Supplementary Information

Supported Ru Olefin Metathesis Catalysts via a Thiolate Tether

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General Remarks

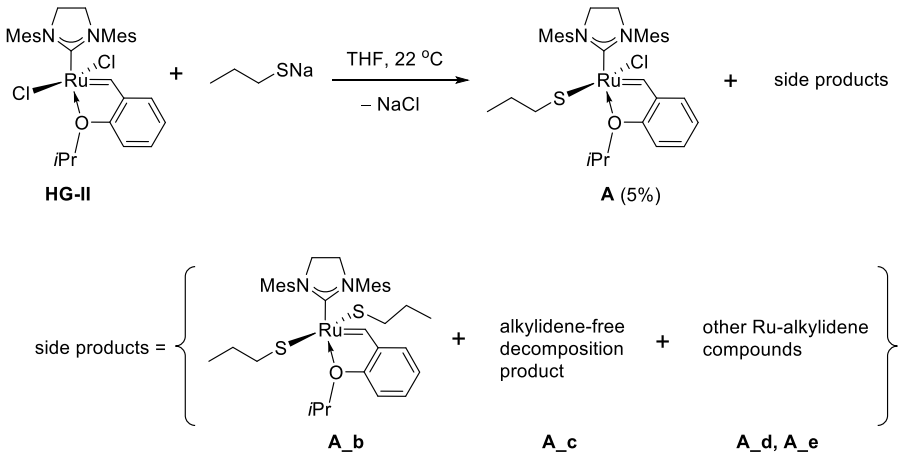
All reactions related to surface-modifications were carried out under Ar using standard Schlenk techniques and dry degassed solvents. TEOS was distilled from Mg. Et_3N was distilled from CaH_2. 1-hexene and 4-Phenyl-1-butene were distilled from Na, degassed and stored for 4 h over activated Selexsorb® CD. Dodecane was distilled from Na and degassed. Methyl oleate was degassed by freeze-pump, stored for 4 h over Selexsorb® CD and then stirred for 3 days with activated alumina.

Elemental analyses were performed under inert atmosphere at the Mikroanalytisches Labor Pascher, Remagen, Germany. Liquid ^1H NMR spectra were recorded on a Bruker AC 300 MHz. Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$ δ = 7.26 ppm; CD_2Cl_2, δ = 5.32 ppm). Liquid ^{13}C NMR spectra were recorded on a Bruker AC 300 MHz operating at 75 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ = 77.16 ppm; CD_2Cl_2, δ = 54.00 ppm). CP-MAS NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer with a conventional double resonance 4 mm CP-MAS probe. The MAS frequency was set to 10 kHz for all the ^1H and ^{13}C experiments reported here. N_2 adsportion-desorption experiments were carried out on a Belsorb Japan system.

Compound **A** and **B** were characterized as described below: NMR spectra were recorded on Bruker Biospin AV 500, and AV III HD 850 spectrometers. The chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard relative to the residual C_6D_5H peaks (δ = 7.16 ppm (proton) and δ = 128.06 ppm (carbon). HRMS (ESI^+) mass spectrum of **B** was recorded by means of a JMS-T100LC AccuTOF™ from JEOL, USA, Inc. (Peabody, MA, USA). (Orthogonal accelerated time of flight single stage reflectron mass analyzer and a dual micro channel plate (MCP) detector). The AccuTOF™ mass spectrometer was operated with an orthogonal electrospray ionization source (ESI), an orthogonal accelerated time of flight (TOF) single stage reflectron mass analyzer and a dual micro channel plate (MCP) detector. Elemental analysis of compound **B** was performed using an Elementar Vario EL III analyzer.

TEOS (tetraethylorthosilicate), HCl, Pluronic 123, TMSBr, Hoveyda-Grubbs 2nd generation catalyst (**HG-II**), sodium thiophenolate, 1-propane thiolate, (3-mercaptopropyl)triethoxysilane, NaF, Et_3N, 4-bromothiophenol, hexamethyldisilazane (HMDS), potassium hexamethyldisilazide (KHMDS) Mg turnings, 4-phenyl-1-butene and 1-hexene were purchased from commercial suppliers (TCI Chemicals, ACROS, Sigma Aldrich, Alfa Aesar) and used as received, unless otherwise stated in paragraph 1 of "General Remarks". Methyl oleate was purchased from Nu-Check Prep, Inc.

Synthesis of ruthenium monothiolate complex A



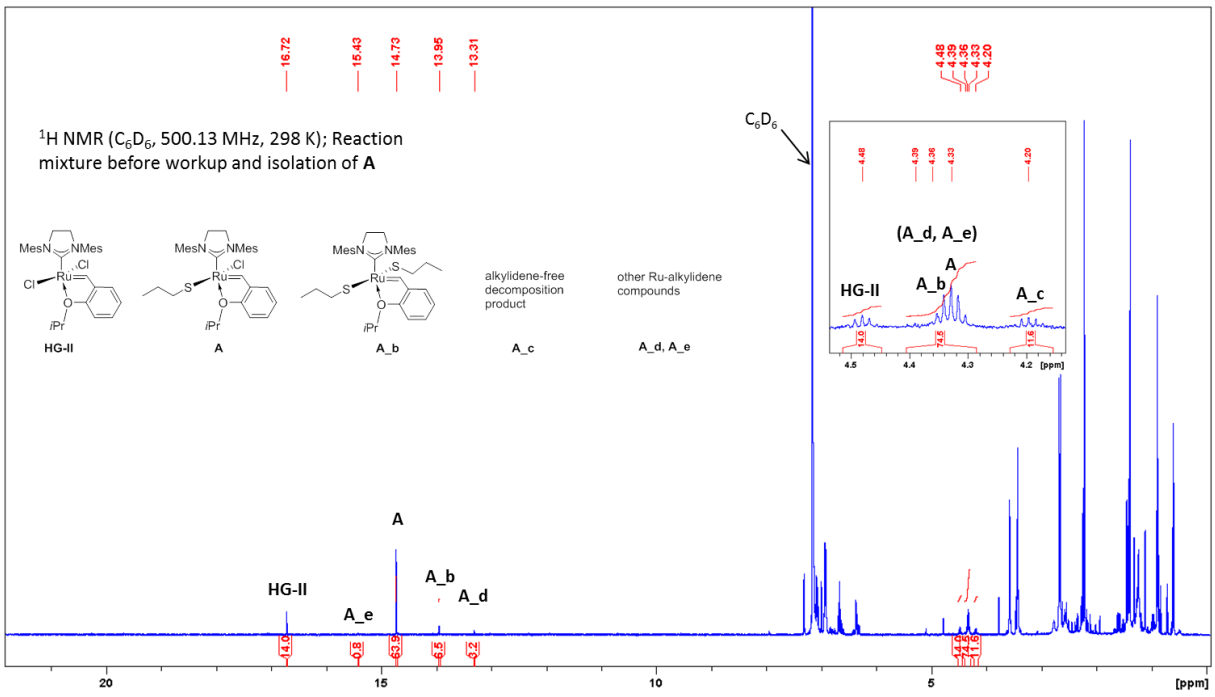
In a glovebox, a 25 mL vial, equipped with a magnetic stirring bar and a screw cap, was charged with Hoveyda-Grubbs second generation catalyst (**HG-II)** (100 mg, 0.16 mmol, 1.0 equivalent) and sodium 1-propanethiolate (15.7 mg, 0.16 mmol, 1.0 equivalent). Tetrahydrofuran (5 mL) was added and the mixture was stirred for five hours at room temperature. The ^{1}H NMR analysis of the reaction mixture in C_6D_6 showed the presence of two main compounds: the monothiolate Ru alkylidene complex **A** (51%, δ = 14.72 ppm (s, Ru=C**H**Ar)) and the starting material **HG-II** (41%, δ = 16.72 ppm (s, Ru=C**H**Ar)). In addition, the corresponding bisthiolate Ru-alkylidene complex **A_b** (5%, δ = 13.73 ppm (s, Ru=C**H**Ar)), and a Ru-alkylidene-free decomposition product (**A_c**) having the septet peak of the isopropoxy moiety at slightly higher field (3%, δ= 4.20 (sep, $^3J_{HH}$ = 6.0, Ar-O-C**H**Me$_2$). The last compound probably derives from the decomposition of the bisthiolate complex **A_b**. Indeed, a new spectrum of the same NMR sample (stored under argon at room temperature for 18 hours) showed a significant percentage increase of **A_c,** while the percentage of **A_b** decreased approximately in the same amount. In contrast, the percentages of the two major compounds (**A** and **HG-II**) were essentially unmodified. To increase the yield of **A**, and additional portion of sodium 1-propanethiolate (6.5 mg, 0.07 mmol, 0.4 equivalents) was added to the reaction mixture and the reaction was stirred at room temperature for another five hours. The ^{1}H NMR analysis of the reaction mixture in C_6D_6 showed an increased percentage of the monothiolate Ru alkylidene complex **A** (64%) along with **HG-II** (14%), **A_b** (7 %), **A_c** (12%), and two new Ru-alkylidene complexes having the proton alkylidene peaks (s, Ru=C**H**Ar) at 15.43 (1%) and 13.31 ppm (3%) respectively.

