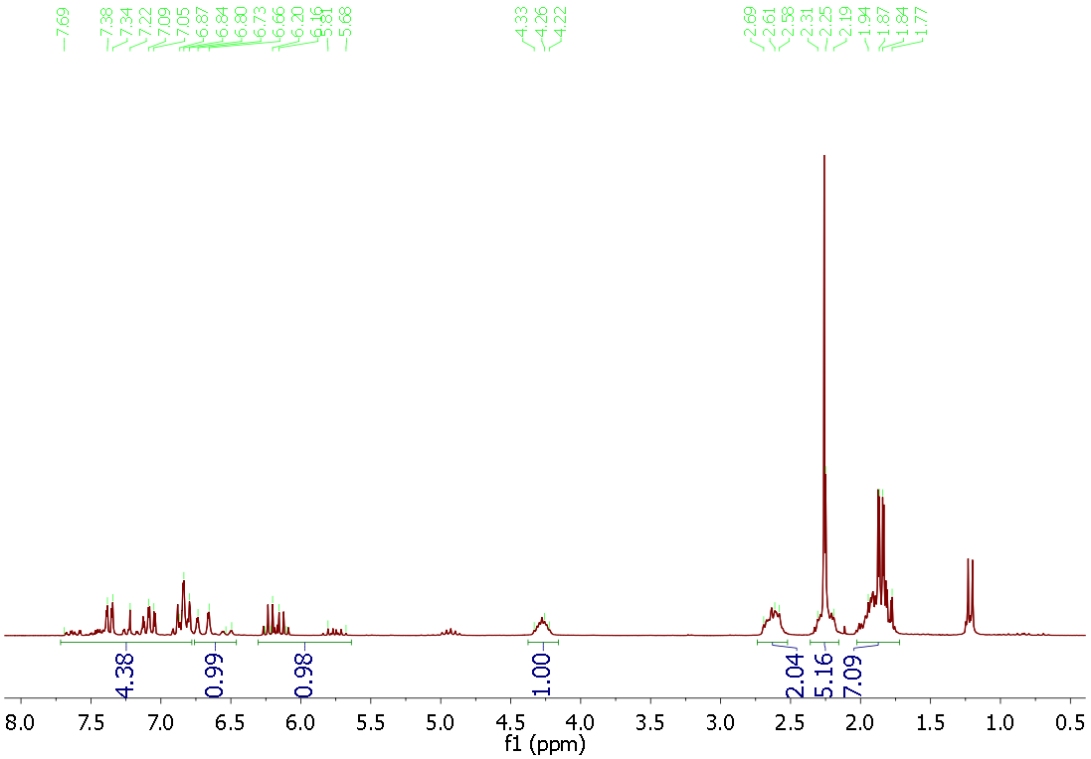
2. Synthesis procedures and analytical data

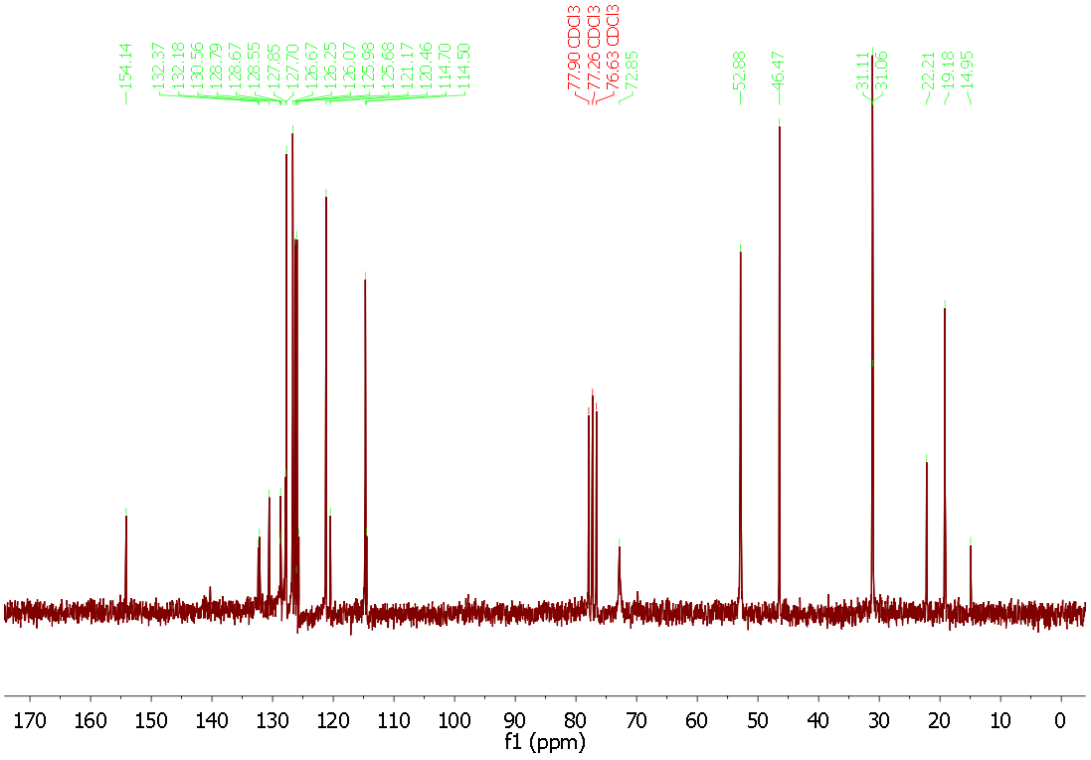
Synthesis of compound 13



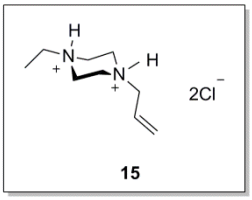
2-Propenyl-phenol was added under argon to a solution of 1-methyl-piperidin-4-ol (2.60 g, 22.6 mmol) and triphenylphosphine (6.52 g, 24.9 mmol) in dry toluene (40 ml). Mixture was cooled down to 0 °C and diizopropyl azodicaroxylate (4.9 ml, 24.9 mmol) was slowly added. When the addition was completed reaction mixture was warmed up to room temperature and stirred for 20 h and then for 4 h at 60 °C. Mixture was cooled down to room temperature, diluted with ethyl acetate (150 ml) and washed with water (200 ml) and with saturated potassium carbonate aq (200 ml). Product was extracted from organic phase with hydrochloric acid aq (0.5 M, 240 ml). Water fraction was then alkalized to pH 10 and product was extracted with dichloromethane (240 ml). Organic phase was washed with water (100 ml), dried with magnesium sulphate, filtered and solvent was evaporated. Crude product was purified by column chromatography (DCM/*c*-hexane/EtOAc/Et_3N 3:3:1:0.1). Evaporation of solvents afforded **13** (4.26 g, 81%) as a yellow oil.

^{1}H (200 MHz, $CDCl_3$) δ ppm: 7.69-6.80 (m, 4H), 6.73-6.49 (m, 1H), 6.26-5.68 (m, 1H), 4.33-4.22 (m, 1H), 2.69-2.58 (m, 2H), 2.31-2.19 (m, 5H), 1.94-1.77 (m, 7H).^{13}C NMR (50 MHz, $CDCl_3$) δ ppm: 154.1, 132.4, 132.2, 130.6, 128.8 , 128.7, 128.5, 127.8, 127.7, 126.7, 126.2, 126.0, 125.7, 121.2, 120.5, 114.7, 114.5, 72.8, 52.9, 46.5, 31.1, 22.2, 19.2, 15.0.





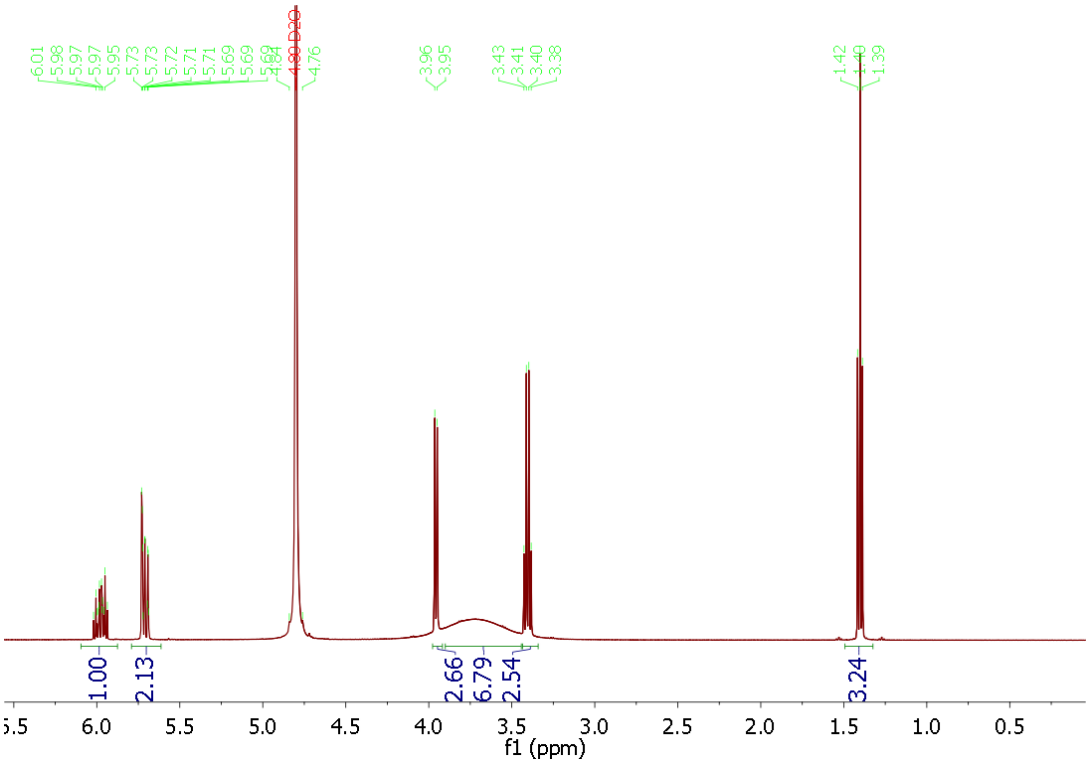
Synthesis of compound 15

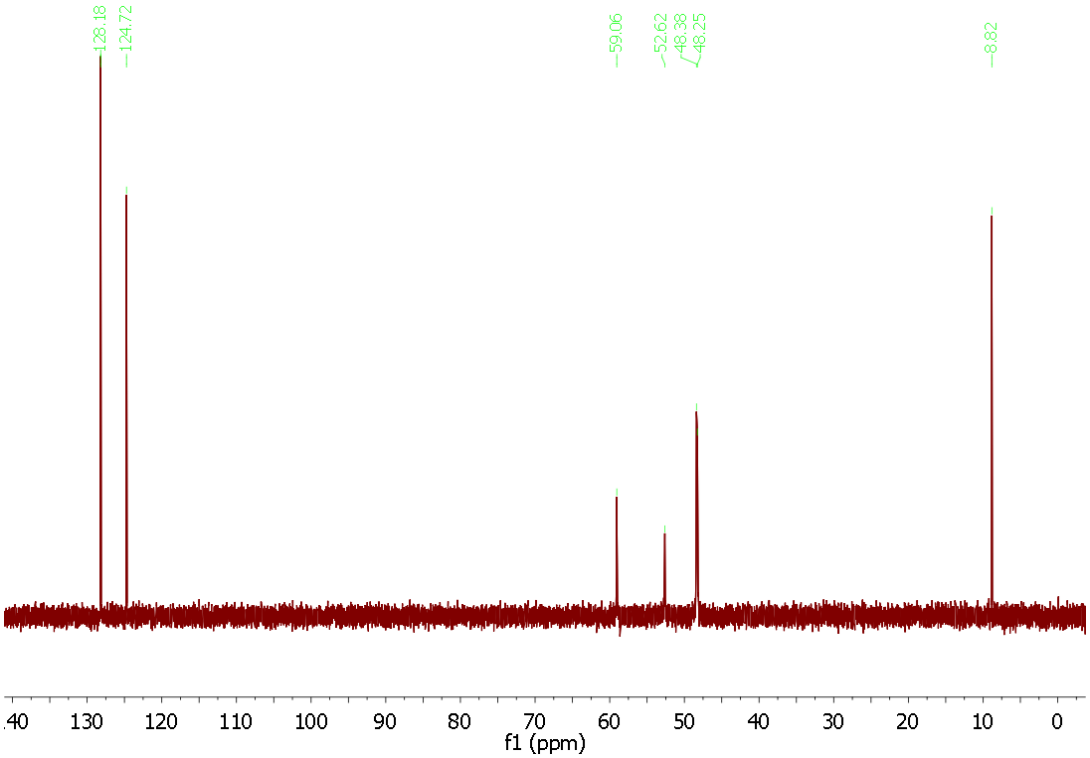


15

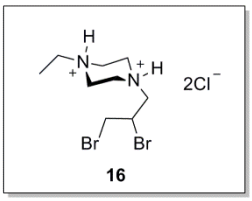
Allyl bromide (68.6 ml, 788 mmol) was slowly added at 0 °C to a solution of *N*-ethyl-piperazine (100 ml, 788 mmol) in dichloromethane (500 ml). When the addition was completed reaction mixture was heated to reflux and stirred at this temperature for 1.5 h. Then it was cooled down to room temperature, washed with sodium hydroxide aq (10%, 350 ml) and dried with magnesium sulfate. Drying agent was filtered off, dichloromethane was evaporated and the residue was dissolved in methanol (100 ml) and hydrochloric acid aq (36%, 157 ml) was added. Removal of solvent and crystallization of crude product from ethanol/diethyl ether mixture afforded product (106 g, 59%) as a colorless crystals.

