Supplementary Information

Catalysts by the meter: rapid screening approach of N-heterocyclic carbene ligand based catalysts

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1 General Experimental

All starting materials and deuterated solvents were obtained from commercial suppliers (Acros Organics, Sigma-Aldrich, abcr, Deutero, euriso-top) and were used without further purification unless otherwise stated.

Anhydrous tetrahydrofurane was prepared using an MBRAUN MB SCS-800 solvent purification system. Anhydrous diethyl ether was distilled over sodium benzophenone ketyl radical under an atmosphere of Ar.

Air- and moisture-sensitive reactions were conducted in oven-dried glassware by using standard Schlenk line or dry-box techniques under an inert atmosphere of N_2 or Ar.

^{1}H NMR spectra were recorded using Bruker ARX-250 (250 MHz), Bruker Avance 300 (300 MHz) and Bruker Avance 500 (500 MHz) spectrometers. ^{13}C NMR spectra were recorded using Bruker Avance 300 (75 MHz) and Bruker Avance 500 (125 MHz) spectrometers. ^{31}P NMR spectra were recorded using Bruker ARX-250 (101 MHz). Chemical shifts are reported in parts per million (ppm) and were calibrated to the residual signals of the deuterated solvents, coupling constants (J) are indicated in Hz.

High-resolution ESI mass spectra (HR ESI-MS) were recorded on a Bruker ApexQe hybrid 9.4 T FT-ICR-MS instrument.

GC and GC/MS measurements were performed on a Thermo Trace GC PolarisQ (San Jose, CA) equipped with a split injector (250°C or 300°C, respectively), a flame-ionisation detector (250°C or 300°C, respectively), and a quadrupole - ion trap mass spectrometer. Electron impact mass spectra (EI GC/MS) were recorded at an ion source temperature of 200°C and electron energy of 70eV using the Xcalibur software package (Thermo, San Jose, California, USA).

Separations where performed on an Agilent J&W HP-5MS column (30 m, i.d. 250 µm, 250 nm film thickness) (Palo Alto, California, USA) or a fused-silica column coated with GE SE-30 (25 m, i.d. 250 µm, 250 nm film thickness), respectively. Helium was used as inert carrier gas. In case of on-column hydrogenations hydrogen was used as reactive carrier gas.

Fused-silica capillaries (i.d. 250 µm, o.d. 365 µm) were purchased from Microquartz (Munich, Germany).

2 Synthetic Procedures and Compound Data

2.1 1-(Allyloxy)-*N,N´*-dimesityl-2,3-diamino-propane (2)

Sodium hydride (441 mg, 18.4 mmol, 2.00 eq) was suspended in anhydrous tetrahydrofurane (12 mL) at 0 °C. *N,N´*-dimesityl-2,3-diamino-1-propanol (3.00 g, 9.20 mmol, 1.00 eq) dissolved in anhydrous tetrahydrofurane (24 mL) was added using a dropping funnel and the solution was allowed to stir for 30 min at 0 °C. Afterwards 3-bromo-1-propene (1.21 g, 10.1 mmol, 1.10 eq) dissolved in anhydrous tetrahydrofurane (15 mL) was added. The solution was stirred for 24 h at 78 °C. Then the mixture was quenched by addition of ethanol, extracted with *n*-pentane and washed with water. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, *n*-hexane : ethyl acetate = 9:1, R_f: 0.65) to get a yellow oil (3.07 g, 8.38 mmol, 91 %).

^{1}H-NMR (300.132 MHz, $CDCl_3$, 25 °C): δ = 2.25-2.30 (m, 18 H, Ar-CH_3), 3.06 (dd, 1 H, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 5.9 Hz, -NH-CH_2-), 3.32 (dd, 1 H, $^2J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 5.7 Hz, NH-CH_2), 3.42-3.46 (m, 1 H, CH), 3.53-3.56 (m, 2 H, O-CH_2-Vinyl), 3.96 (d, 2 H, $^3J_{H,H}$ = 5.3 Hz, CH_2-O), 5.16-5.30 (m, 2 H, CH=CH_2), 5.84-5.97-(m, 1 H, C*H*=CH_2), 6.84 (s, 4 H, Ar-H) ppm.