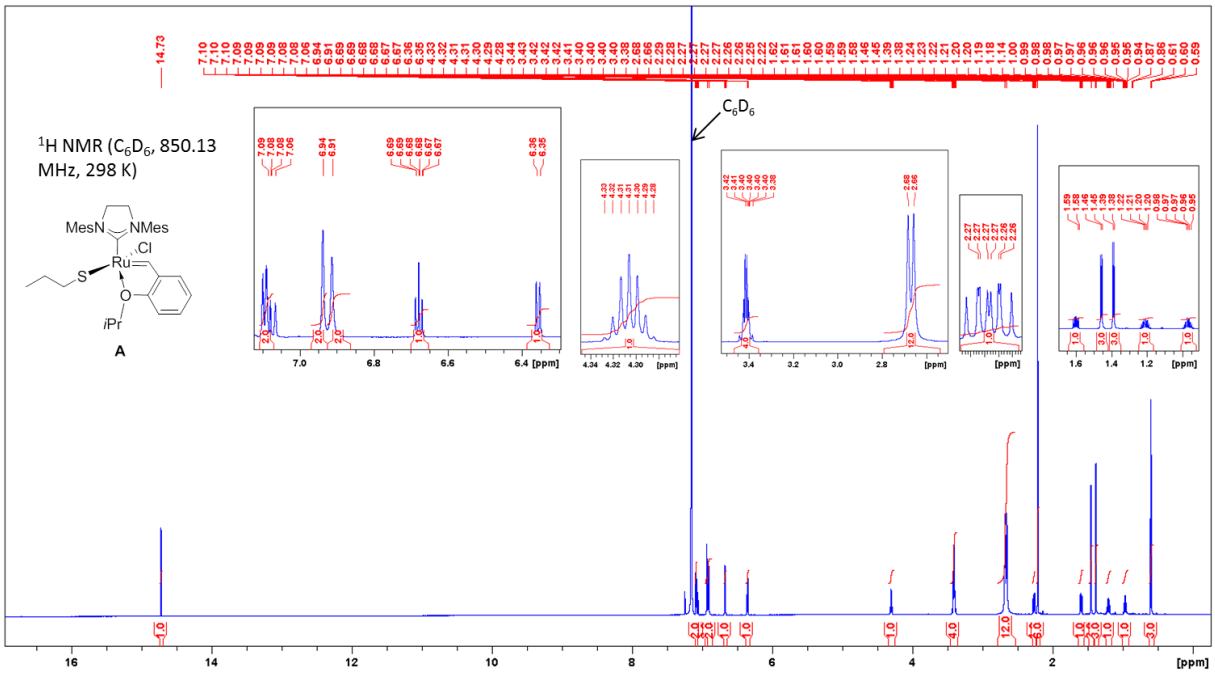
The solvent was removed under reduced pressure, and the residue was extracted with pentane (about 15 mL), and filtered through a short pad of celite. The resulting dark-green solution was placed in the freezer (–32 °C) for two days. The first and second crop dark-green crystals and the supernatant solution were analyzed by ^{1}H NMR. The composition was the following: first crop crystals (**HG-II** (3 %), **A** (92%), **A_b** (2%), **A_c** (3%)), second crop crsytals (**HG-II** (3 %), **A** (88 %), **A_b** (2%), **A_c**

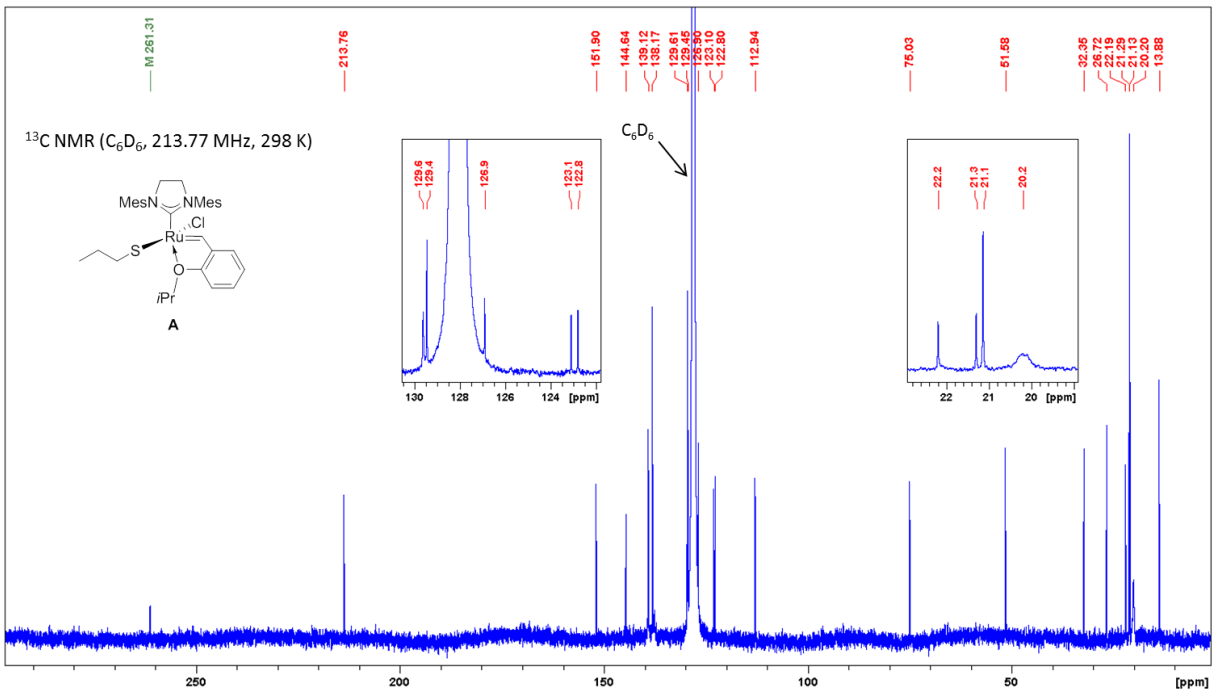
(7%)), solution: (**A** (52%), **A_b** (13%), **A_c** (34%), and **A_d** (1%)). The solution was discarded, while the two crops of crystals were separately recrystallized.

The crystals were first dissolved in toluene. The solvent was then removed by vacuum, and the residue was extracted with pentane and filtered through a pad of celite. Finally, the two filtrates were put in the freezer at −32 C for two days. Crystals and solutions were analyzed by ^{1}H NMR and the cleanest fractions were again recrystallized using the same procedure. This purification procedure was repeated two more times with fractions of increasingly higher purity. In the end, three fractions of the pure title compound **A** were obtained (5.5 mg (overall weight); 5% of yield).