^{1}H NMR (500 MHz, D_2O) δ ppm: 6.01-5.95 (m, 1H), 5.73-5.69 (m, 2H), 3.95 (d, 2H, *J* = 7.5Hz), 3.93-3.45 (bs, 8H), 3.40 (q, 2H, *J* = 7.5Hz), 1.40 (t, 3H, *J* = 7.5Hz).^{13}C NMR(125 MHz, D_2O) δ ppm: 128.2, 124.7, 59.1, 52.6, 48.4, 48.3, 8.7. HRMS (ESI) calcd for $C_9H_{18}N_2$ ($[M+H]^+$) *m/z* 155.1548 found 155.1553.





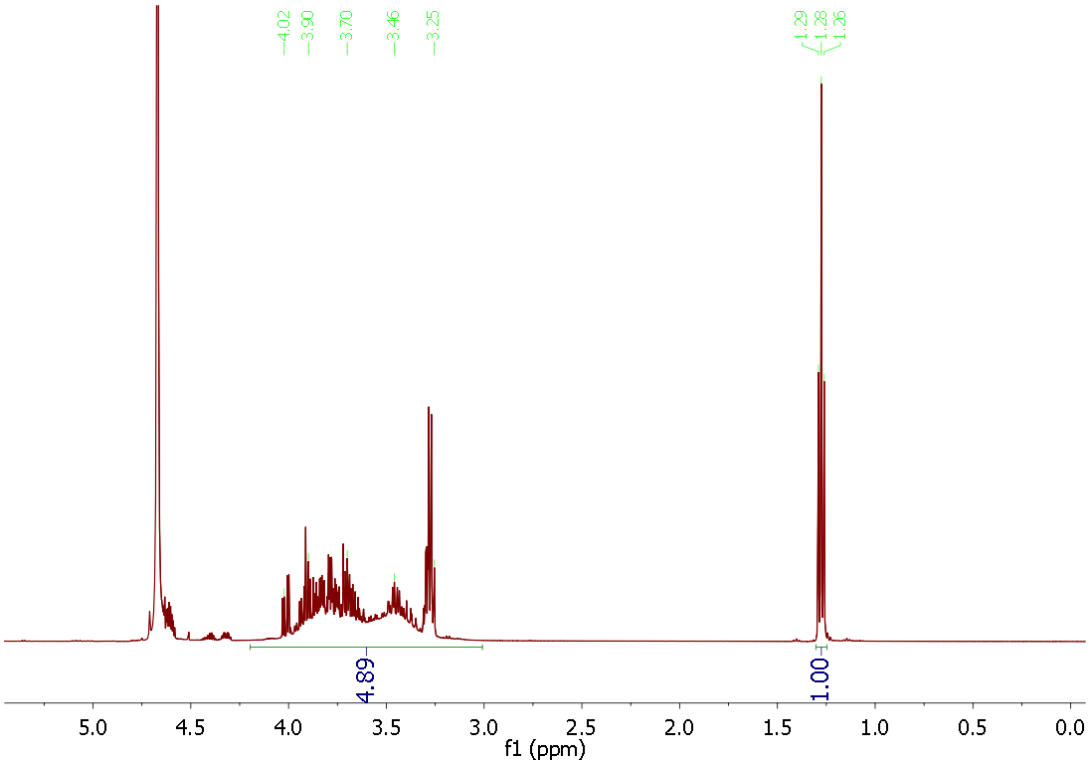
Synthesis of compound 16

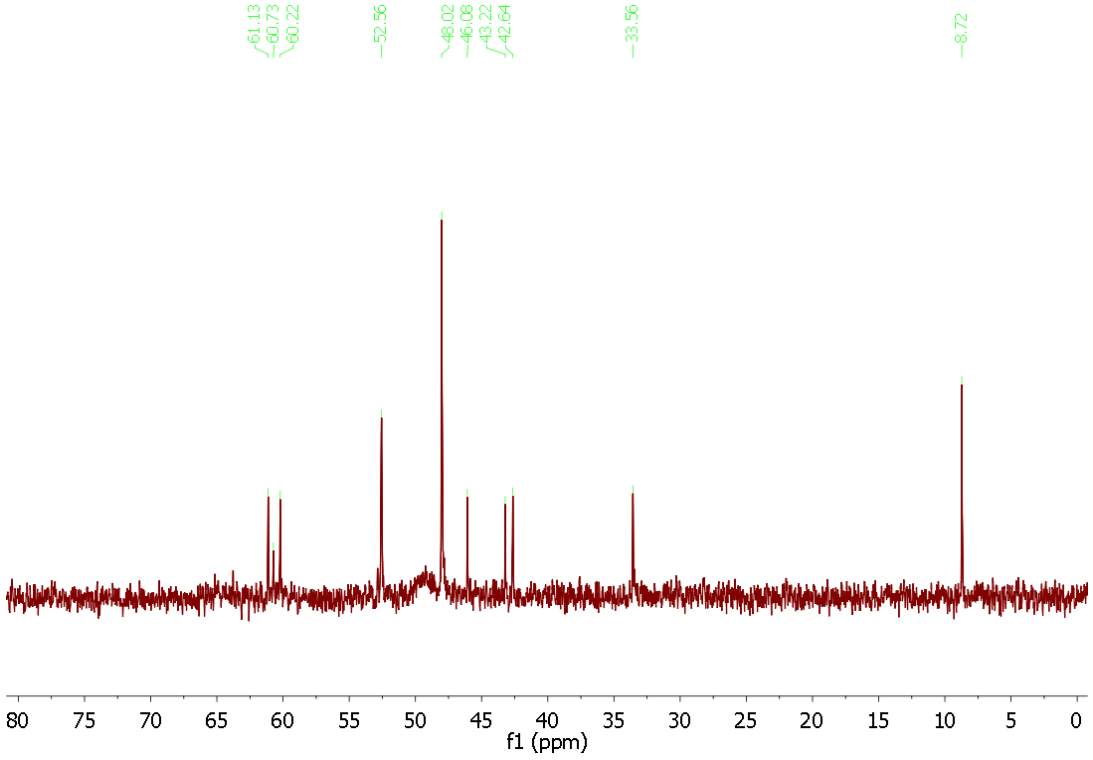


16

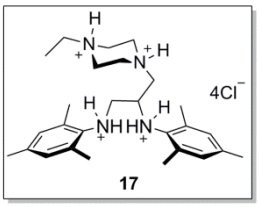
Bromine (23.9 ml, 462 mmol) was slowly added at 50 °C to a solution of **15** (105 g, 462 mmol) in water (200 ml) at such a rate that the temperature did not exceed 60 °C. When the addition was completed water was evaporated to dryness. Recrystallization of crude product from ethanol afforded **16** (127 g, 71%) as a colorless crystals.

^{1}H NMR (500 MHz, D_2O) δ ppm: 4.02-3.25 (m, 15H), 1.40 (t, 3H, *J* = 7.5Hz). ^{13}C NMR (125 MHz, D_2O) δ ppm: 61.1, 60.7, 60.2, 52.6, 48.0, 46.1, 43.2, 42.6, 33.6, 8.7. HRMS (ESI) calcd for $C_9H_{18}Br_2N_2$ ($[M+H]^+$) *m/z* 314.9946 found 314.9934.



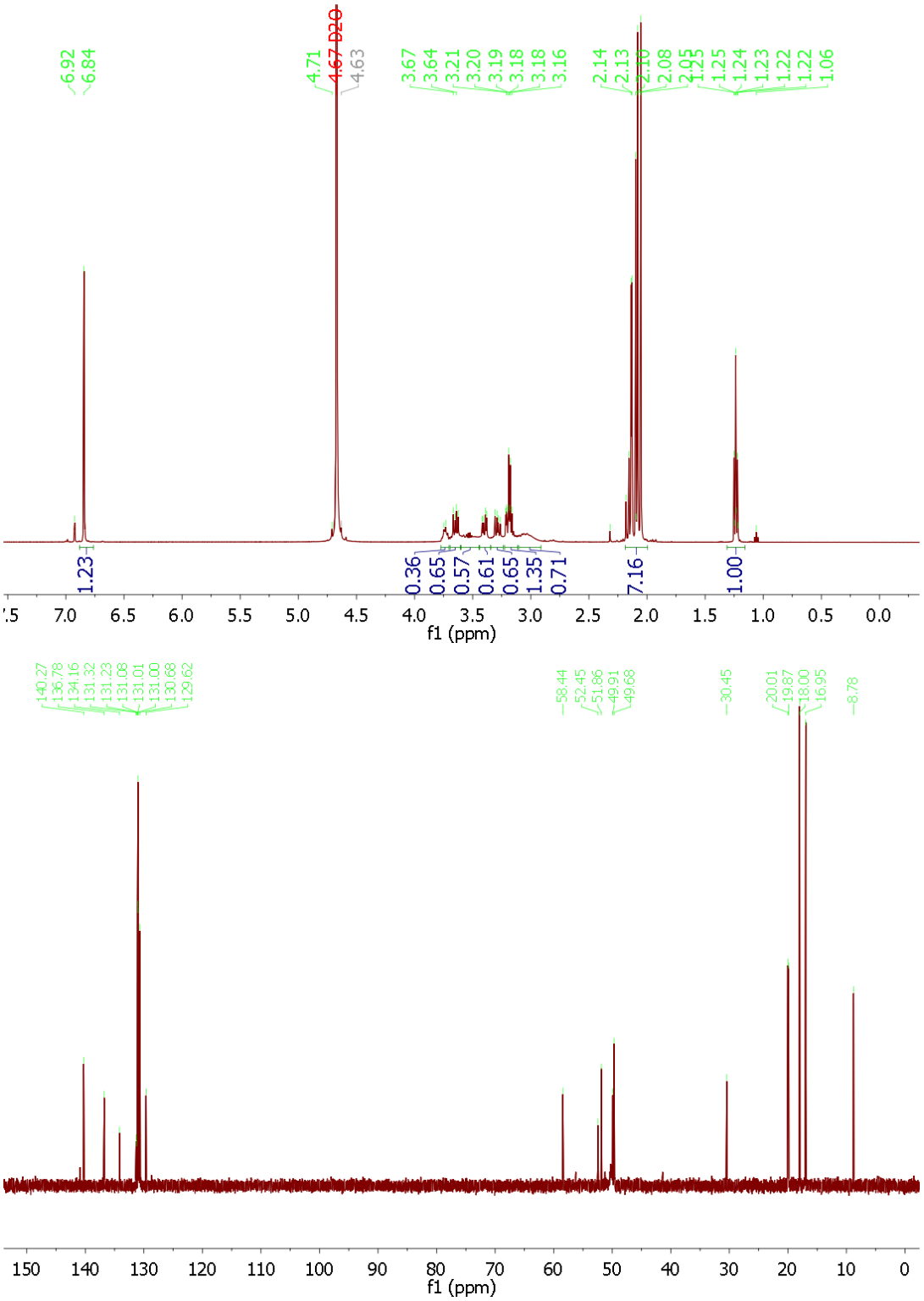


Synthesis of compound 17

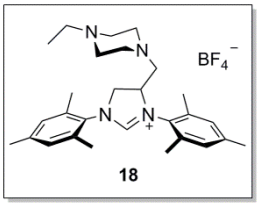


Compound **16** (50.0 g, 129 mmol) and 2,4,6-trimethylaniline (146.0 ml, 1034 mmol) was heated together at 125 °C for 24 h. Reaction mixture was then cooled down to room temperature and alkalized with sodium hydroxide aq (15%, 190 ml). Product was extracted with dichloromethane (300 ml). Organic fraction was washed with water (100 ml) and dried with magnesium sulfate. Drying agent was filtered off and solvent was evaporated. Then excess of 2,4,6-trimethylaniline was removed under reduced pressure (3 mbar). Crude product was dissolved in methanol (200 ml) and hydrochloric acid aq (36%, 51.3 ml) was added. Removal of solvent and crystallization of crude product from acetone (500 ml) afforded **17** (46.3 g, 62%) as a white solid.

^{1}H NMR (500 MHz, D_2O) δ ppm: 6.84 (s, 4H), 3.75-3.71 (m, 1H), 3.67-3.62 (m, 2H), 3.60-3.44 (m, 2H), 3.42-3.38 (m, 2H), 3.31-3.26 (m, 2H), 3.22-3.19 (m, 4H), 3.10-2.92 (m, 2H), 2.31-2.18 (m, 20H), 1.37 (t, 3H, *J* = 7.5Hz). ^{13}C NMR (125 MHz, D_2O) δ ppm: 140.3, 136.8, 134.2, 131.3, 131.2, 131.1, 131.0, 130.7, 129.6, 58.4, 52.4, 51.9, 49.9, 49.7, 30.4, 20.0, 19.9, 18.0, 16.9, 8.8. HRMS (ESI) calcd for $C_{27}H_{43}N_4$ ($[M+H]^+$) *m/z* 423.3488 found 423.3473.