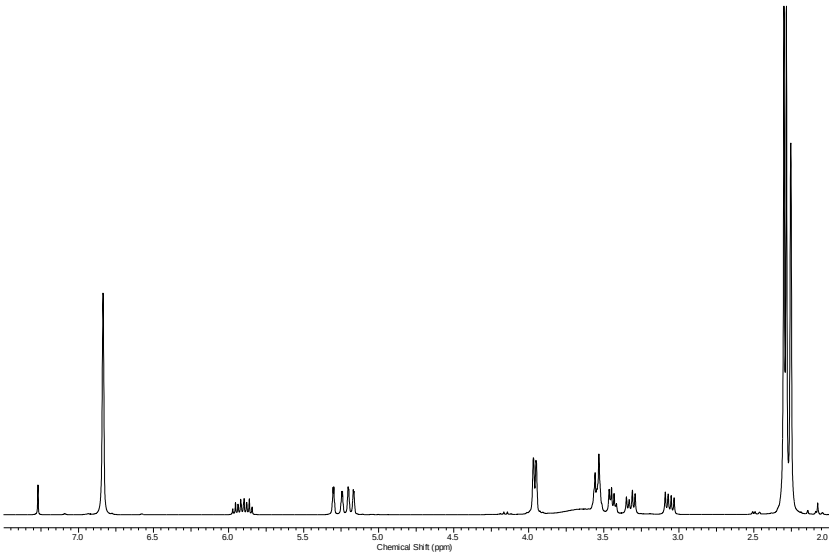

Fig. S1 ^{1}H-NMR of 1-(Allyloxy)-*N,N´*-dimesityl-2,3-diamino-propane **2**.

^{13}C-NMR (75.54 MHz, $CDCl_3$, 25 °C): δ = 18.7, 19.2, 20.9, 21.0, 51.3, 57.0, 71.1, 72.7, 117.4, 129.7, 129.8, 130.0, 130.3, 131.2, 131.7, 134.9, 142.1, 144.0 ppm.

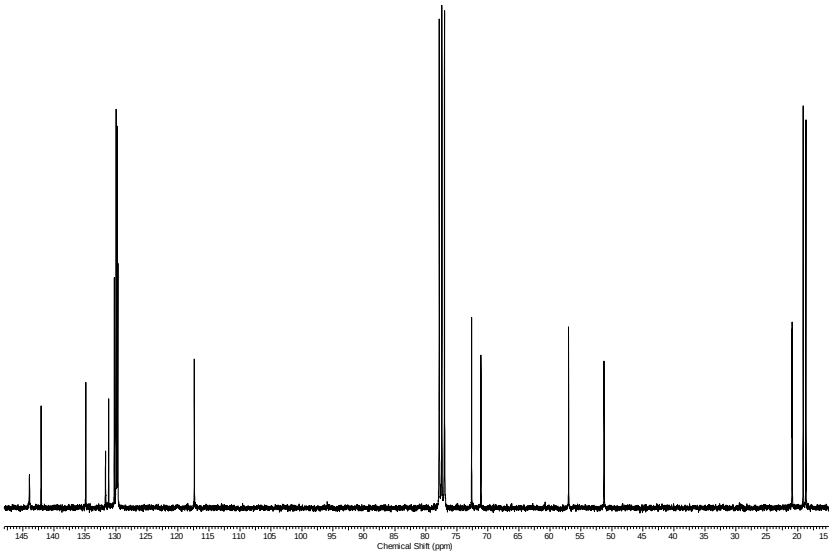

Fig. S2 ^{13}C-NMR of 1-(Allyloxy)-*N,N´*-dimesityl-2,3-diamino-propane **2**.

HR-MS (ESI+): $[M+H]^+$: *m/z* = 367.27449 $(C_{24}H_{35}N_2O)^+$, calculated: *m/z* = 367.27494.

2.2 3-(Allyloxymethyl)-1,3-dimesityl-4,5-dihydro-1*H*-imidazol-3-ium-tetrafluoroborate (3)

2 (2.95 g, 8.07 mmol, 1.00 eq), ammonium tetrafluoroborate (847 mg, 8.07 mmol, 1.00 eq) and triethyl orthoformate (15.5 g, 17.0 mL, 104 mmol, 13.0 eq) were heated to 120 °C for 16 h. After addition of diethyl ether (100 mL) the white precipitate was filterd out through a glas frit, washed with diethyl ether and recrystallized from dichloromethane/diethyl ether yield **3** as colorless powder (3.60 g, 7.75 mmol, 96 %).