^{1}H NMR (500.13 MHz, C_6D_6, 300 K): δ = 14.73 (s, 1H), 7.11-7.07 (m, 2H), 6.94 (s, 2H), 6.91 (s, 2H), 6.68 (dt, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 0.6, 1H), 6.36 (d, $^{3}J_{HH}$ 8.0, 1H), 4.31 (sep, $^{3}J_{HH}$ = 6.1 1H), 3.45-3.37 (m, 4H), 2.68 (s, 6H), 2.66 (s, 6H), 2.27 (ddd, , $^{2}J_{HH}$ = 12.8, $^{3}J_{HH}$ 8.0, $^{3}J_{HH}$ 6.9, 1H), 2.22 (s, 6H), 1.60 (ddd, , $^{2}J_{HH}$ = 12.8, $^{3}J_{HH}$ 8.1, $^{3}J_{HH}$ 5.9, 1H), 1.46 (d, $^{3}J_{HH}$ = 6.3 3H), 1.39 (d, $^{3}J_{HH}$ = 6.0 3H), 1.25-1.17 (m, 1H), 1.00-0.93 (m, 1H), 0.60 (t, $^{3}J_{HH}$ 7.3, 1H). ^{13}C{^{1}H} NMR (231.77 MHz, C_6D_6, 300 K): δ = 261.3, 213,8, 151.9, 144.6, 139.1, 138.2, 129.6, 129.4, 126.9, 123.1, 122.8, 112.9, 75.0, 51.6, 32.4, 26.7, 22.2, 21.3, 21.1, 20.2 (br), 13.9. HRMS (ESI+): calculated for $C_{34}H_{45}N_2O^{102}RuS$ $[M\text{-}Cl]^+$: m/z = 631.2299, found: m/z = 631.2327.




^{1}H NMR (C_6D_6, 850.13 MHz, 298 K)
MesN
NMes
Cl
Ru
S
O
iPr
A
C_6D_6
[ppm]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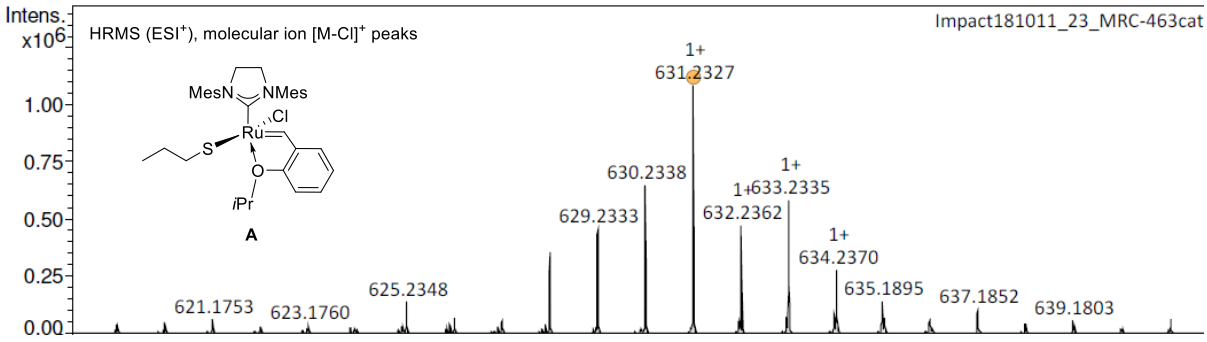
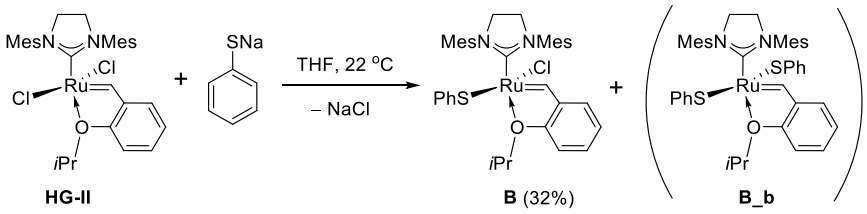
MesN
NMes
Cl
Ru
S
O
iPr
A
C_6D_6
[ppm]


Intens.
x10^6
HRMS (ESI$^+$), molecular ion [M-Cl]$^+$ peaks
Impact181011_23_MRC-463cat
MesN
NMes
Cl
Ru
S
O
iPr
A
1+
631.2327
630.2338
629.2333
1+
633.2335
632.2362
1+
634.2370
635.1895
637.1852
639.1803
625.2348
621.1753
623.1760

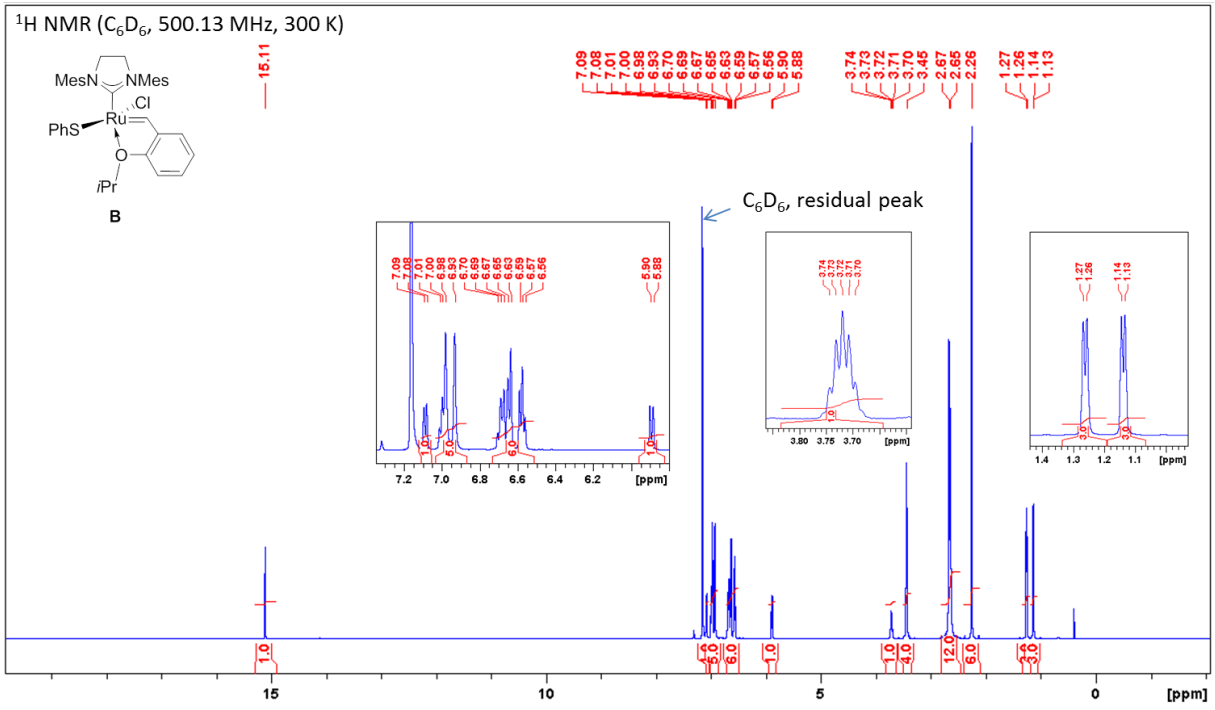
Synthesis of ruthenium monothiolate complex B