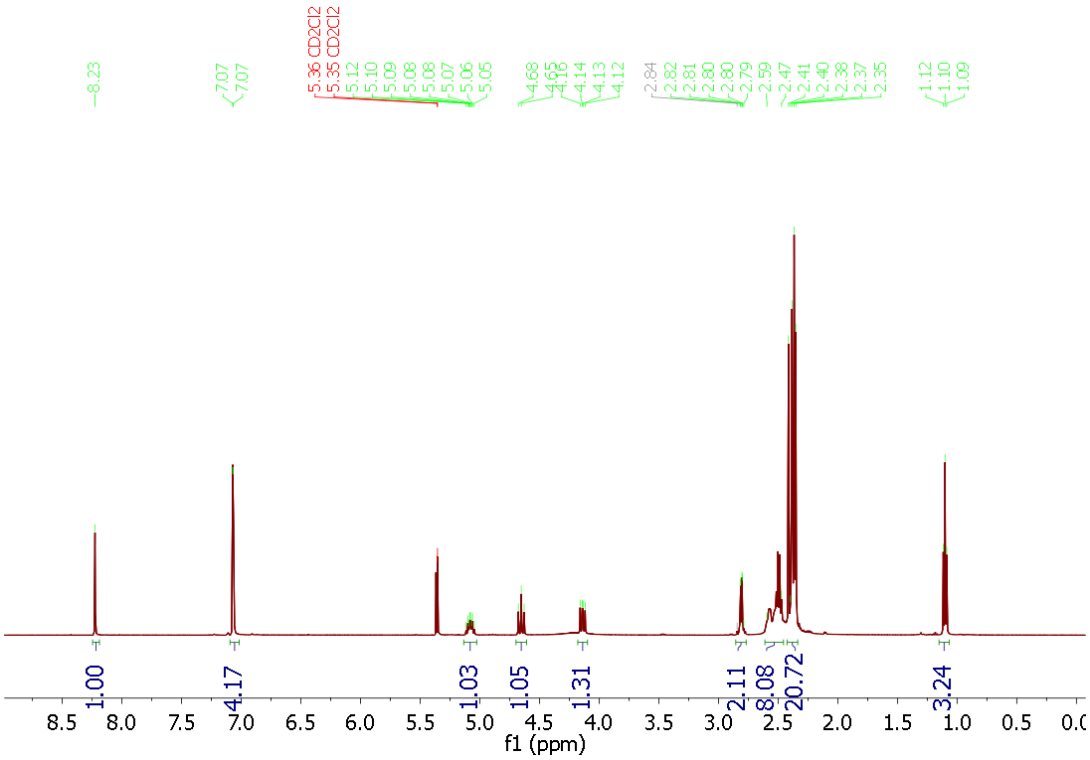


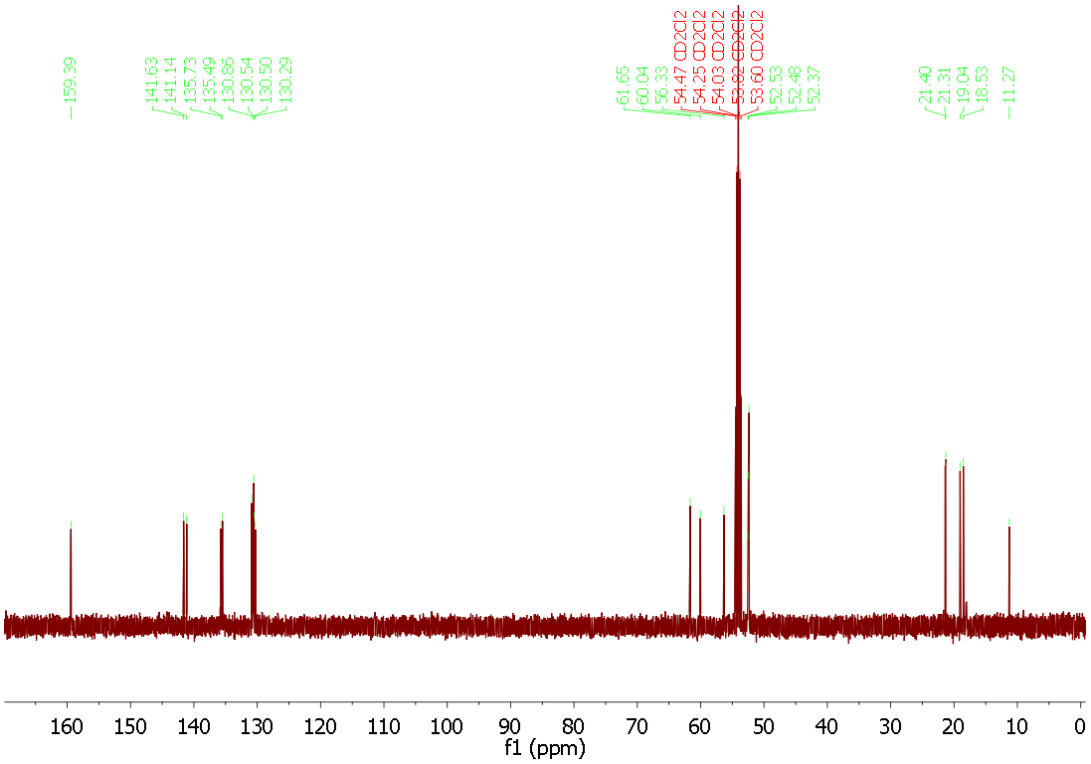
Synthesis of compound 18



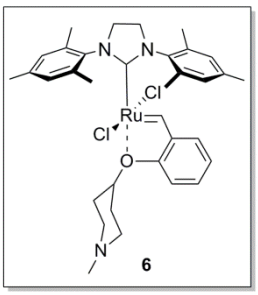
Solution of **17** (72.3 g, 124 mmol) in mixture of triethyl orthoformate (103 ml, 620 mmol) and methanol (170 ml) was stirred at 90 °C for 3 h. After evaporation of solvents, crude product was dissolved in water (100 ml) and solution of ammonium tetrafluoroborate (19.5 g, 186 mmol) in water (200 ml) and sodium hydroxide aq (5%, 180 ml) were added. After extraction of product with dichloromethane (300 ml), organic fraction was dried with sodium sulfate. Drying agent was filtered off and solvent was evaporated. Crude product was purified by recrystallization from dichloromethane/tetrachloromethane mixture to afford **18** (50.5 g, 78%) as a white crystals.

^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm: 8.23 (s, 1H), 7.07 (d, 4H, *J* = 1.5Hz), 5.12-5.05 (m, 1H), 4.68-4.65 (m, 1H), 4.16-4.12 (m, 1H), 2.82-2.80 (m, 2H), 2.59-2.47 (m, 8H), 2.41-2.35 (m, 20H), 1.10 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (125 MHz, CD_2Cl_2) δ ppm: 159.4, 141.6, 141.1, 135.7, 135.5, 130.9, 130.5, 130.5, 130.3, 61.6, 60.0, 56.3, 52.5, 52.5, 52.4, 21.4, 21.3, 19.0, 18.5, 11.3. HRMS (ESI) calcd for $C_{28}H_{41}N_4$ ($[M+H]^+$) *m/z* 433.3331 found 433.3342.



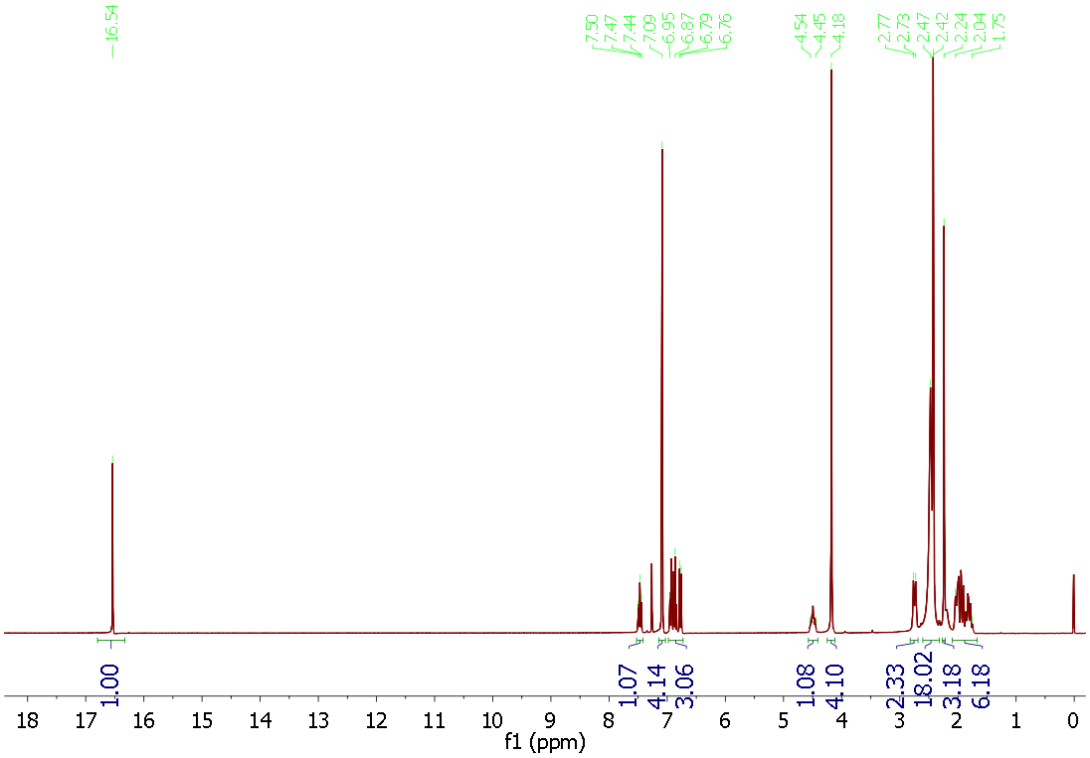


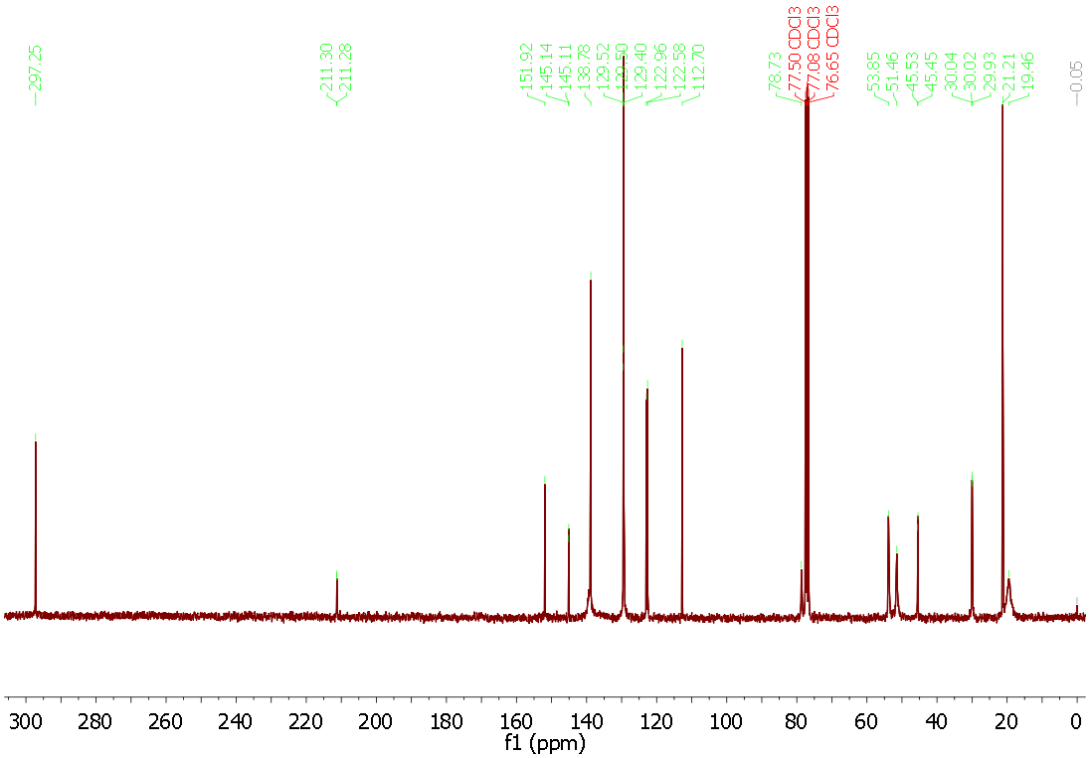
Synthesis of complex 6



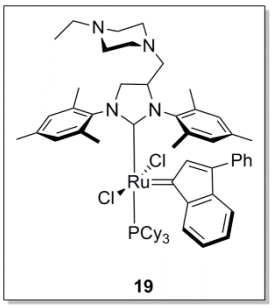
Compound **13** (0.321 g, 1.39 mmol) and CuCl (0.187 g, 1.89 mmol) were placed in a Schlenk flask. The flask was filled with argon and then dry toluene (20 ml) was added. Afterwards **Ind-II** (1.173 g, 1.26 mmol) was added and the resulting solution was stirred at 80 °C for 20 min. The reaction mixture was cooled down to room temperature and concentrated under vacuum. The resulting material was dissolved in a minimum amount of EtOAc and the insoluble white solid filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuum, and the crude catalyst was purified by flash chromatography (*c*-hexane/EtOAc 7:3). Removal of solvents afforded complex **6** (0.408 g, 48%) as a green solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 16.54 (s, 1H), 7.50-7.47 (m, 1H), 7.09 (s, 4H), 6.95-6.76 (m, 3H), 4.54-4.45 (m, 1H), 4.18 (s, 4H), 2.77-2.73 (m, 2H), 2.47-2.42 (m, 18H), 2.24 (s, 3H), 2.04-1.75 (m, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 297.3, 211.3 (d), 151.9, 145.1, 138.8, 129.5, 129.4, 123.0, 122.6, 112.7, 78.7, 53.8, 53.7, 51.5, 45.5, 45.4, 30.0, 29.9, 21.2, 19.5. HRMS (ESI) calcd for $C_{34}H_{43}N_3OClRu$ ($[M\text{-}Cl]^+$) *m/z* 646.2138 found 646.2145.