^{1}H-NMR (300.132 MHz, $CDCl_3$, 25 °C): δ = 2.31-2.41 (m, 18 H, Ar-CH_3), 3.45-3.49 (dd, 1 H, $^2J_{H,H}$ = 11.7 Hz, $^3J_{H,H}$ = 1.5 Hz, CH_2-O), 3.63-3.68 (dd, 1 H, $^2J_{H,H}$ = 11.7 Hz, $^3J_{H,H}$ = 2.2 Hz, CH_2-O), 4.02-4.04 (m, 2 H, O-CH_2-Vinyl), 4.37-4.43 (dd, 1 H, $^2J_{H,H}$ = 12.1 Hz, $^3J_{H,H}$ = 7.7 Hz N-CH_2), 4.70-4.78 (t, 1 H, $^2J_{H,H}$ = 12.1 Hz, N-CH_2), 5.19-5.29 (m, 3 H, CH=CH_2, N-CH), 5.80-5.94 (m, 1 H, C*H*=CH_2), 6.97-6.99 (m, 4 H, Ar-H), 7.79 (s, 1 H, N-CH=N) ppm.

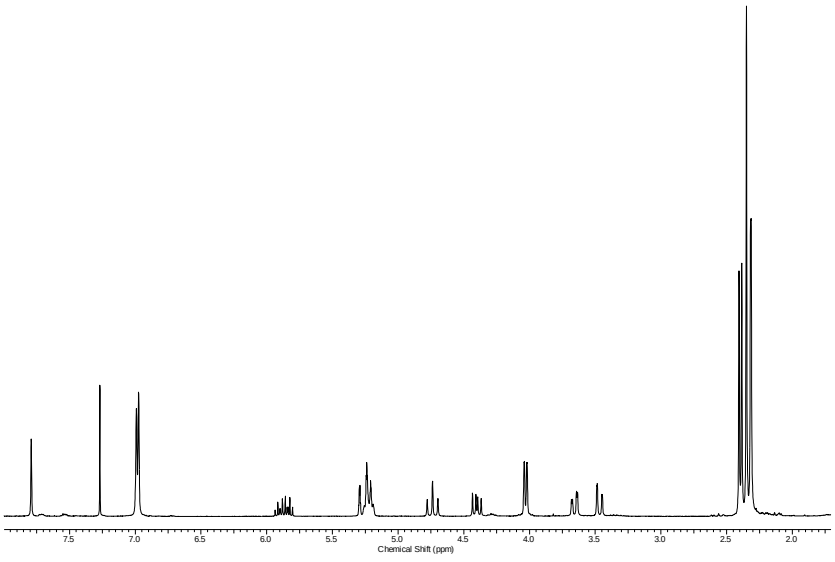

Fig. S3 ^{1}H-NMR of 3-(Allyloxymethyl)-1,3-dimesityl-4,5-dihydro-1*H*-imidazol-3-ium-tetrafluoroborate **3**.