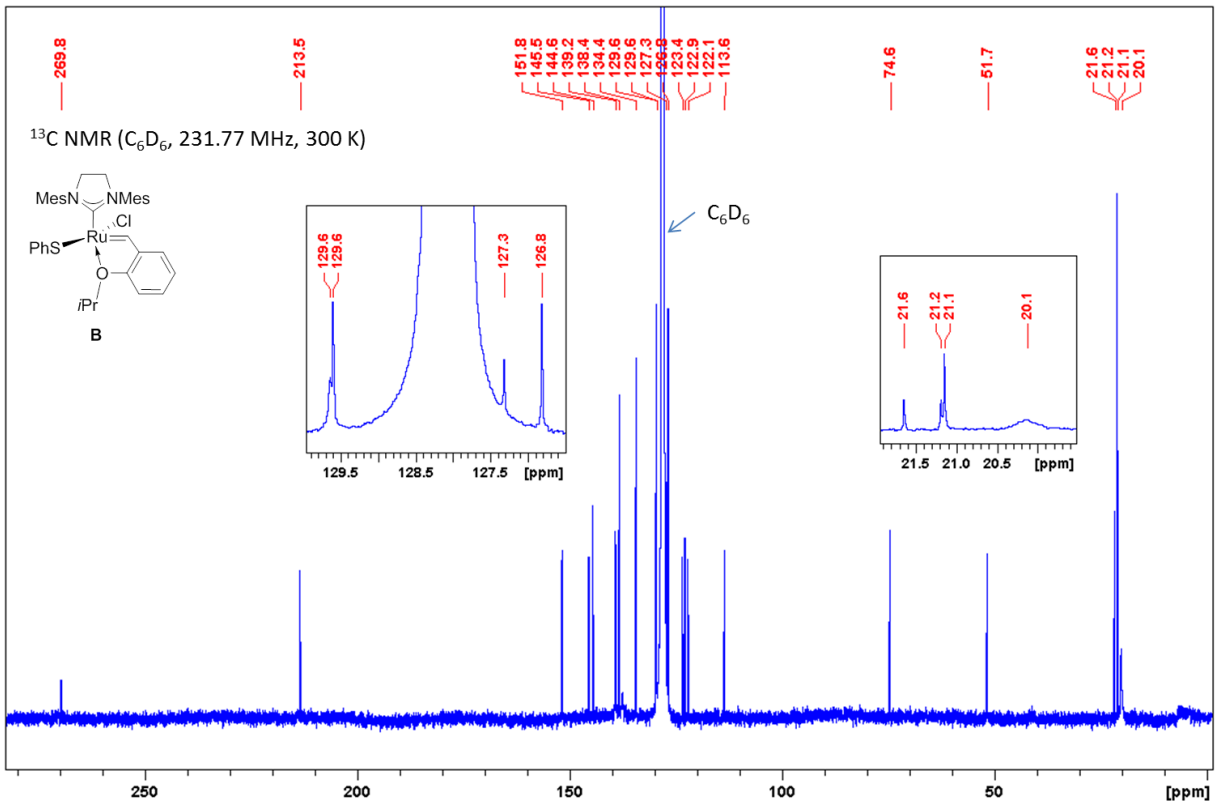


In a glovebox, a 25 mL vial, equipped with a magnetic stirring bar and a screw cap, was charged with Hoveyda-Grubbs second generation catalyst (**HG-II)** (100 mg, 0.16 mmol, 1 equivalent), and tetrahydrofuran (2 mL). The mixture was stirred at room temperature for about 1 minute until a homogeneous solution was obtained. In another 25 mL vial, equipped with a magnetic stirring bar and a screw cap, sodium thiophenolate (27.5 mg, 0.208 mmol, 1.3 equivalents) was dissolved in tetrahydrofuran (5 mL). The latter solution was slowly added in six fractions (of about 0.8 ml each) to the solution of **HG-II** in a time of an hour. The mixture was stirred at room temperature for additional two hours. The ^{1}H NMR analysis of the reaction mixture in C_6D_6 showed the presence of two main compounds: the Ru monothiolate **B** (79%, δ = 15.11 ppm (s, Ru=C**H**Ar)) and the Ru-bisthiolate **B_b** (19%, δ = 14.11 ppm (s, Ru=C**H**Ar)), along with residual starting material **HG-II** (2%, δ = 16.72 ppm (s, Ru=C**H**Ar)). The solvent was removed under reduced pressure. The residual was dissolved in toluene (about 3 mL), and then filtered through a short pad of celite. To the filtrate was added pentane (15 mL) and the resulting dark-green mixture was placed in the freezer (–32 °C) for two days. The dark-green crystals (59 mg) were isolated, washed three times with pentane and dried under vacuum. A sample was dissolved in C_6D_6 and analyzed by ^{1}H NMR spectroscopy. The following composition was determined: **B** (96%), **B_b** (2.5%), and **HG-II** (1.5%).

Since, the percentage of **HG-II** in the crystallized material (1.5%) was only slightly lower than that in the reaction mixture (2%), we decided to remove the residual **HG-II** by reaction with sodium thiophenolate. The crystallized material was dissolved in tetrahydrofuran (5 mL). Then a solution of sodium thiophenolate, prepared by dissolving 1.8 mg in 2.7 ml of THF, was added in small portions until the ^{1}H NMR analysis of the mixture showed a negligible content of the dichloride precursor **HG-II**. In total 2.2 mL of sodium thiophenolate solution was added during a time of 12 hours. The following composition was determined by ^{1}H NMR spectroscopy: **B** (82%), **B_b** (18%), and **HG-II** (< 0.05%). The solvent was removed under reduced pressure. The residual was dissolved in toluene (about 3 mL), and the solution filtered through a short pad of celite. To the filtrate was added pentane (20 mL) and the resulting dark-green mixture was placed in the freezer (–32 °C) for two days. The dark-green crystals (49 mg) were isolated and washed three times with pentane, dried under reduced pressure, and a sample was analyzed by ^{1}H NMR spectroscopy. The analysis of the spectrum showed

the presence of the Ru-monothiolate **B** as the main component (97.5%) and the Ru-bisthiolate **B_b** (2.5%) as the only impurity. This material was dissolved in toluene (about 3 mL). Pentane (20 mL) was added and the mixture was placed in the freezer (–32 °C) for two days. The dark-green crystals were isolated, washed three times with pentane and dried under reduced pressure to give 36 mg (32%) of the title compound **B**. ^{1}H NMR (500.13 MHz, C_6D_6, 300 K): δ = 15.11 (s, 1H), 7.09 (d, $^{3}J_{HH}$ = 7.5 1H), 7.03-6.88 (m, 5H), 6.72-6.53 (m, 6H), 5.89 (d, $^{3}J_{HH}$ = 8.3 1H), 3.72 (sep, $^{3}J_{HH}$ = 6.0 1H) 3.45 (s br, 4H), 2.67 (s, 6H), 2.65 (s, 6H), 2.26 (s, 6H), 1.26 (d, $^{3}J_{HH}$ = 6.0 3H) , 1.14 (d, $^{3}J_{HH}$ = 6.0 3H). ^{13}C{^{1}H} NMR (231.77 MHz, C_6D_6, 300 K): δ = 269.8, 213,5, 151.8, 145.5, 144.6, 139.2, 138.4, 134.4, 129.64, 129.60, 127.3, 126.8, 123.4, 122.9, 122.1, 113.6, 74.6, 51.7, 21.6, 21.2, 21.1, 20.1. Elemental analysis, calculated (%) for $C_{37}H_{43}ClN_2ORuS$: C, 63.46, H, 6.19, N, 4.00; found (%): C, 63.90, H, 6.06, N, 3.71. HRMS (ESI+): calculated for $C_{37}H_{44}{}^{35}ClN_2O^{102}RuS$ $[M + H]^+$: m/z = 701.19063, found: m/z = 701.19177.