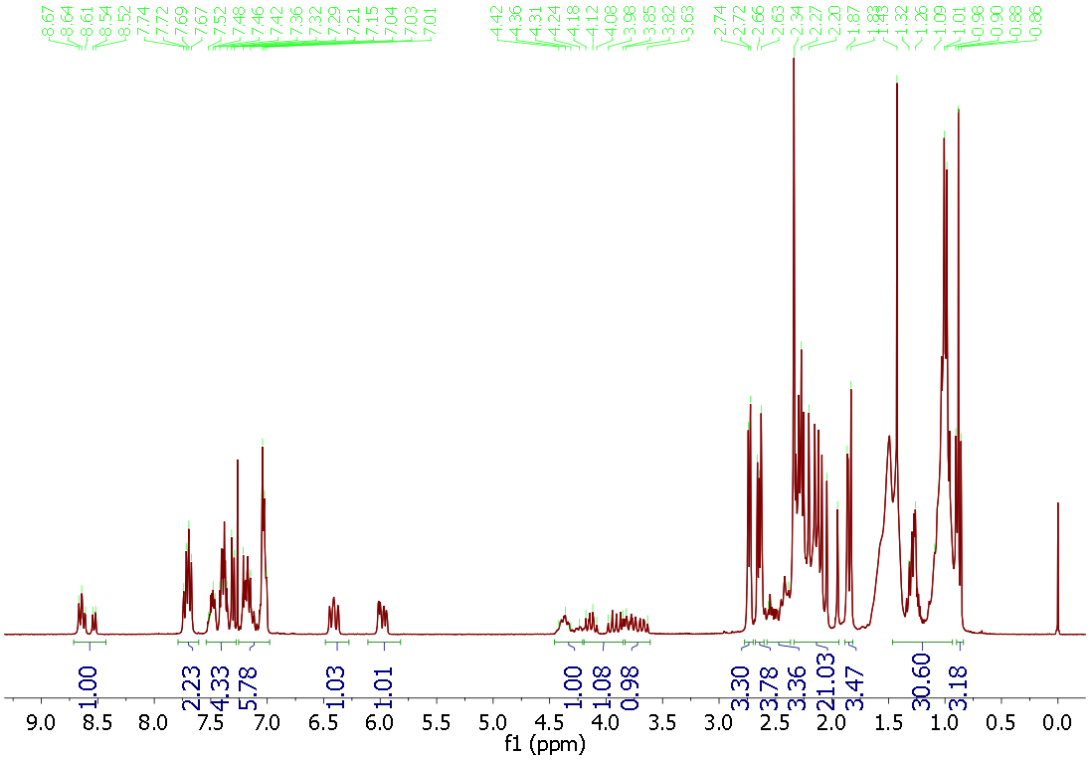
Synthesis of complex 19

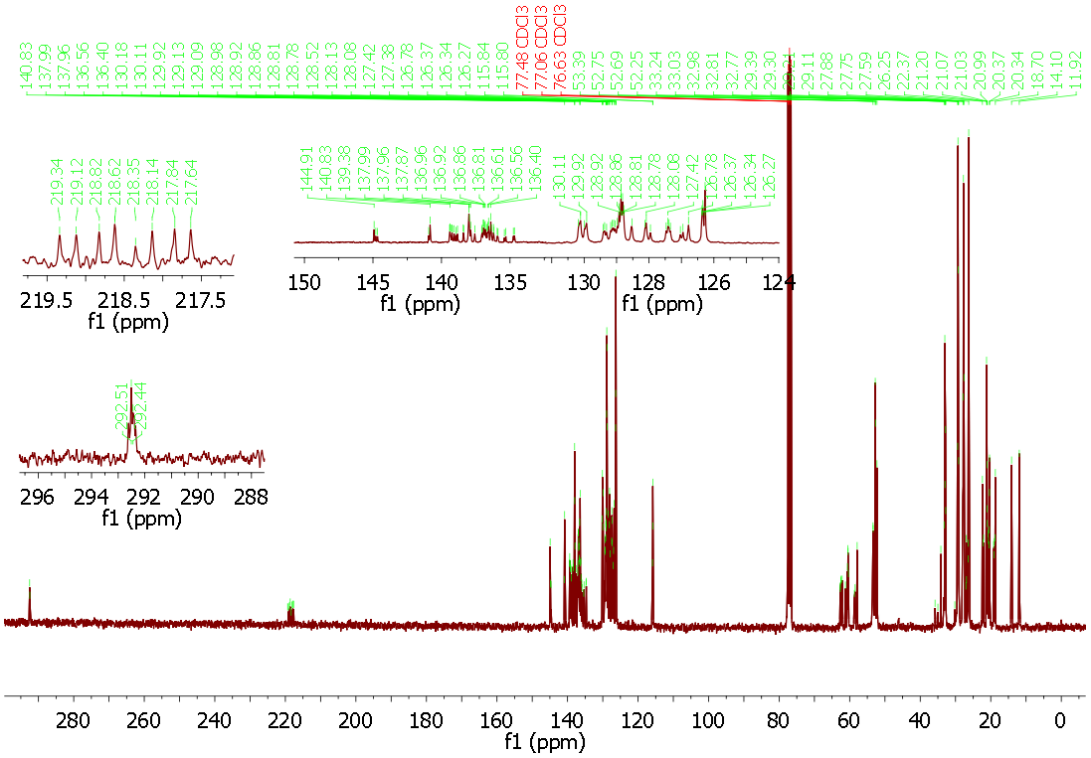


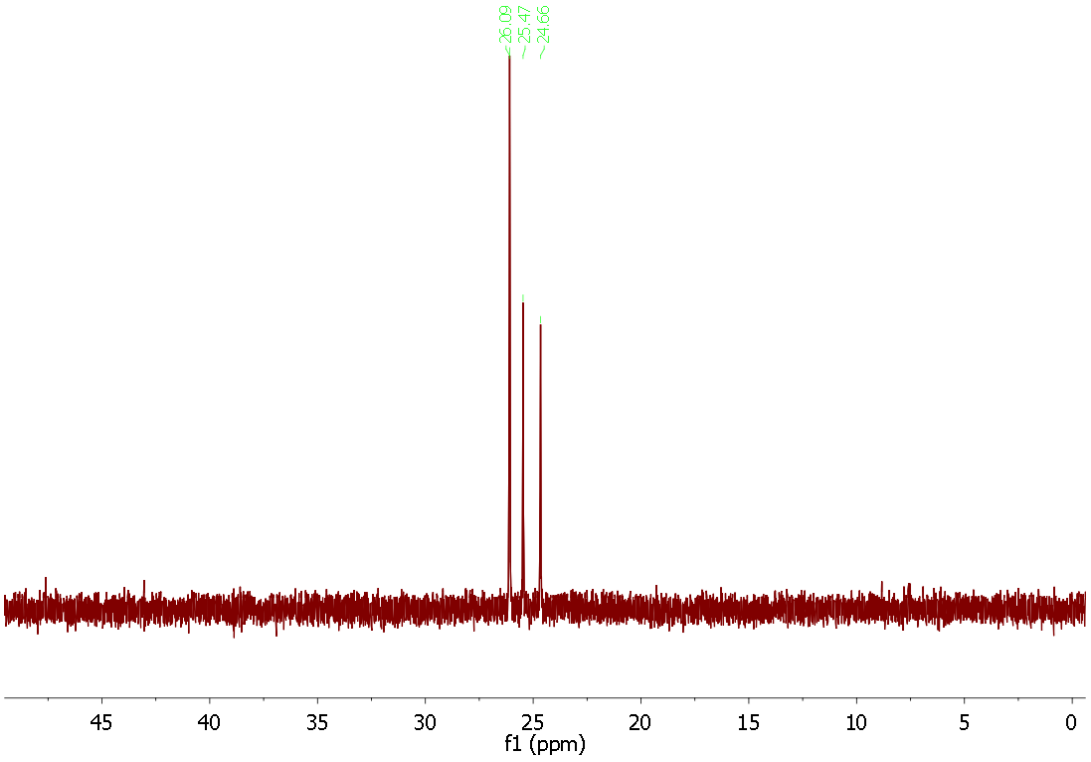
19

Potassium *t*-amylate (1.7 M in toluene, 2.26 ml, 3.85 mmol) was added at room temperature to a suspension of **18** (2.00 g, 3.85 mmol) in dry hexane (40 ml) under argon. Reaction mixture was stirred at room temperature for 1 h, then **Ind-I** (2.54 g, 2.75 mmol) was added and stirring was continued at reflux for 1 h. After cooling down, reaction mixture was filtered through a short pad of silica gel (*c*-hexane/EtOAc 8:2). Solvents were evaporated, crude catalyst was washed with *n*-pentane and dried under vacuum to afford complex **19** (2.51 g, 85%) as a dark red solid.

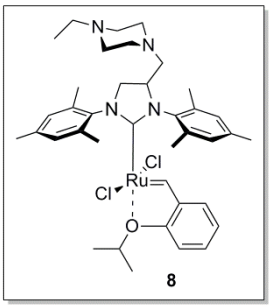
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 8.67-8.52 (m, 1H), 7.74-7.67 (m, 2H), 7.52-7.29 (m, 4H), 7.22-7.00 (m, 5H), 6.45-6.37 (m, 1H), 6.02-5.94 (m, 1H), 4.42-4.24 (m, 1H), 4.18-3.85 (m, 1H), 3.82-3.63 (m, 1H), 2.74-2.72 (m, 3H), 2.66-2.63 (m, 3H), 2.56-2.39 (m, 3H), 2.34-1.95 (m, 21H), 1.87-1.83 (m, 3H), 1.43-0.98 (m, 30H), 0.88 (t, 3H, *J* = 7.2Hz). ^{31}P NMR (124.5 MHz, $CDCl_3$) δ ppm: 26.09, 26.47, 24.66. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 292.5-292.4 (m), 219.4-217.7 (m), 144.9, 144.8, 144.7, 140.9, 140.8, 139,1, 138.9, 138.8, 138.4, 138.0, 137.9, 137.6, 137.0, 136.9, 136.7, 136.4, 136.2, 136.9, 135.4, 135.3, 134.8, 134.7, 130.1, 129.9, 129.4, 129.3, 128,9, 128.8, 128.6, 128.1, 128.0, 127.4, 127.1, 127.0, 126.8, 126.4, 126.3, 115.9, 115.8, 62.7, 62.5, 62.1, 61.2, 60.6, 60.5, 60.4, 58.7, 58.5, 57.9, 53.4, 52.3, 33.2, 33.0, 32.8, 29.3, 29.2, 29.1, 27.9, 27.7, 27.6, 26.3, 21.2, 14.1, 11.9. HRMS (ESI) calcd for $C_{61}H_{83}N_4PClRu$ ($[M\text{-}Cl]^+$) *m/z* 1039.5087 found 1039.5063.