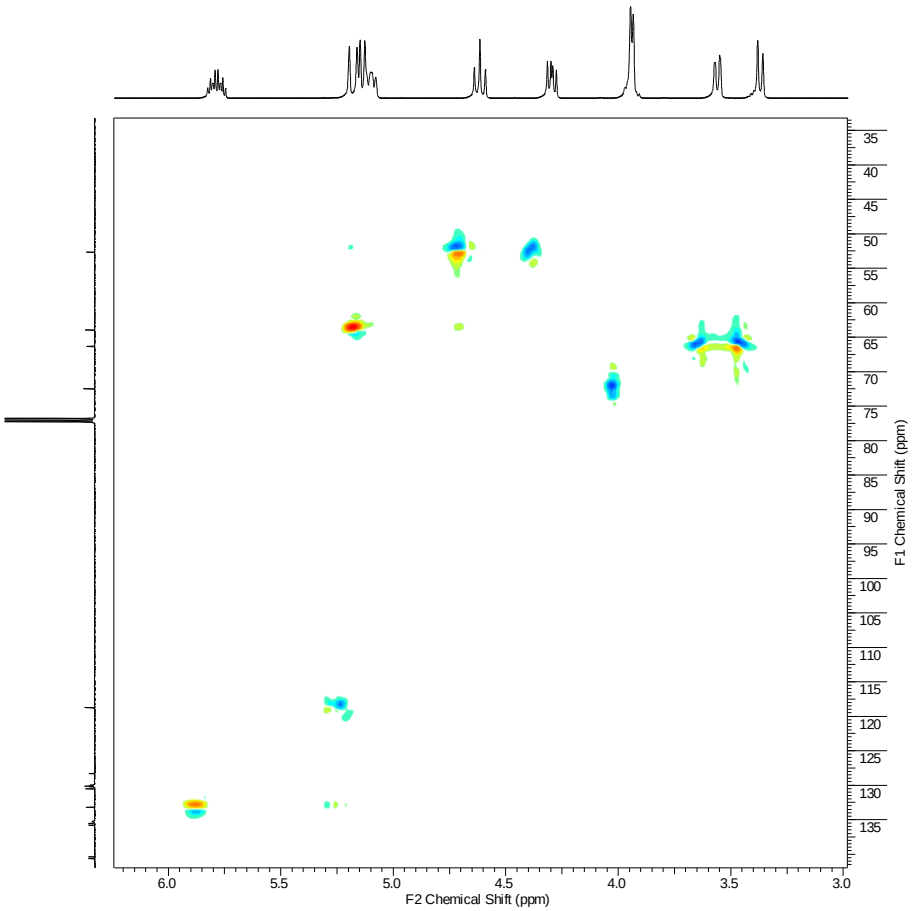

Fig. S4 ^{1}H, ^{13}C-HSQC of 3-(Allyloxymethyl)-1,3-dimesityl-4,5-dihydro-1*H*-imidazol-3-ium-tetrafluoroborate **3**. The N-CH_2 proton peaks are showing an unusual pattern in the ^{1}H-NMR spectrum (apparently a triplett, which is caused by overlap of a double dublett and a double dublett, which show the same coupling constants), which has been confirmed by the here presented spectrum.

^{13}C-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 17.3, 17.6, 18.2, 20.9, 21.0, 52.1, 64.0, 66.3, 72.5, 118.9, 128.9, 130.1, 130.6, 133.1, 135.6, 140.5, 140.8, 157.9 ppm.

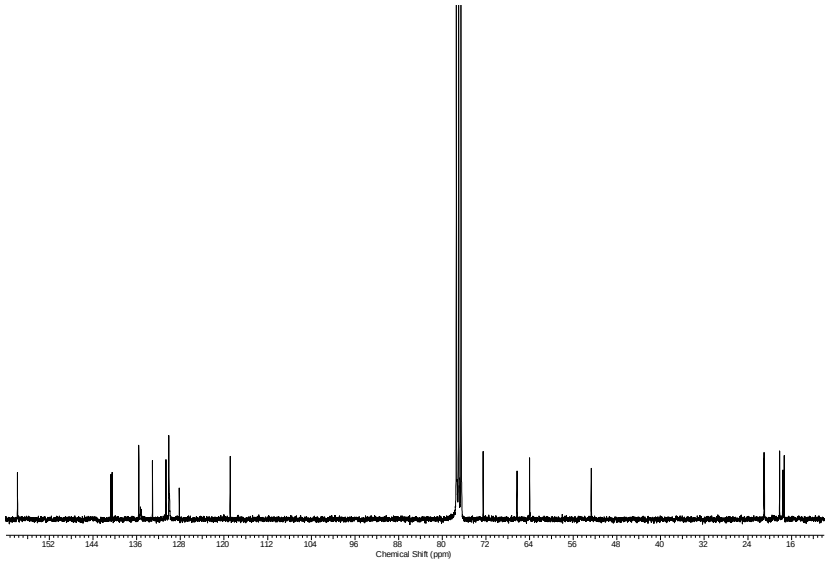

Fig. S5 ^{13}C-NMR of 3-(Allyloxymethyl)-1,3-dimesityl-4,5-dihydro-1*H*-imidazol-3-ium-tetrafluoroborate **3**.