269.8
213.5
151.8
145.5
144.6
139.2
138.4
134.4
129.6
129.6
127.3
126.8
123.4
122.9
122.1
113.6
74.6
51.7
21.6
21.2
21.1
20.1
^{13}C NMR (C_6D_6, 231.77 MHz, 300 K)
MesN
NMes
Cl
PhS
Ru
O
iPr
B
C_6D_6
129.6
129.6
127.3
126.8
129.5
128.5
127.5
[ppm]
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20.5
[ppm]
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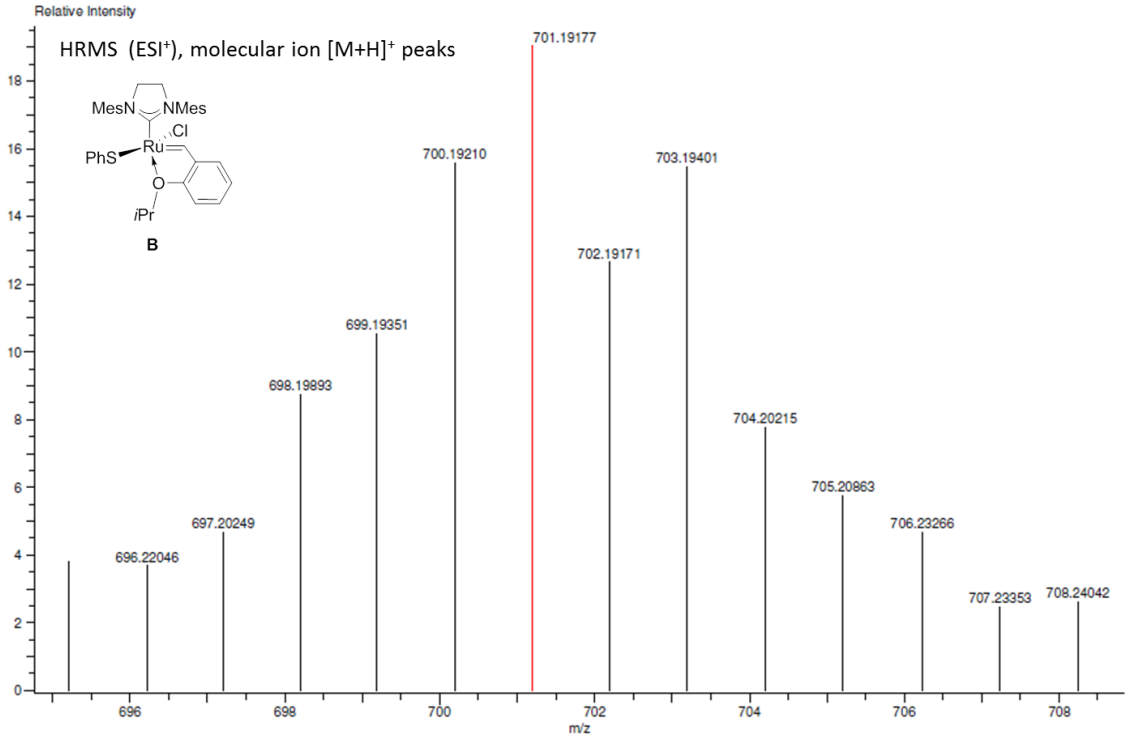
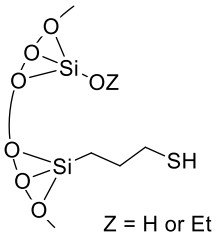
200
150
100
50
[ppm]


Relative Intensity
HRMS (ESI$^+$), molecular ion $[M+H]^+$ peaks
MesN
NMes
Cl
PhS
Ru
O
iPr
B
701.19177
700.19210
703.19401
702.19171
699.19351
698.19893
704.20215
705.20863
706.23266
697.20249
696.22046
707.23353
708.24042
18
16
14
12
10
8
6
4
2
0
696
698
700
702
704
706
708
m/z

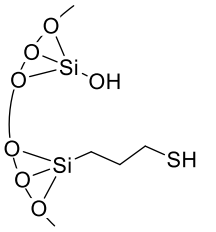
Synthesis of Mat-PrSH

(EtO)Mat-Pr-SH



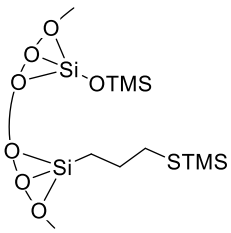
A mixture of Pluronic® P123 (8.4 g), H_2O (333 mL) and HCl 37% (878 µL) was stirred for 4 h in a 500 mL glass round-bottomed flask, until a clear solution was obtained, and subsequently added into a mixture of TEOS (20 mL, 90 mmol) and (3-mercaptopropyl)triethoxysilane (582 µL, 2.2 mmol) contained in a 1 L glass round-bottomed flask equipped with a mechanical stirrer. The reaction mixture was stirred for 2 h at room temperature and then warmed up to 45 °C, at which NaF (154 mg, 3.67 mmol) was added. The mixture was stirred at this temperature for 72 h. The resulting solid was filtered and washed with H_2O (2 x 200 mL), EtOH (1 x 200 mL), acetone (1 x 200 mL) and Et_2O (2 x 200 mL). The surfactant was removed by Soxhlet extraction with EtOH during 48 h. The solid was then filtered, washed with acetone (2 x 200 mL) and Et_2O (2 x 200 mL) and dried at 135 °C under vacuum (10^{-5} mm Hg). 5.7 g of **(EtO)Mat-Pr-SH** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 3.7, 3.4, 1.8, 1.0 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 57.8, 25.1, 14.3, 8.8 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 1019.7 m^2/g, $d_{p,BJH}$: 8.06 nm.

(HO)Mat-Pr-SH



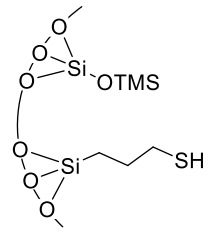
Material **(EtO)Mat-Pr-SH** (5.2 g) was suspended in HCl 2 M (500 mL), warmed up to 45 °C and stirred for 2h. After filtration, washing with H_2O (2 x 200 mL), EtOH (1 x 200 mL), acetone (1 x 200 mL) and Et_2O (2 x 200 mL) and drying at 135 °C under vacuum (10^{-5} mm Hg), 4.4 g of **(HO)Mat-Pr-SH** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 3.2, 1.9 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 25.3, 8.8 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 1014.6 m^2/g, $d_{p,BJH}$: 8.06 nm; Elemental analysis: Si 41.2 %, S 1.2 %.