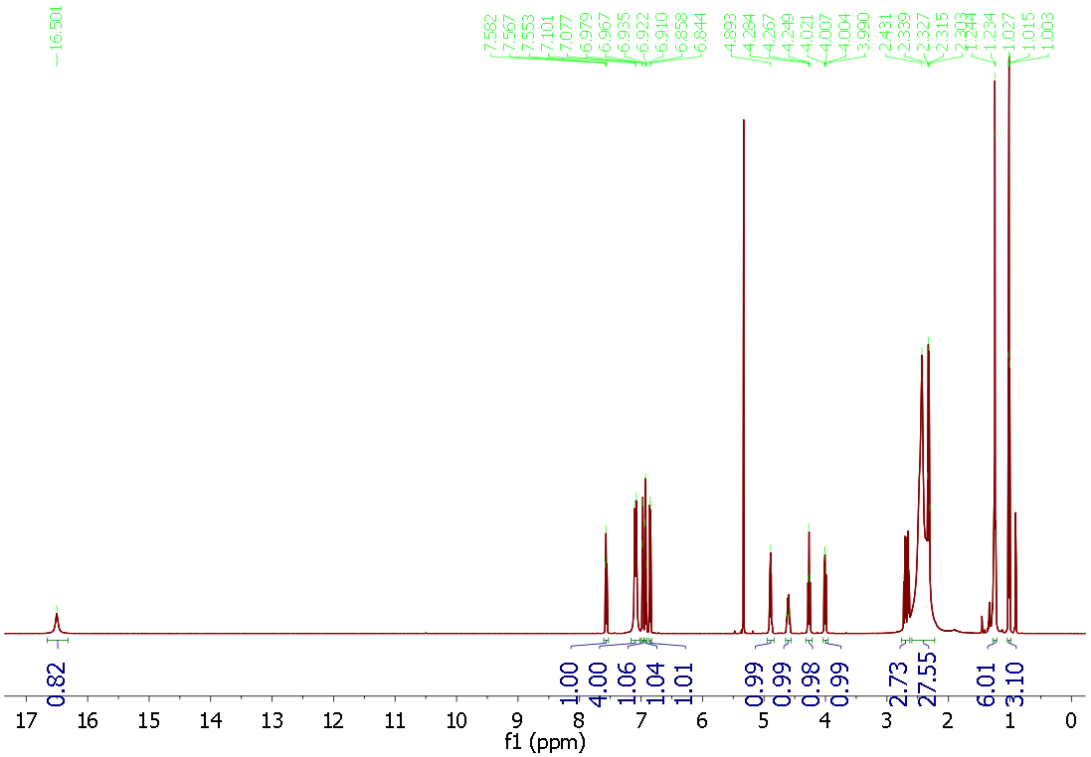
Synthesis of complex 8

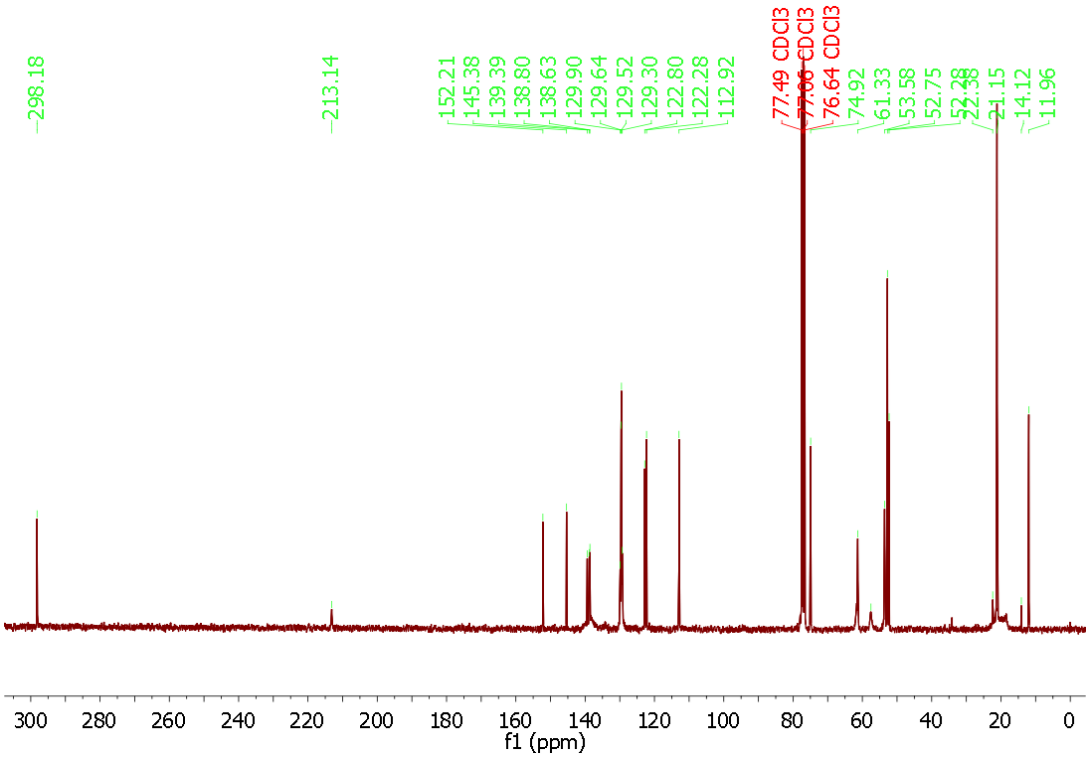


8

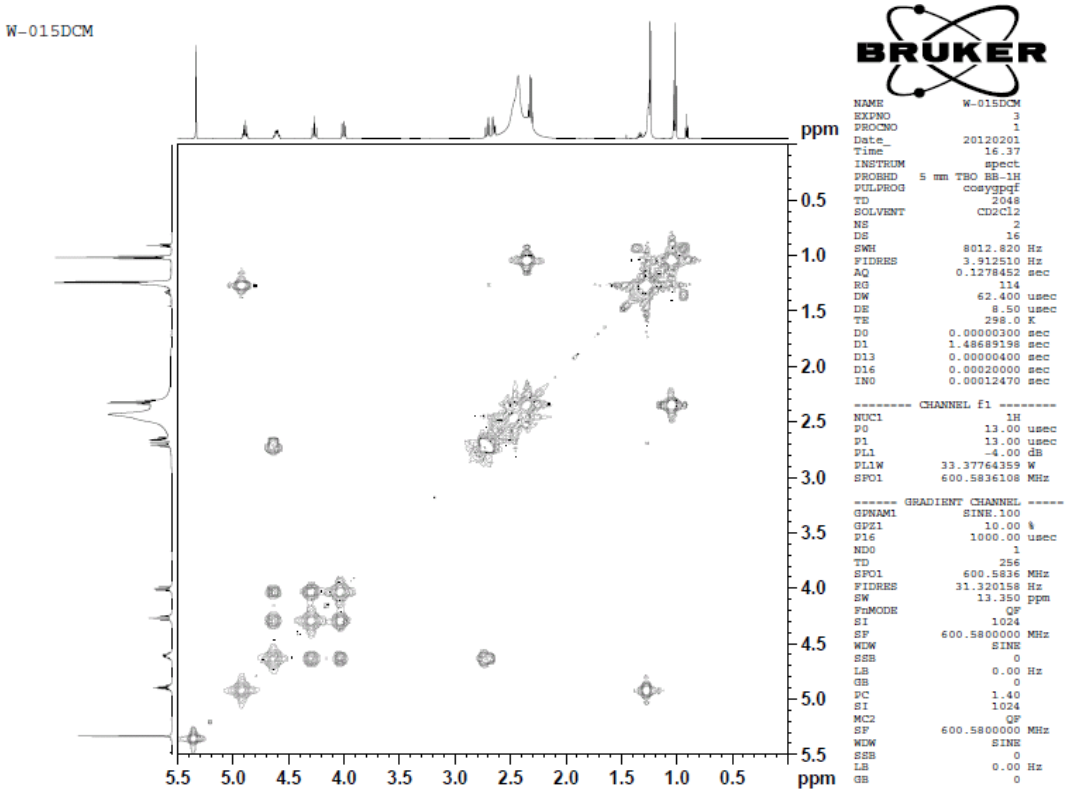
Compound **20** (0.143 g, 0.81 mmol) and CuCl (0.121 g, 1.22 mmol) were placed in a Schlenk flask. The flask was filled with argon and then dry toluene (20 ml) was added. Afterwards complex **19** (0.876 g, 0.81 mmol) was added and the resulting solution was stirred at 80 °C for 20 min. The reaction mixture was cooled down to room temperature and concentrated under vacuum. The resulting material was dissolved in a minimum amount of EtOAc and the insoluble white solid filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuum, and the crude catalyst was purified by flash chromatography (*c*-hexane/EtOAc 7:3). Removal of solvents afforded complex **8** (0.420 g, 68%) as a green solid.

^{1}H NMR (600 MHz, CD_2Cl_2) δ ppm: 16.50 (s, 1H), 7.58-7.55 (m, 1H), 7.10-7.07 (m, 4H), 6.98-6.97 (m, 1H), 6.93-6.91 (m, 1H), 6.85 (d, 1H, *J* = 8.4Hz), 4.89 (heptet, 1H, *J* = 6.6 Hz), 4.63-4.58 (m, 1H), 4.27 (*pseudo*t, 1H, *J* = 10.8 Hz), 4.02-3.99 (m, 1H), 2.73-2.64 (m, 2H), 2.60-2.30 (m, 28H), 1.24 (d, 6H, *J* = 6.0Hz), 1.01 (t, 3H, NCH_2CH_3, *J* = 7.2Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 298.2, 213.1, 152.2, 145.4, 139.4, 138.8, 138.6, 129.9, 129.6, 129.5, 129.3, 122.8, 122.3, 112.9, 74.9, 61.3, 57.5, 53.6, 52.8, 52.3, 22.4, 21.2, 14.1, 12.0. HRMS (ESI) calcd for $C_{38}H_{52}N_4ONaCl_2Ru$ ($[M+Na]^+$) *m/z* 775.2459 found 775.2436.

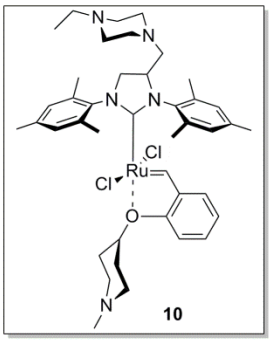




Extended COSY spectra of **8**

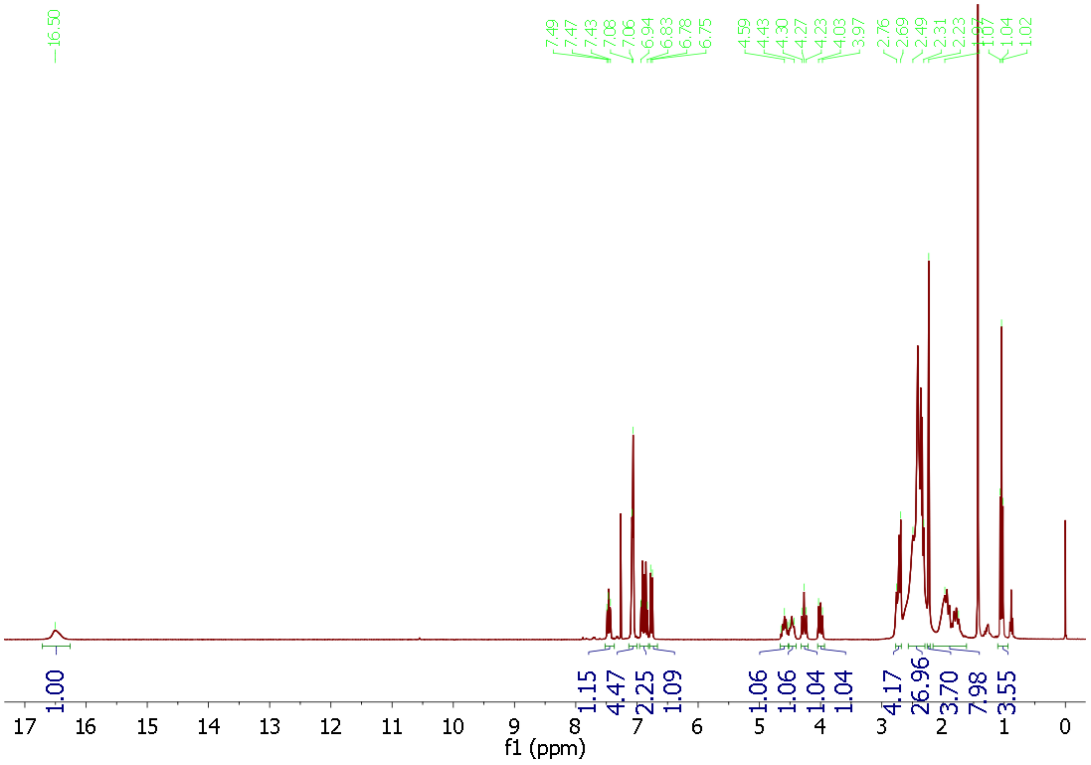


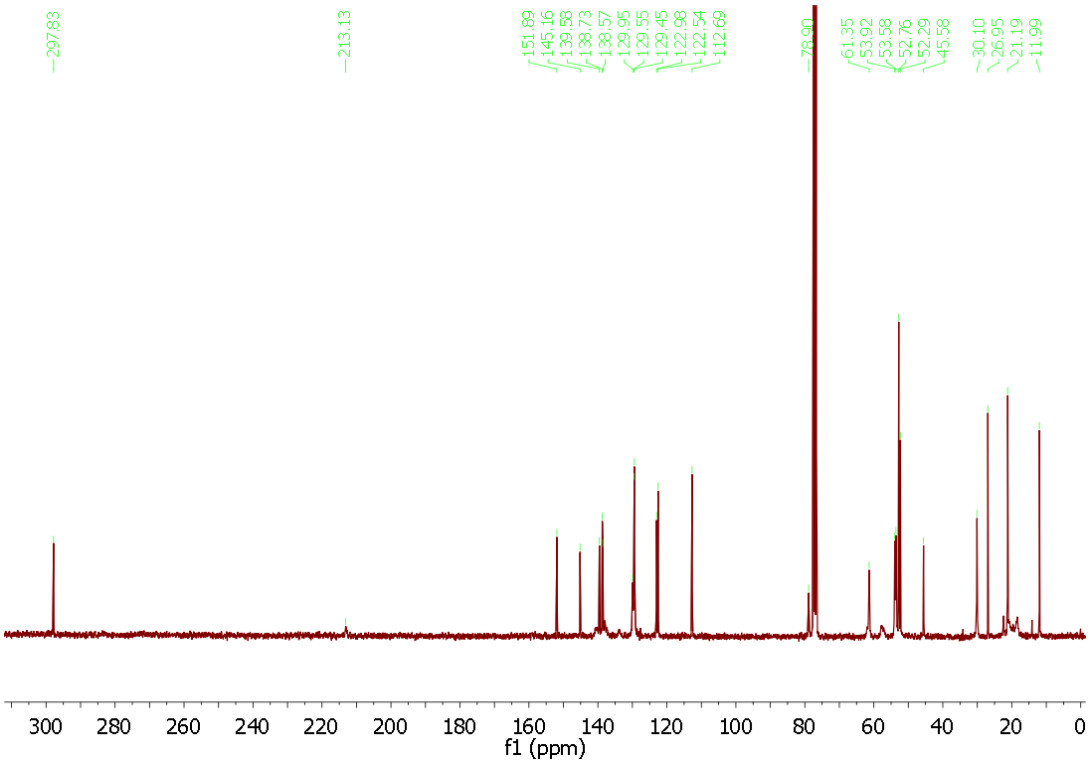
Synthesis of complex 10



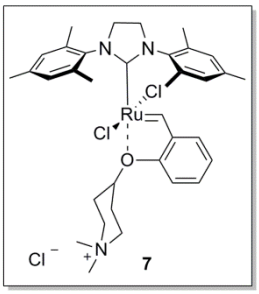
The same procedure as described for complex **8** was employed to afford complex **10** as a green solid in 37% yield. Column chromatography was performed using mixture of *c*-hexane/EtOAc 1:1.

0.280 g (37%) – green solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 16.50 (s, 1H), 7.49-7.43 (m, 1H), 7.09-7.06 (m, 4H), 6.94-6.83 (m, 2H), 6.76 (d, 1H, *J* = 8.1Hz), 4.65-4.54 (m, 1H), 4.50-4.43 (m, 1H), 4.27 (*pseudo*t, 1H, *J* = 10.5Hz), 4.03-3.97 (m, 1H), 2.76-2.69 (m, 4H), 2.49-2.31 (m, 26H), 2.23 (s, 3H), 1.97-1.75 (m, 8H), 1.04 (t, 3H, *J* = 7.2Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 297.8, 213.1, 151.9, 145.2, 139.6, 138.7, 138.6, 130.0, 129.6, 129.5, 123.0, 122.5, 112.7, 78.9, 61.4, 53.9, 53.6, 52.8, 52.3, 45.6, 30.1, 26.9, 21.2, 12.0. HRMS (ESI) calcd for $C_{41}H_{57}N_5OClRu$ ($[M\text{-}Cl]^+$) *m/z* 772.3295 found 772.3283.