HR-MS (ESI+): $[M\text{-}BF_4]^+$: *m/z* = 377.25869 $(C_{25}H_{33}N_2O)^+$, calculated: *m/z* = 377.25874

2.3 1,3-Dimesityl-5-(propyloxymethyl)-4,5-dihydro-1*H*-imidazol-3-ium-poly(dimethylsiloxane) (4)

In a 20 mL Schlenk tube **3** (153 mg, 0.33 mmol, 1.00 eq), hydridomethyldimethylpoly-siloxane (468 mg, 0.29 mmol, 0.88 eq, 10,2 % Si-H groups), and Karstedt´s catalyst (12 µl) were suspended in anhydrous tetrahydrofurane (40 mL). The mixture was stirred in an ultrasonic bath for 4 h under argon atmosphere. Afterwards the solvent was evaporated and the residue was passed through a short silica gel column (dichlormethane : methanol = 20:1). The solvent was evaporated to give a yellow oil (603 mg).

^{1}H-NMR (300.132 MHz, $CDCl_3$, 25 °C): δ = -0.12-0.28 (m, 219 H, Si-CH_3), 0.45-0.50 (m, 2 H, Si-CH_2), 1.56-1.60 (m, 2 H, Si-CH_2-CH_2), 2.32-2.43 (m, 18 H, Ar-CH_3), 3.43-3.48 (m, 2 H, O-CH_2-CH_2), 3.60-3.68 (m, 2 H, CH-CH_2-O), 4.29-4.45 (m, 1 H, N-CH_2), 4.69 (m, -Si-H), 4.76-4.87 (m, 1 H, N-CH_2), 5.19-5.37 (m, 1 H, N-C*H*), 6.99 (s, 4 H, Ar-H), 7.81 (s, 1 H, N-CH=N) ppm.

2.4 3-(Propyloxy)-*N,N*`-dimesitylpropane-1,2-diamine-poly(dimethylsiloxane) (6)

In a 20 mL Schlenk tube **2** (62.0 mg, 0.17 mmol, 1.00 eq), hydridomethyldimethylpolysiloxane (156 mg, 0.11 mmol, 0.65 eq, 10,2% Si-H groups) and Karstedt´s catalyst (10 µl) were suspended in anhydrous tetrahydrofurane (10 mL). The mixture was stirred in an ultrasonic bath for 4 h under argon atmosphere. Afterwards the solvent was evaporated and the residue was passed through a short silica gel column (dichloromethane : methanol = 20:1). The solvent was evaporated to give a yellow oil (195 mg).

^{1}H-NMR (300.132 MHz, $CDCl_3$, 25 °C): δ = 0.06-0.10 (m, Si-CH_3), 0.48-0.53 (m, 2 H, Si-CH_2), 1.53-1.57 (m, 2 H, Si-CH_2-CH_2-), 2.23-2.26 (m, 18 H, Ar-CH_3), 3.01-3.07 (m, 1 H, NH-CH_2), 3.31-3.51 (m, 5 H, NH-CH_2, CH-CH_2-O, O-CH_2-CH_2), 3.74-3.78 (m, 1 H, NH-C*H*), 4.69-4.70 (m, Si-H), 5.39-5.42 (m, NH), 6.81 (s, 4 H, Ar-H) ppm.