(TMSO)Mat-Pr-STMS

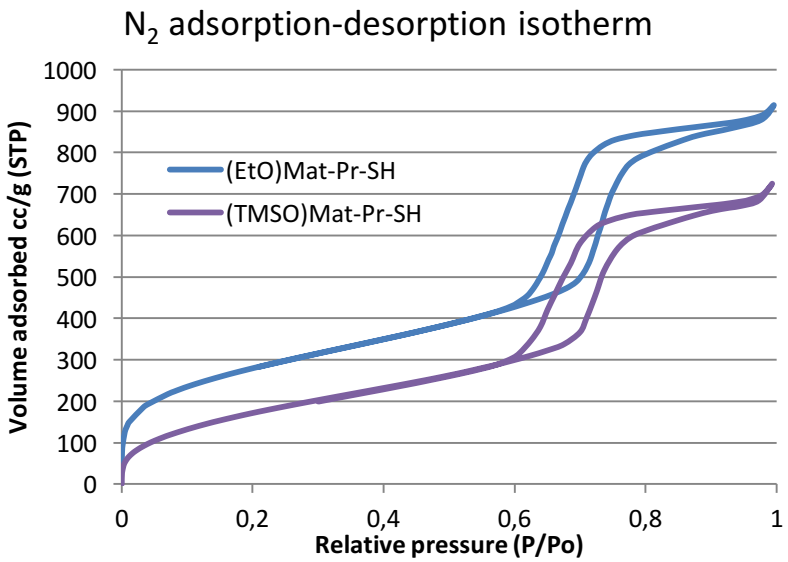


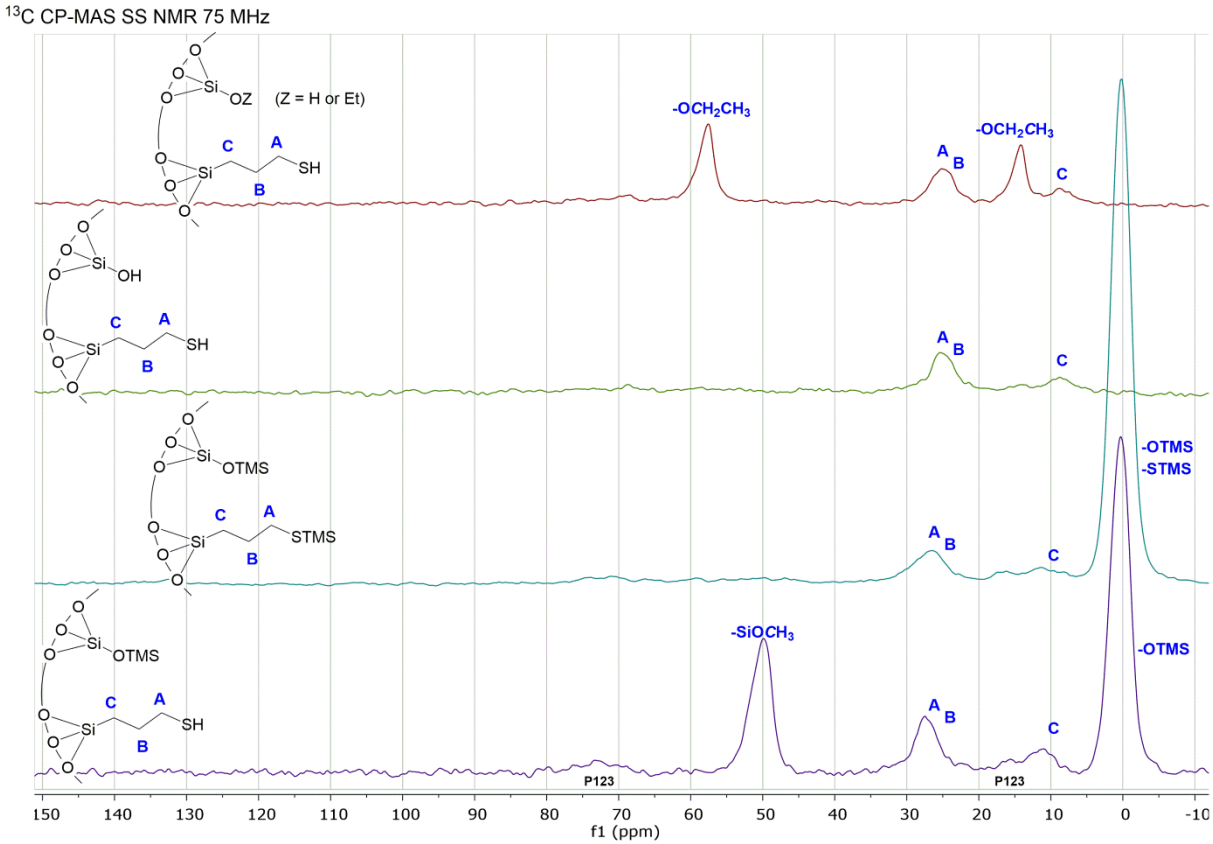
Material **(HO)Mat-Pr-SH** (3.5 g) was suspended in dry toluene (225 mL) and dry Et_3N (47 mL) under Ar, whereupon TMSBr (22 mL) was added. The mixture was stirred at room temperature for 48 h. The solid was filtered under Ar, washed with dry toluene (2 x 50 mL), dry MeOH (4 x 50 mL) and dry Et_2O (2 x 50 mL) and then dried at 135 °C under vacuum (10^{-5} mm Hg). 3.5 g of **(TMSO)Mat-Pr-STMS** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 3.5, 0.1 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 26.7, 11.5, 0.3 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 592.7 m^2/g, $d_{p,BJH}$: 8.06 nm.

(TMSO)Mat-Pr-SH (Mat-PrSH)



Material **(TMSO)Mat-Pr-STMS** (2.0 g) and K_2CO_3 (53 mg) were suspended in dry MeOH (50 mL) and stirred under Ar at room temperature overnight. The solid was filtered under Ar, washed with dry MeOH (3 x 50 mL), dry acetone (1 x 50 mL) and dry Et_2O (2 x 50 mL) and then dried at 135 °C under vacuum (10^{-5} mm Hg). 1.8 g of **(TMSO)Mat-Pr-SH** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 3.4, 0.1 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 49.9 (MeO- on the surface), 27.5, 11.0, 0.3 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 675.0 m^2/g, $d_{p,BJH}$: 7.05 nm; Elemental analysis: Si 37.4 %, S 1.0 %.

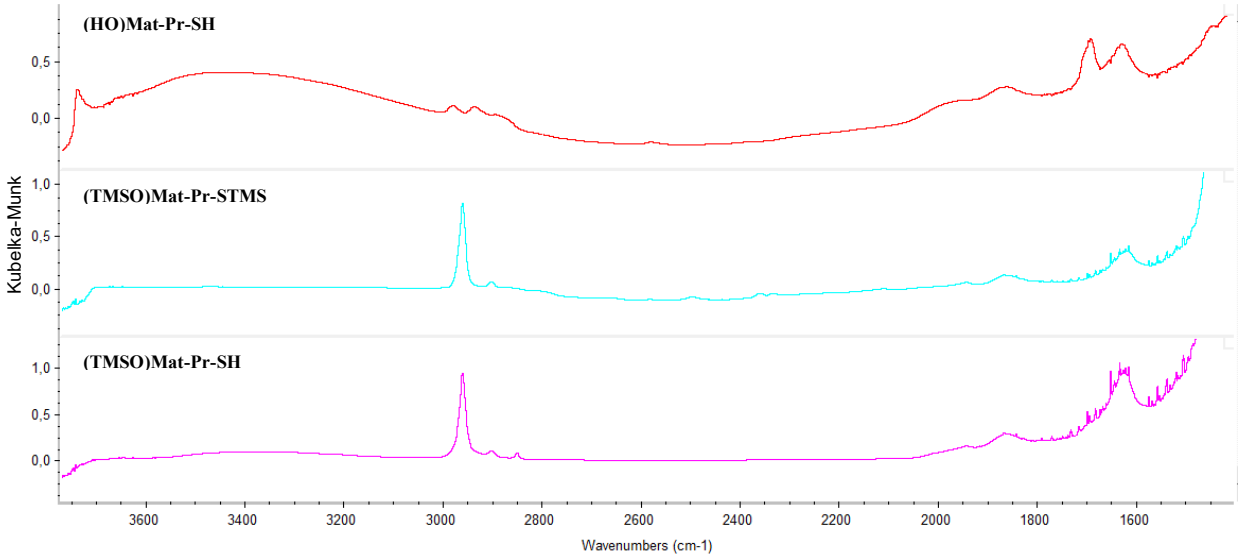




Contact time: 2 ms; recycle delay: 5 s; number of scans: 11k.

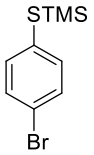
[The-$SiOCH_3$ groups are formed by methylation of surface –OH located in small micropores, which were not methylated during the treatment with TMSBr due to the bulkiness of this latter]

DRIFT of the materials:



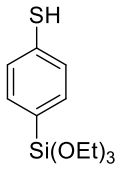
Synthesis of material B

((4-bromophenyl)thio)trimethylsilane



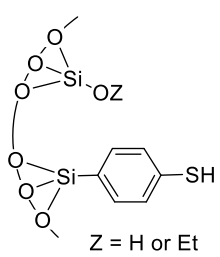
A mixture of 4-bromothiophenol (10 g, 52.9 mmol), saccharine (70 mg, 0.4 mmol) and chloroform (100 mL) was warmed up to reflux temperature under Ar, whereupon HMDS (12.5 mL, 59.6 mmol) was added. The reaction was refluxed for 3 h. After cooling the mixture to room temperature, the solvent was removed under vacuum to give 13.4 g (97% yield) of ((4-bromophenyl)thio)trimethylsilane as clear white crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 0.27 (s, 9H) ppm. Known compound.[1]

4-(triethoxysilyl)benzenethiol



A mixture of Mg turnings (1 g, 37 mmol), TEOS (6.5 mL, 29.1 mmol) and THF (10 mL) were refluxed under Ar for 15 min. Then, still at reflux temperature, 1,2-dibromoethane (0.5 mL) and ((4-bromophenyl)thio)trimethylsilane (3.5 g, 13.4 mmol) were added in this order. After 3 h, the reaction was cooled down to room temperature and 2.5 mL of TMSCl were added. The solvent was removed under vacuum. Then, EtOH (6 mL) was added and the mixture was filtered under Ar. Finally, the EtOH was removed under vacuum to give 3.0 g (83% yield, 85% NMR purity) of a colorless liquid which tends to crystallize, identified as 4-(triethoxysilyl)benzenethiol. The impurities present correspond to the TMS-protected product and the partially hydrolyzed triethoxysilane. However, since the TMS-protection and the silane will be completely hydrolyzed in the next step, the compound was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 3.72 (q, *J* = 7.0 Hz, 6H), 1.11 (t, *J* = 7.0 Hz, 9H) ppm.