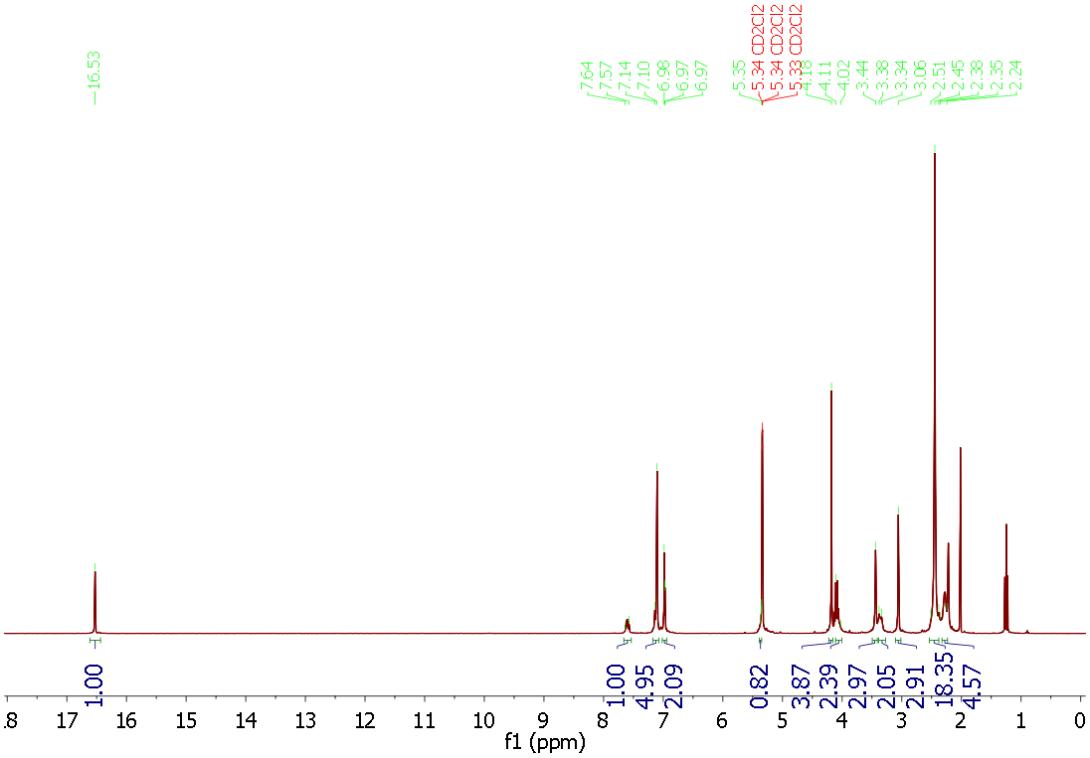


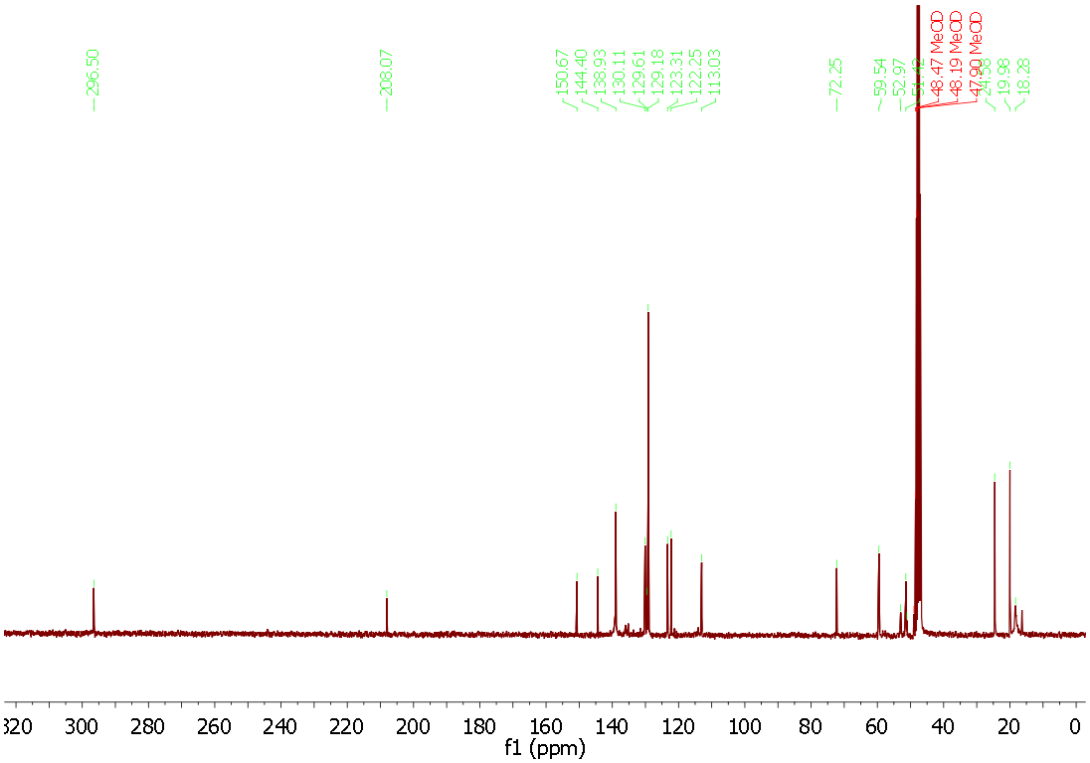
Synthesis of complex 7



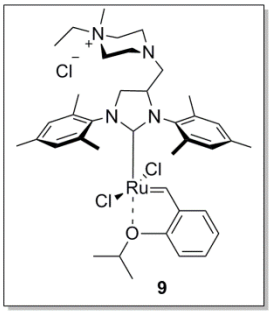
Complex **6** (0.224 g, 0.33 mmol) was placed under argon in pressure flask and dry methanol (3 ml) was added. Mixture was cooled down to –30 °C and cold liquid chloromethane (ca 3 ml) was added. Mixture was slowly warmed up to room temperature, then placed in oil bath heated to 50 °C and stirred for 60 h. After that time flask was opened carefully to remove chloromethane and mixture was concentrated. Residue was purified by filtration through a short plug of aluminium oxide (neutral, Brockman grade I, ethyl acetate/methanol 19:1). Solvents were evaporated, catalyst was washed with ethyl acetate twice and dried on vacuum to afford complex **7** (0.220 g, 91 %) as a green solid. Solubility in neat water: 2 mg/ml.

^{1}H NMR (300 MHz, CD_2Cl_2) δ ppm: 16.66 (s, 1H), 7.64-7.57 (m, 1H), 7.14-7.10 (m, 5H), 6.98-6.97 (m, 2H), 5.37-5.35 (m, 1H), 4.19 (s, 4H), 4.11-4.02 (m, 2H), 3.44 (s, 3H), 3.38-3.34 (m, 2H), 3.06 (s, 3H), 2.51-2.38 (m, 18H), 2.35-2.24 (m, 4H). ^{13}C NMR (75.4 MHz, MeOD) δ ppm: 296.5, 208.1, 150.7, 144.4, 138.9, 130.1, 129.6, 129.2, 123.3, 122.3, 113.0, 72.3, 59.5, 53.0, 51.4, 24.6, 20.0, 18.3, 16.3. HRMS (ESI) calcd for $C_{35}H_{46}N_3OCl_2Ru$ ($[M\text{-}Cl]^+$) *m/z* 696.2061 found 696.2070.





Synthesis of complex 9

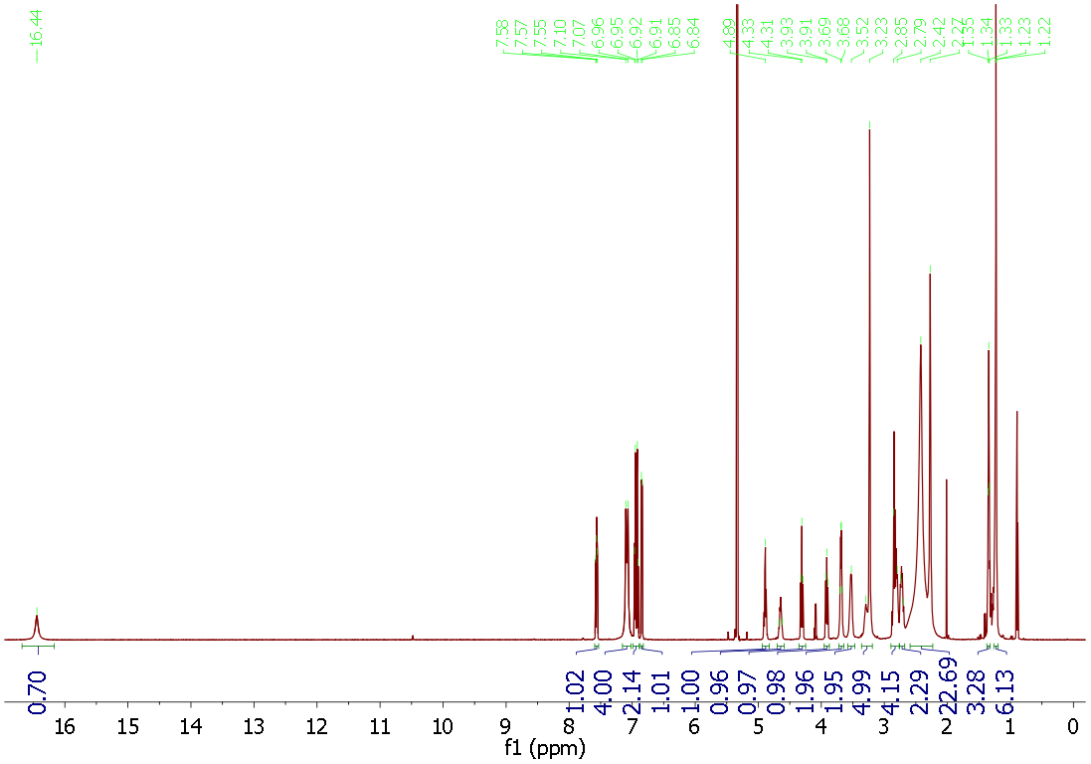


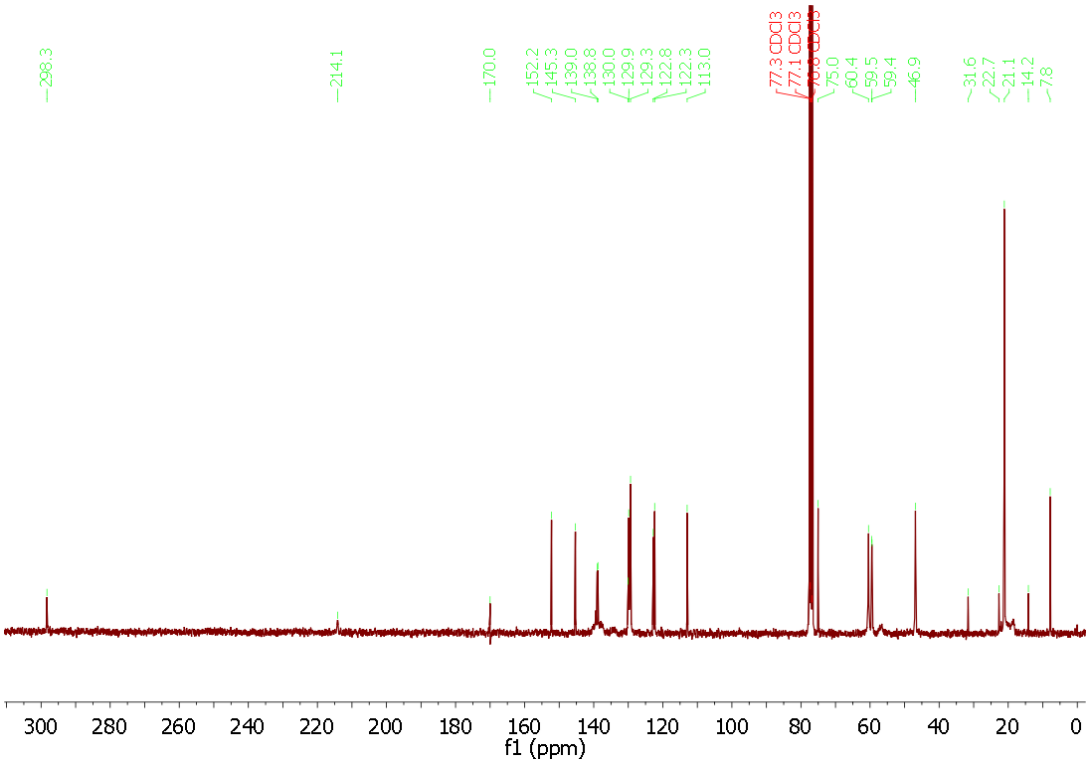
9

The same procedure as described for complex **7** was employed to afford complex **9** as a green solid in 84% yield.