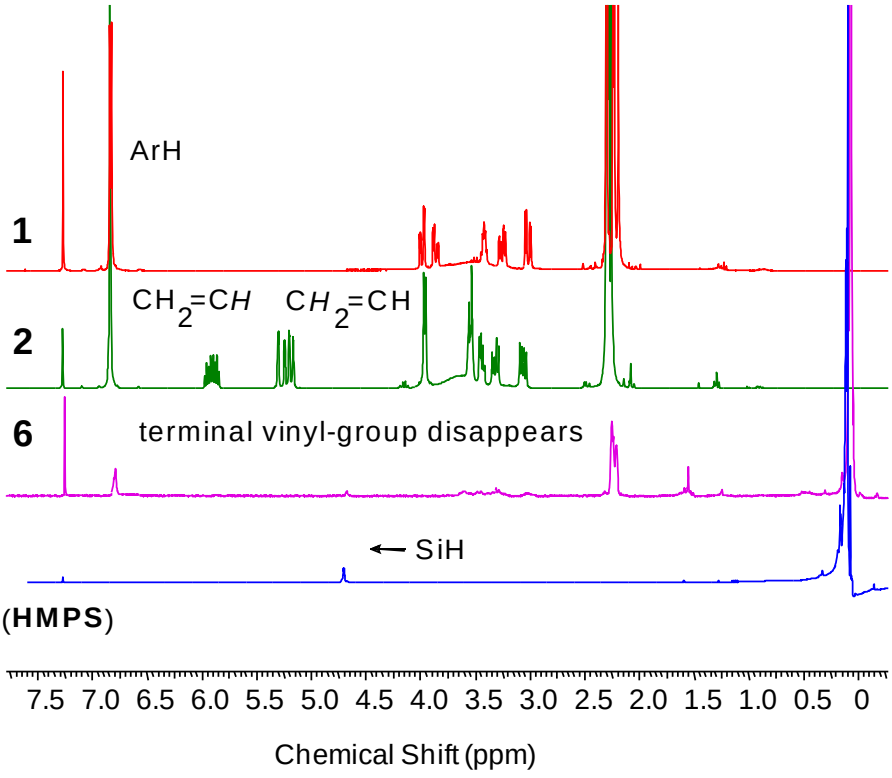

Fig. S6 Reaction control by ^{1}H-NMR of the conversion of **1** to **2**, and immobilization of **2** to hydridomethyldimethylpolysiloxane forming polymer **6**.

2.5 1,3-Dimesityl-4-(propyloxymethyl)-2-(pentafluorophenyl)-imidazolidine-poly-(dimethylsiloxane) (7)

6 (195 mg, part of **2**: 62.0 mg, 0.17 mmol, 1.00 eq) and pentafluoro benzaldehyd (43.0 mg, 0.22 mmol, 1.30 eq) were dissolved in tetrahydrofurane (1.00 mL) and acetic acid (0.10 mL). The reaction mixture was stirred for 24 h and the solvent was removed under reduced pressure. The obtained red oil (250 mg) was directly used in the next step without further purification.

2.6 Benzyliden[1,3-bismesityl-4-propyloxymethyl-2-imidazolidinylidene] (tricyclohexylphosphine) ruthenium (II)-poly-(dimethylsiloxane) (5)

Pathway A: 4 (203 mg, part of **3**: 140 mg, 0.33 mmol, 1.00 eq) and KO*t*Bu (27.0 mg, 0.24 mmol, 0.70 eq) were dissolved in anhydrous THF (1 mL) and stirred for 1 h at room temperature. The yellow reaction mixture was added dropwise via a drain tube to a solution of $(PCy_3)_2RuCl_2CH_2Ph$ (35.1 mg, 0.43 mmol, 1.30 eq) in toluene (1 mL). The solution was stirred for 3 h at 80 °C. The solvent was removed under reduced pressure.

Pathway B: **7** (250 mg, part of **2**: 62.0 mg, 0.17 mmol, 1.00 eq) and $(PCy_3)_2RuCl_2CH_2Ph$ (97.4 mg, 0.18 mmol, 0.70 eq) were dissolved in anhydrous toluene (10 mL). The solution was stirred at 80 °C. ^{31}P-NMR reaction control indicated completion after 4 h (cf. Fig. S2). The solvent was removed under reduced pressure.