(EtO)Mat-Ph-SH

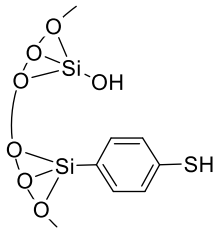


A mixture of Pluronic® P123 (8.4 g), H_2O (333 mL) and HCl 37% (878 µL) was stirred for 4 h in a 500 mL glass round-bottomed flask, until a clear solution was obtained, and subsequently added into a mixture of TEOS (20 mL, 90 mmol) and as 4-(triethoxysilyl)benzenethiol (0.6 g, 2.2 mmol) contained in a 1 L glass round-bottomed flask equipped with a mechanical stirrer. The reaction mixture was stirred for 2 h at room temperature and then warmed up to 45 °C, at which NaF (154 mg, 3.67 mmol) was added. The mixture was stirred at this temperature for 72 h. The resulting solid was filtered and washed with H_2O (2 x 200 mL), EtOH (1 x 200 mL), acetone (1 x 200 mL) and Et_2O (2 x 200 mL). The surfactant was removed by Soxhlet extraction with EtOH during 48 h. The solid was then filtered, washed with acetone (2 x 200 mL) and Et_2O (2 x 200 mL) and dried at 135 °C

[1] A.R. Bassindale, D.R.M. Walton, *J. Organometal. Chem.* **1970,** *25*, 389-393.

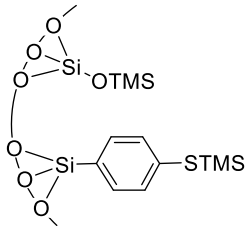
under vacuum (10^{-5} mm Hg). 6.0 g of **(EtO)Mat-Ph-SH** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 7.4, 6.9, 3.7, 1.0 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 132.7, 126.0, 57.7, 14.3 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 940.5 m^2/g, $d_{p,BJH}$: 8.06 nm.

(HO)Mat-Ph-SH



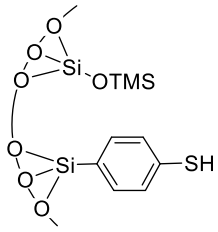
Material **(EtO)Mat-Ph-SH** (5.6 g) was suspended in HCl 2 M (500 mL), warmed up to 45 °C and stirred for 2h. After filtration, washing with H_2O (2 x 200 mL), EtOH (1 x 200 mL), acetone (1 x 200 mL) and Et_2O (2 x 200 mL) and drying at 135 °C under vacuum (10^{-5} mm Hg), 4.8 g of **(HO)Mat-Ph-SH** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 7.4, 7.0 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 132.8, 126.0 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 957.9 m^2/g, $d_{p,BJH}$: 8.06 nm; Elemental analysis: Si 40.0 %, S 0.73 %.

(TMSO)Mat-Ph-STMS

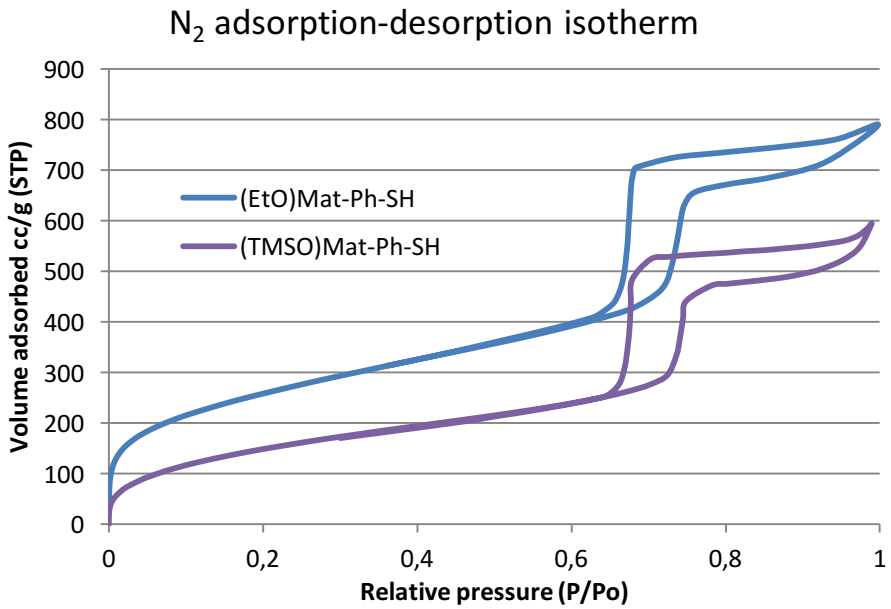


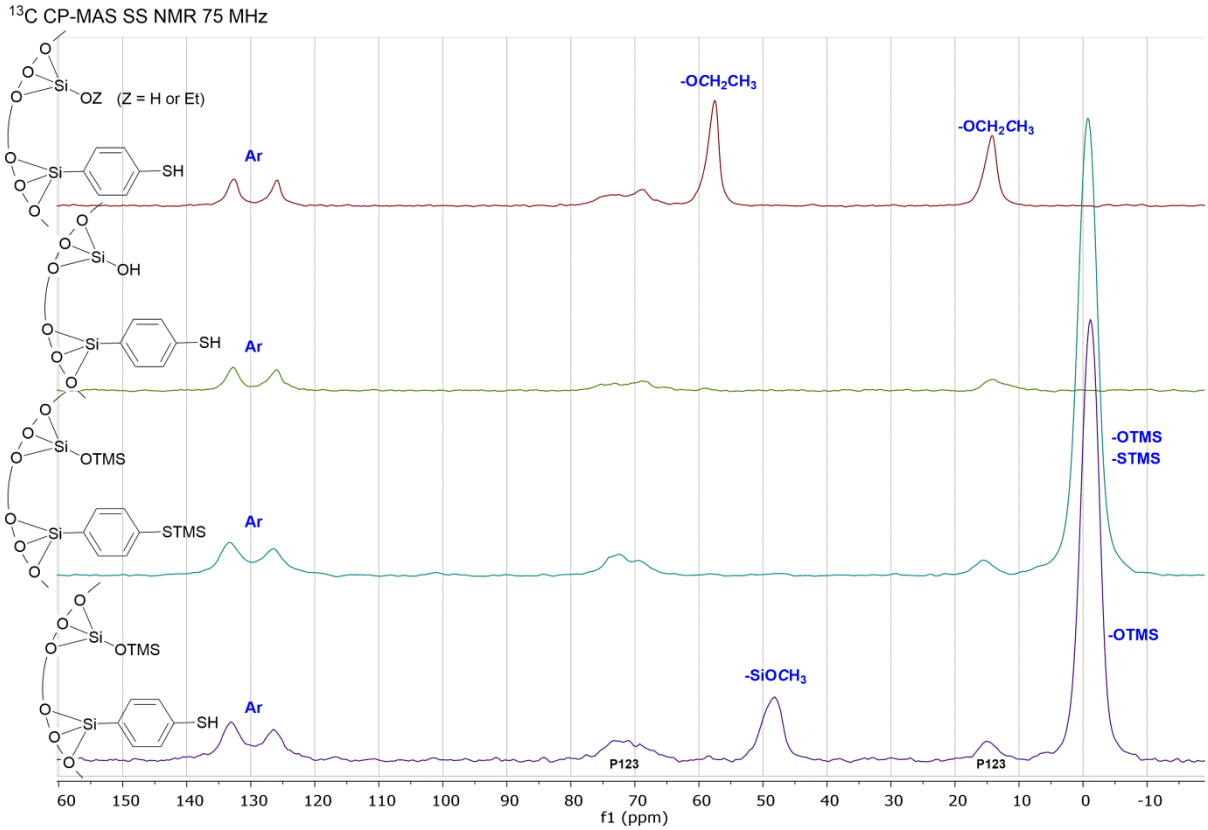
Material **(HO)Mat-Ph-SH** (3.0 g) was suspended in dry toluene (250 mL) and dry Et_3N (40 mL) under Ar, whereupon TMSBr (18.5 mL) was added. The mixture was stirred at room temperature for 48 h. The solid was filtered under Ar, washed with toluene (2 x 50 mL), dry MeOH (4 x 50 mL) and dry Et_2O (2 x 50 mL) and then dried at 135 °C under vacuum (10^{-5} mm Hg). 3.5 g of **(TMSO)Mat-Ph-STMS** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 7.6, 6.9, 0.0 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 133.4, 126.5, -0.8 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 553.5 m^2/g, $d_{p,BJH}$: 8.06 nm.