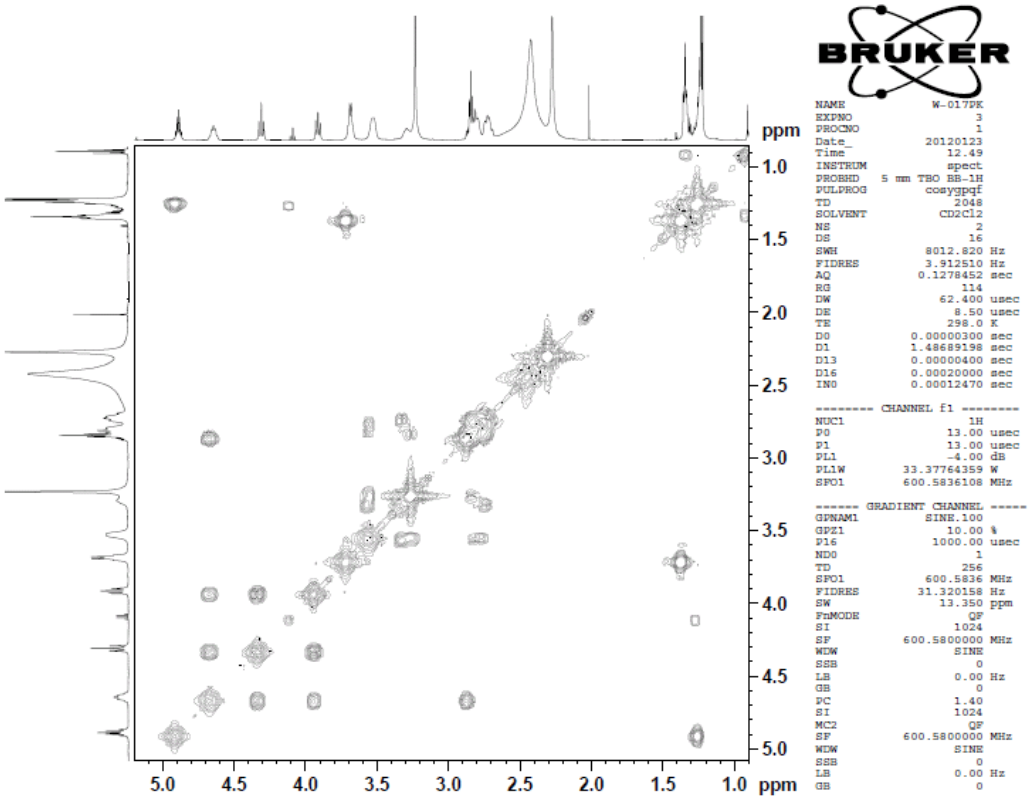
Solubility in neat water: 3 mg/ml.

0.290 g (97%) – green solid; ^{1}H NMR (600 MHz, CD_2Cl_2) δ ppm: 16.44 (s, 1H), 7.58-7.55 (m, 1H), 7.10-7.07 (m, 4H), 6.96-6.91 (m, 2H) 6.84 (d, 1H, *J* = 7.8Hz), 4.89 (heptet, 1H, *J* = 6.0Hz), 4.67-4.62 (m, 1H), 4.31 (*pseudo*t, 1H, *J* = 10.2Hz), 3.91 (*pseudo*t, 1H, *J* = 9.6Hz), 3.70-3.67 (m, 2H, NCH_2CH_3), 3.52 (bs, 2H), 3.29-3.23 (m, 5H), 2.85-2.79 (m, 4H), 2.79-2.74-2.69 (m, 2H), 2.42-2.27 (m, 18 H), 1.34 (t, 3H, *J* = 6.6Hz, NCH_2CH_3), 1.22 (d, 6H, *J* = 6.0Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 298.3, 214.1, 170.0, 152.2, 145.3, 139.0, 138.8, 130.0, 129.9, 129.4, 122.8, 122.3, 113.0, 75.0, 60.4, 59.5, 59.4, 46.9, 31.6, 22.7, 21.1, 14.2, 7.8. HRMS (ESI) calcd for $C_{39}H_{55}N_4OCl_2Ru$ ($[M\text{-}Cl]^+$) *m/z* 767.2796 found 767.2802.

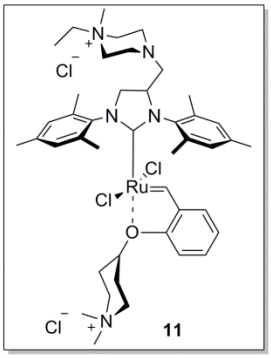




Extended COSY spectra of **9**



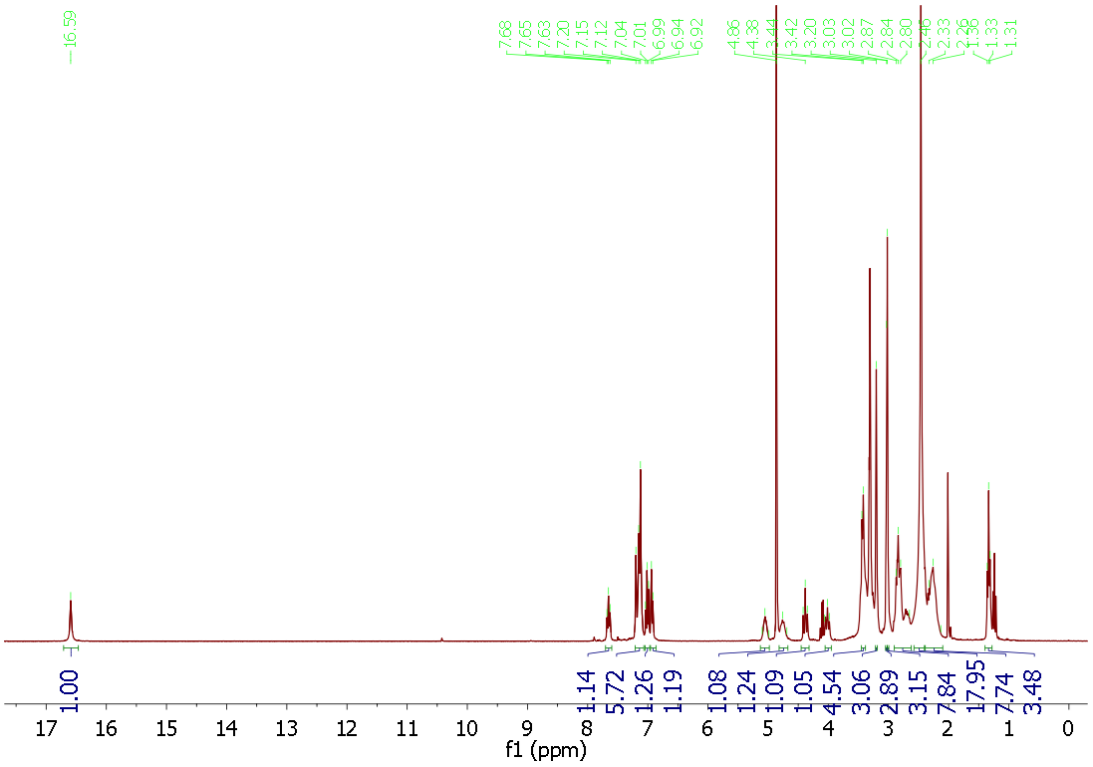
Synthesis of complex 11

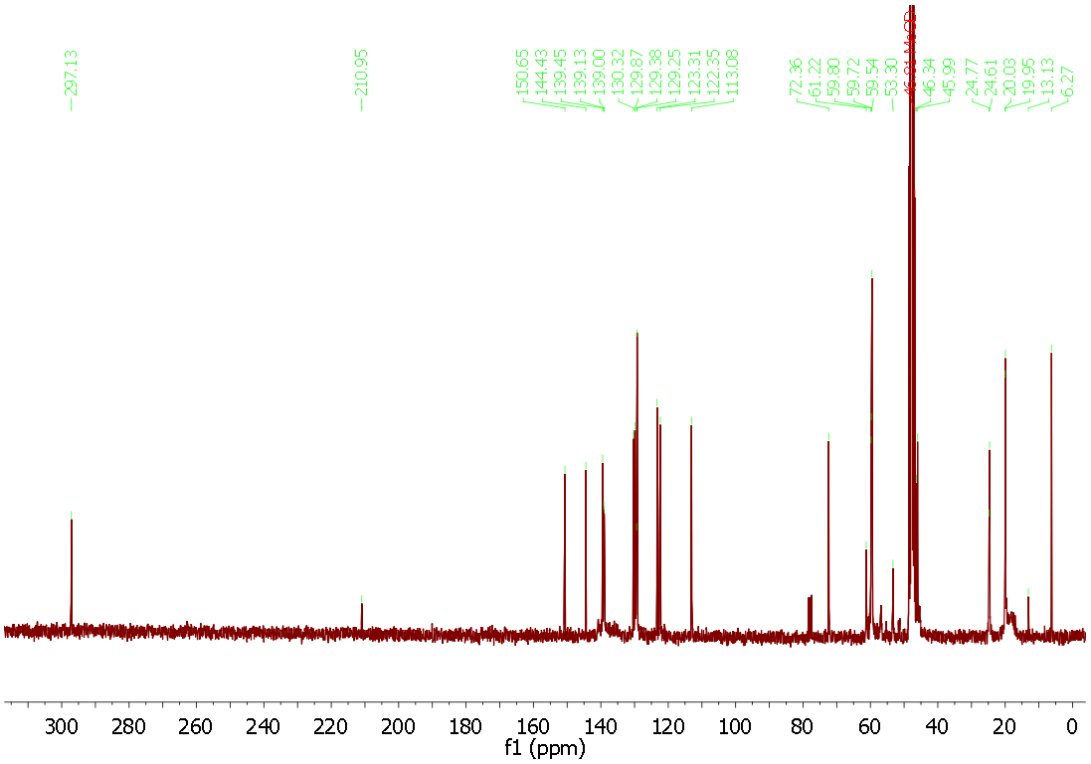


The same procedure as described for complex **7** was employed to afford complex **11** as a green solid in 93% yield.

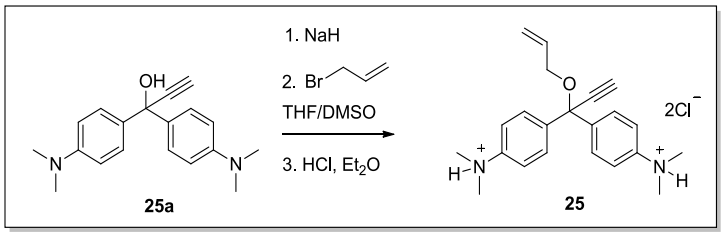
Solubility in neat water: 35 mg/ml.

0.370 g (93%) – green solid; ^{1}H NMR (300 MHz, MeOD) δ ppm: 16.59 (s, 1H), 7.68-7.63 (m, 1H), 7.20-7.12 (m, 5H), 7.04-7.00 (m, 1H), 6.94-6.91 (m, 2H), 5.10-5.01 (m, 1H), 4.80-4.69 (m, 1H), 4.38 (*pseudo*t, 1H, *J* = 10.5Hz), 4.02-4.00 (m, 1H), 3.44-3.42 (m, 4H), 3.20 (s, 3H), 3.04 (s, 3H), 3.02 (s, 3H), 2.87-2.60 (m, 8H), 2.47 (bs, 18H), 2.35-2.15 (m, 8H), 1.33 (t, 3H, *J* = 6.9Hz). ^{13}C NMR (75.4 MHz, MeOD) δ ppm: 297.1, 211.0, 150.7, 144.4, 139.5, 139.1, 139.0, 130.3, 129.9, 129.4, 129.3, 123.3, 122.4, 113.1, 72.4, 61.2, 59.8, 59.7, 59.5, 53.3, 46.3, 46.0, 24.8, 24.6, 20.0, 19.9, 13.1, 6.3. LRMS (ESI) calcd for $C_{43}H_{64}N_5OCl_2Ru$ ([M-2Cl]$^{2+}$) *m/z* 418.6 found 418.6.