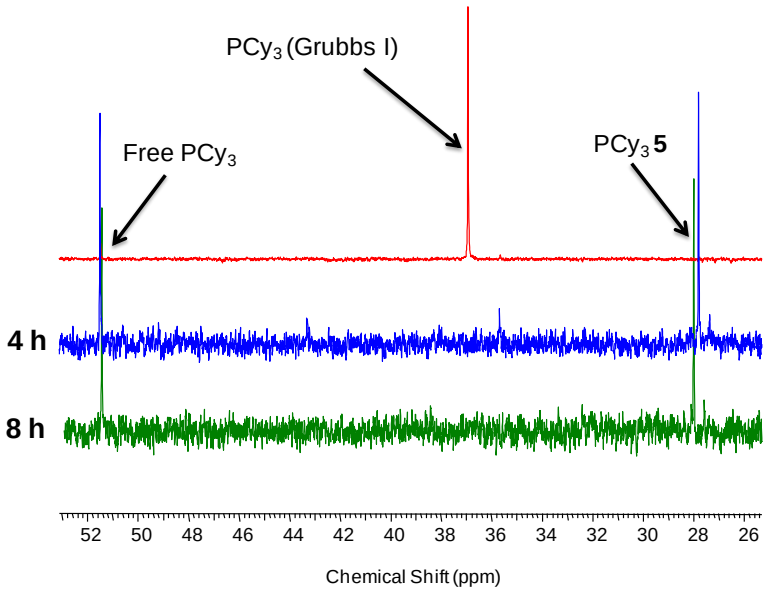

Fig. S7 Reaction control by ^{31}P-NMR of the formation of benzyliden[1,3-bismesityl-4-propyloxymethyl-2-imidazolidinylidene] (tricyclohexylphosphine) ruthenium (II)-poly-(dimethylsiloxane) **5** starting from compound **7** by thermal carbene formation and in situ ligand exchange of PCy_3 against the bonded benzyliden[1,3-bismesityl-4-propyloxymethyl-2-imidazolidinylidene] moiety at 80°C after 4 and 8 h. The ^{31}P-NMR spectrum of the Grubbs 1st generation catalyst has been included as reference.

3 Coating of fused-silica columns (Pathway C)

3.1 Coationg of a fused-silica column with 3-(propyloxy)-*N,N`*-dimesitylpropane-1,2-diamine-poly(dimethylsiloxane) (8)

3-(Propyloxy)-4,5-dimesitylpropane-1,2-diamine-poly(dimethylsiloxane) **6** (8.60 mg) was dissolved in absolute diethyl ether (2.0 mL) to be used as coating solution. Capillaries were coated by the static method described by Grob.[1] A 10 m fused-silica capillary (i.d. 250 µm) was coated with this solution giving a 250 nm film at the inner wall of the capillary. Immobilization was achieved by a temperature program starting at 40°C for 5 min, then heating up to 180°C for 10 min at a rate of 0.5 K/min. Capillaries were flushed with absolute solvents before activation or conversion with organometallic compounds to remove non-bonded or decomposed materials.

3.2 Preparation of the ring closing metathesis (RCM)-catalyst column (9 → 10)

Pentafluorobenzaldehyd (20 mg, 0.10 mmol) and acetic acid (0.10 mL) were dissolved in absolute *n*-pentane (2.0 mL). A 1 m fused-silica capillary **8** was coated with this solution at 60 °C to obtain the immobilized carbene ligand with a film thickness of 250 nm at the inner wall of the capillary. Afterwards the capillary was rinsed with *n*-pentane (1.0 mL) to remove formed pentafluorobenzene. In the next step Grubb´s catalyst 1st generation (4.0 mg, 0.05 mmol) was dissolved in absolute *n*-pentane (2.0 mL). The capillary was flushed with this solution to achieve a ligand exchange and to obtain an immobilized Grubb´s 2nd generation type catalyst. Then the capillary was flushed with argon to remove solvents and volatile components.

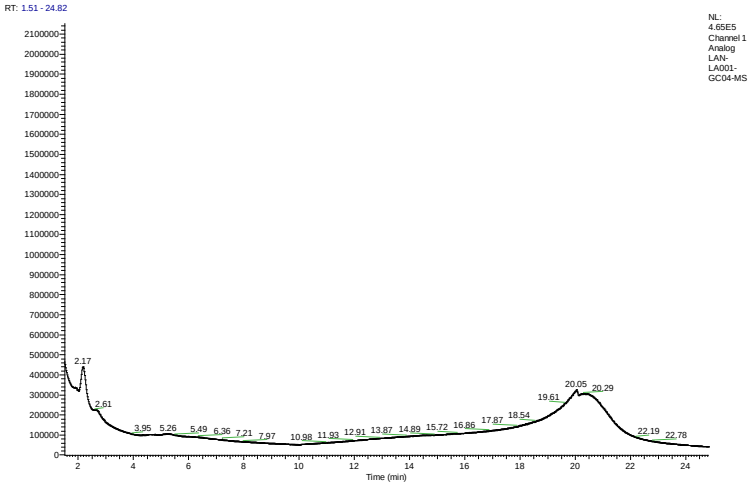

Fig. S8 Formation of pentafluorobenzene detected by GC/ MS.