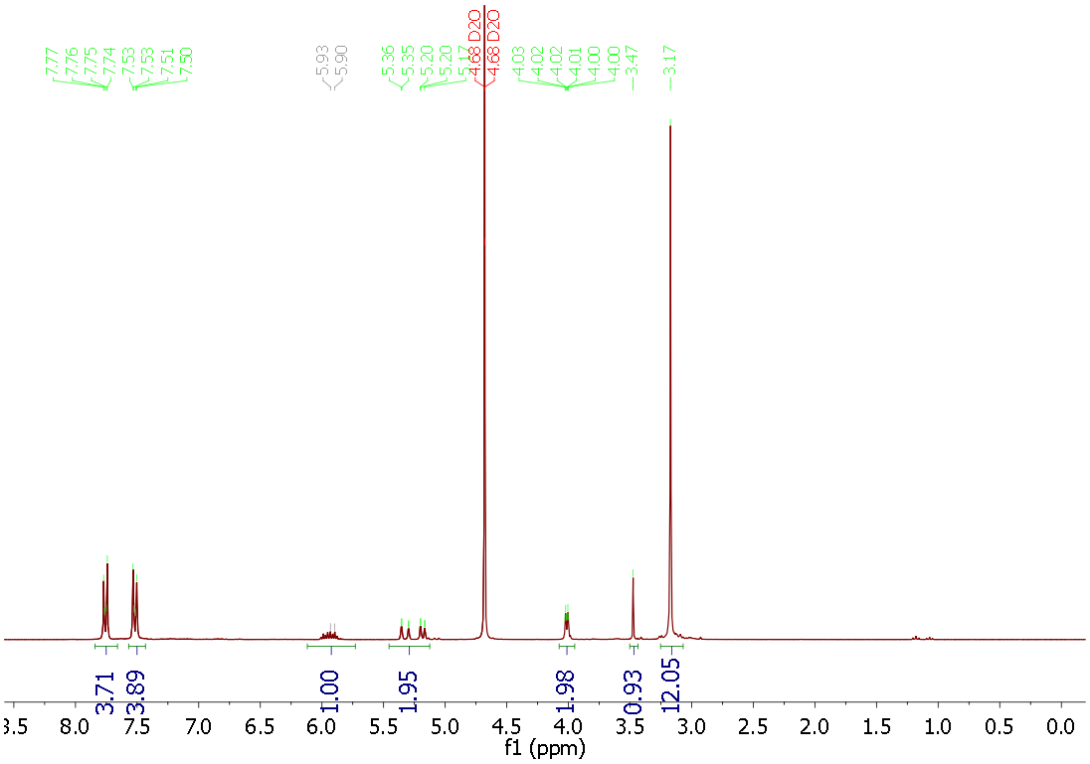
Synthesis of compound 26

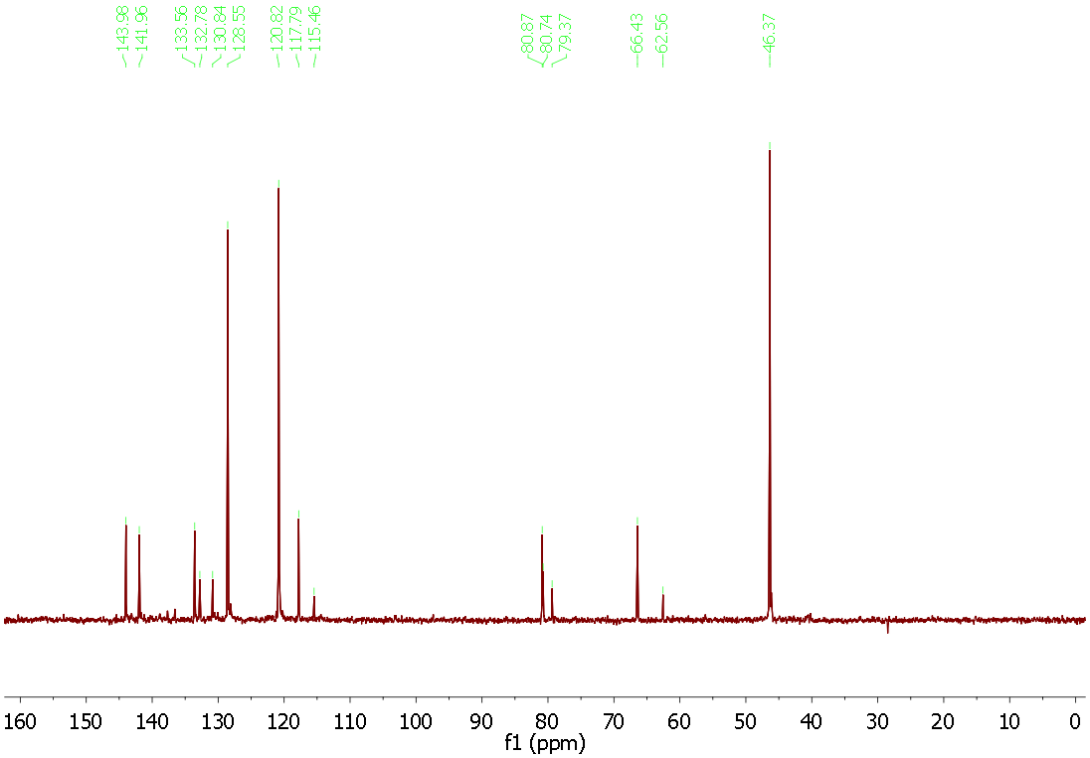


NaH (0.015 g, 0.37 mmol) was added at −10 °C to a solution of **25a**[4] (0.100 g, 0.34 mmol) in THF/DMSO 9:1 (4 ml). Reaction mixture was warmed up to room temperature and stirred for 1 h. Then it was cooled down to −10 °C and allyl bromide (0.044 ml, 0.51 mmol) was added in one portion. After that, mixture was stirred at room temperature for 1 h. Solvents were removed under reduced pressure and crude product was filtered through a short pad of silica gel (eluent: *c*-hex/AcOEt 8:2). After evaporation of solvents, product was dissolved in diethyl ether (5 ml) and HCl (1M in Et_2O, 0.625 ml) was added at 0 °C. White solid was filtered off, washed with Et_2O (2x5 ml) and dried on vacuum to afford 2**5** (0.114 g, 82 %) as a green solid (product changed colour from white to green during work up).

^{1}H NMR (300 MHz, D_2O) δ ppm: 7.77-7.75 (m, 4H), 7.53-7.50 (m, 4H), 6.01-5.88 (m, 1H), 5.36-5.17 (m, 2H), 4.03-4.00 (m, 2H), 3.47 (s, 1 H), 3.17 (s, 12H). ^{13}C NMR (75.4 MHz, D_2O) δ ppm: 144.0, 142.0, 133.6, 132.8, 130.9, 128.6, 120.9, 117.8, 115.5, 80.9, 80.7, 79.4, 66.4, 62.6, 46.4. HRMS (ESI) calcd for $C_{22}H_{26}N_2O$ ($[M+H]^+$) *m/z* 335.2123 found 335.2130.

[4] A.J. Curtis, Ch.D. Gabbutt, B.M. Heron, C. Kilner, *Tetrahedron Letters*, **2011**, *52*, 708-710.





3. General procedures for metathesis reactions

RCM of DEDAM in DCM – catalyst extraction – Isomerization in D_2O

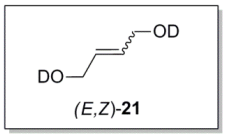
Complex **11** (6.0 mg, 1 mol%) was added under air to a solution of **27** (158 mg, 0.66 mmol) in dichloromethane (6.5 ml). Reaction mixture was stirred at reflux for 30 minutes then cooled down to room temperature and extracted with D_2O (6.5 ml) for 10 minutes. Organic fraction was separated and dried with magnesium sulphate. Solvent was removed under vacuum to afford **28** (135 mg, 97%) as a colorless oil. To green D_2O (Z)-**21** (58 mg, 0.66 mmol) was added and 0.7 ml of resulted solution was transferred to NMR vial. After 1h at room temperature the yield of (E)-**21** was 94%

Representative procedure of metathesis in D_2O

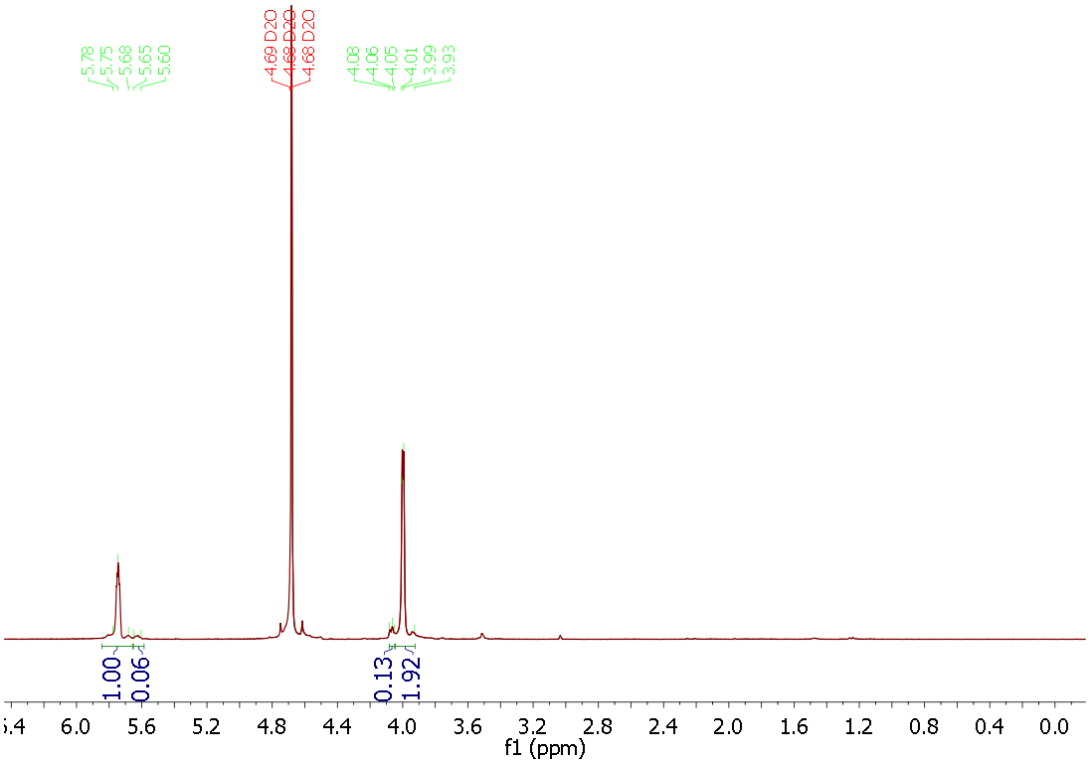
Flask equipped with a magnetic stirring bar was charged with substrate **22** (8.7 mg, 0.15 mmol) and non-degassed D_2O (1.5 ml). Next to this solution catalyst was added (0.6 mg, 0.75 µmol). Reaction mixture was stirred at 25°C for a defined period of time. Next 0.7 ml of reaction mixture was transferred to an NMR tube. Yield was determined using NMR method.

4. Analytical data of metathesis products

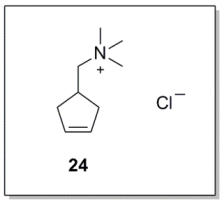
E-**21** + *Z*-**21**: ^{1}H NMR (300 MHz, D_2O) δ ppm: 5.78-5.68 (m, 2H, *E*-**21**), 5.65-5.60 (m, 2H, *Z*-**21**), 4.08-4.05 (m, 4H, *Z*-**21**), 4.01-3.93 (m, 4H, *E*-**21**).



(*E*,*Z*)-**21**



24: ^{1}H NMR (300 MHz, D_2O) δ ppm: 5.64 (s, 2H), 3.43 (d, 2H, *J* = 6.0Hz), 3.05 (s, 9H), 2.76-2.66 (m, 1H), 2.63-2.56 (m, 2H), 2.15-2.05 (m, 2H).



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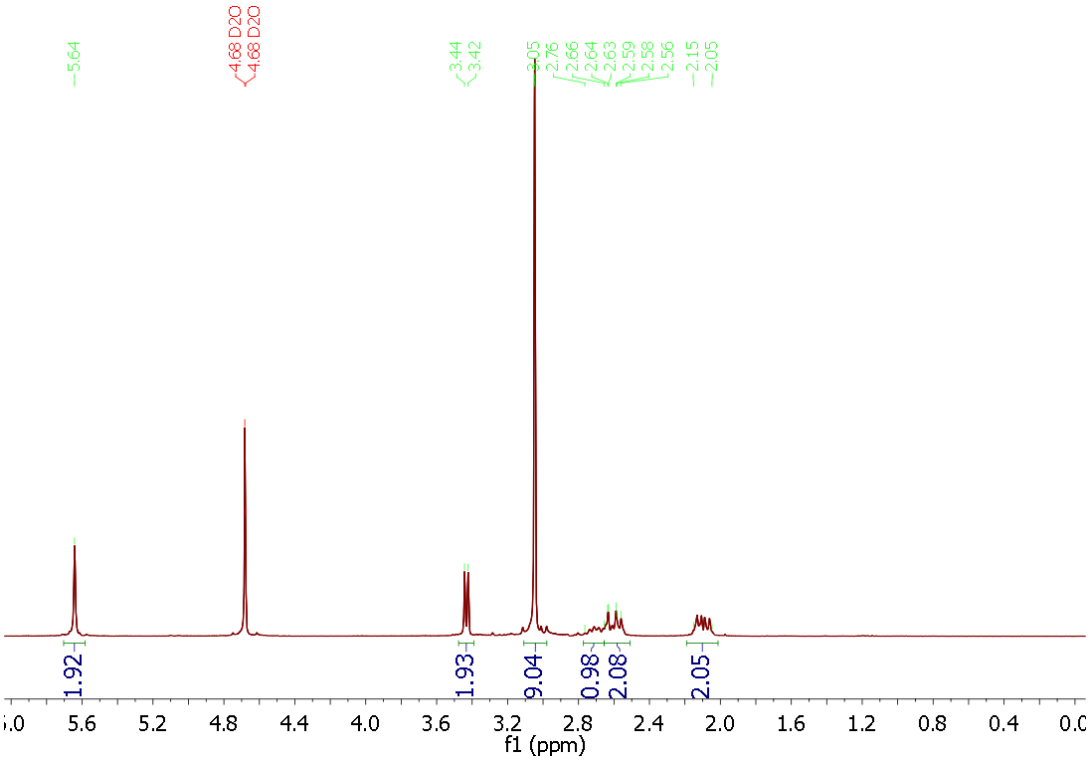
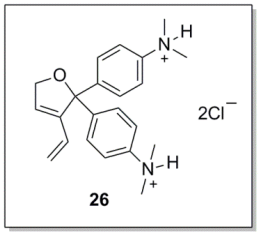


26: ^{1}H NMR (500 MHz, D_2O): δ = 7.53-7.51 (m, 4H), 7.48-7.45 (m, 4H), 6.32 (bs, 1H), 6.20 (dd, 1H, *J* = 18 Hz, *J* = 11.5 Hz), 5.17 (d, 1H, *J* = 17.5 Hz), 5.07 (d, 1H, *J* = 11 Hz), 4.74 (bs, 2H), 3.20 (s, 12H); ^{13}C NMR (50 MHz, D_2O): δ = 144.4, 141.9, 140.9, 130.1, 128.6, 126.9, 120.5, 118.9, 94.0, 74.0, 46.5. HRMS (ESI) calcd for $C_{22}H_{26}N_2O$ ([M+H]$^+$) m/z 335.2123 found 335.2128.



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