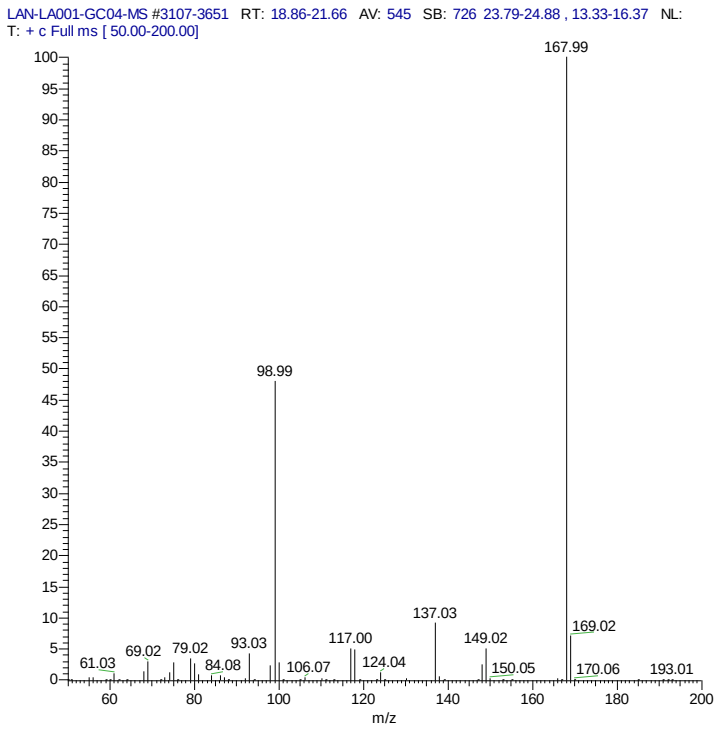

Fig. S9 EI mass spectrum of pentafluorobenzene detected by GC/ MS at a retention time interval between 19 and 21.6 min.

3.3 Preparation of the hydrogenation catalyst column (9 → 11)

Pentafluorobenzaldehyd (20 mg, 0.10 mmol) and acetic acid (0.10 mL) were added to absolute *n*-pentane (2.0 mL). A 1 m fused-silica capillary **8** was flushed with this solution at 60 °C to obtain the immobilized carbene ligand. Afterwards the capillary was rinsed with *n*-pentane (1.0 mL) to remove formed pentafluorobenzene. AuCl·Me_2S (6.0 mg, 0.03 mmol) was dissolved in absolute dichloromethane and was immobilized by purging this solution through the capillary at 60°C. Then the capillary was flushed with argon.

4 Catalytic on-column reactions

4.1 On-column ring closing metathesis experiments

Ring closing metathesis (RCM) experiments of the *N*,*N*-diallyltrifluoroacetamide to *N*-trifluoroacetylpyrrolidine were performed by on-column reaction gas chromatography. A fused-silica capillary of only 10 cm coated with the immobilized RCM-catalyst **10** was employed. This capillary was coupled between a pre-separation column coated with GE SE-30 (1 m, i.d. 250 µm, 250 nm film thickness) and an HP-5MS separation column (30 m, i.d.

250 µm, 250 nm film thickness) to separate the reaction mixture formed on the catalytically active column. All measurements were repeated 3 times at each temperature in steps of 5 K between 50-105 °C and constant pressure (80 kPa).

4.2 On-column hydrogenation experiments

Hydrogenations of nitrobenzene to aniline were performed on a 10 cm silica-capillary coated with immobilized Au(I)-catalyst **11.** This capillary was coupled between a pre-separation column coated with GE SE-30 (1 m, i.d. 250 µm, 250 nm film thickness) and a fused silica-capillary coated with GE SE-30 (25 m, i.d. 250 µm, 250 nm film thickness) to separate the reaction mixture formed on the catalytically active column. Hydrogen was used as reactive carrier gas. All measurements were repeated 3 times at each temperature in steps of 5 K between 80-95 °C and variation of the inlet pressure between 40-60 kPa.

5 References

1 K. Grob, in *Making and Manipulating Capillary Columns for Gas Chromatography*, Huethig, Heidelberg, 1986.