(TMSO)Mat-Ph-SH (Mat-PhSH)



Material **(TMSO)Mat-Ph-STMS** (2.0 g) and K_2CO_3 (53 mg) were suspended in dry MeOH (50 mL) and stirred under Ar at room temperature overnight. The solid was filtered under Ar, washed with dry MeOH (3 x 50 mL), dry acetone (1 x 50 mL) and dry Et_2O (2 x 50 mL) and then dried at 135 °C under vacuum (10^{-5} mm Hg). 1.7 g of **(TMSO)Mat-Ph-SH** were obtained as a white powder. ^{1}H SS NMR (300 MHz): δ 7.6, 6.9, 0.0 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 133.1, 126.4, 48.4 (MeO-on the surface), -1.0 ppm; Nitrogen adsorption-desorption isotherm: $a_{S,BET}$: 573.6 m^2/g, $d_{p,BJH}$: 8.06 nm; Elemental analysis: Si 35.2 %, S 0.6 %.

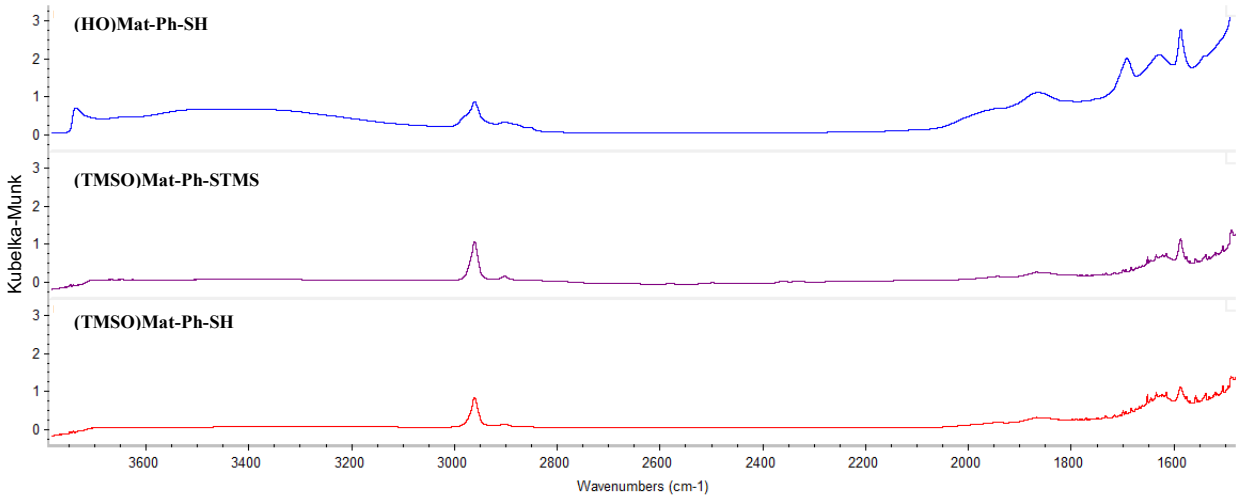




Contact time: 2 ms; recycle delay: 2 s; number of scans: 11k.

[The-$SiOCH_3$ groups are formed by methylation of surface –OH located in small micropores, which were not silylated during the treatment with TMSBr due to the bulkiness of this latter]

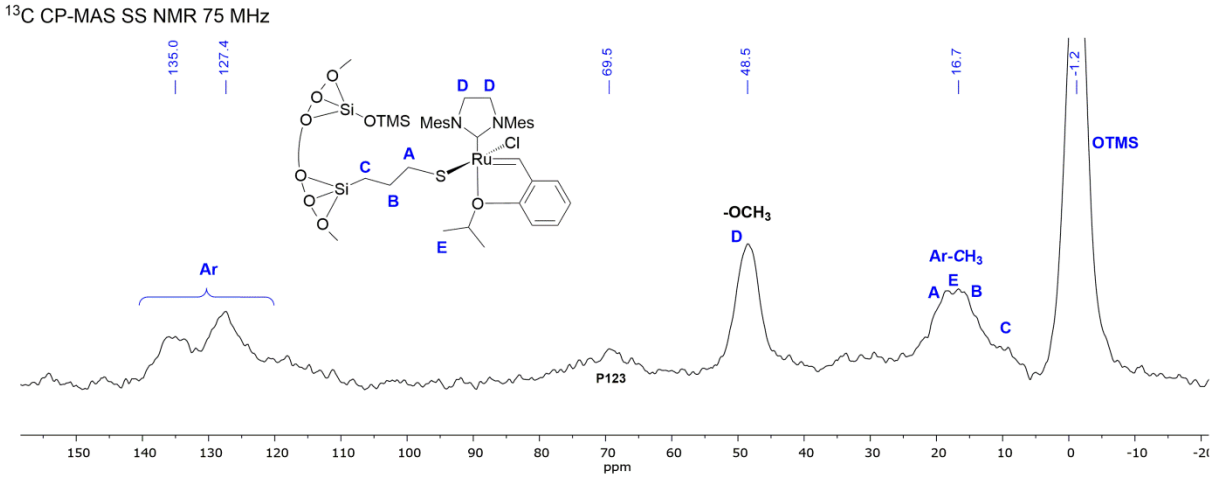
DRIFT of the materials:



General procedure for the catalyst immobilization

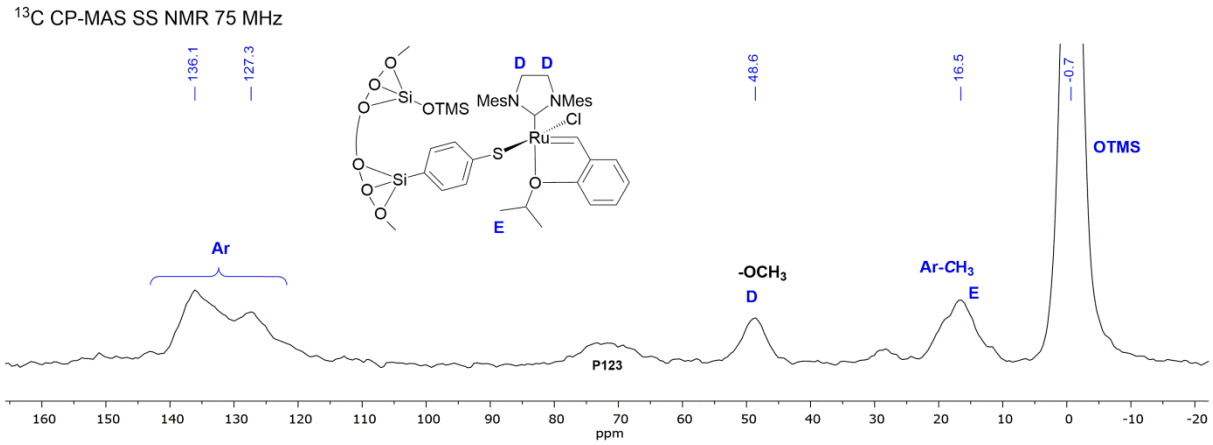
Material **Mat-PrSh** or **Mat-PhSh** (400 mg), dry toluene (4 mL) and KHMDS (0.5 M solution in toluene, 1 mL) were stirred for 2 h at room temperature under Ar atmosphere. The solvent was filtered off and the material washed with more toluene (3 x 8 mL). To the dry material, a solution of **HG-II** (125 mg) in toluene (8 mL) was added. The mixture was stirred for 20 h at room temperature. Subsequently, the solvent was filtered off and the material washed with dry DCM (3 x 10 mL). The material was dried under high vacuum for 20 h.

Mat-A: ^{1}H SS NMR (300 MHz): δ 8.52, 6.55, 3.43, 0.04 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 135.0, 127.4, 48.5, 16.7, -1.2 ppm; Elemental analysis: S 0.84 %, Ru 1.33 %.



Contact time: 1 ms; recycle delay: 5 s; number of scans: 14k.

Mat-B: ^{1}H SS NMR (300 MHz): δ 6.96, 3.31, -0.14 ppm; ^{13}C CP-MAS SS NMR (75 MHz): δ 136.1, 127.3, 48.6, 16.5, -0.7 ppm; Elemental analysis: S 0.53 %, Ru 1.24 %.



Contact time: 5 ms; recycle delay: 2 s; number of scans: 25k.

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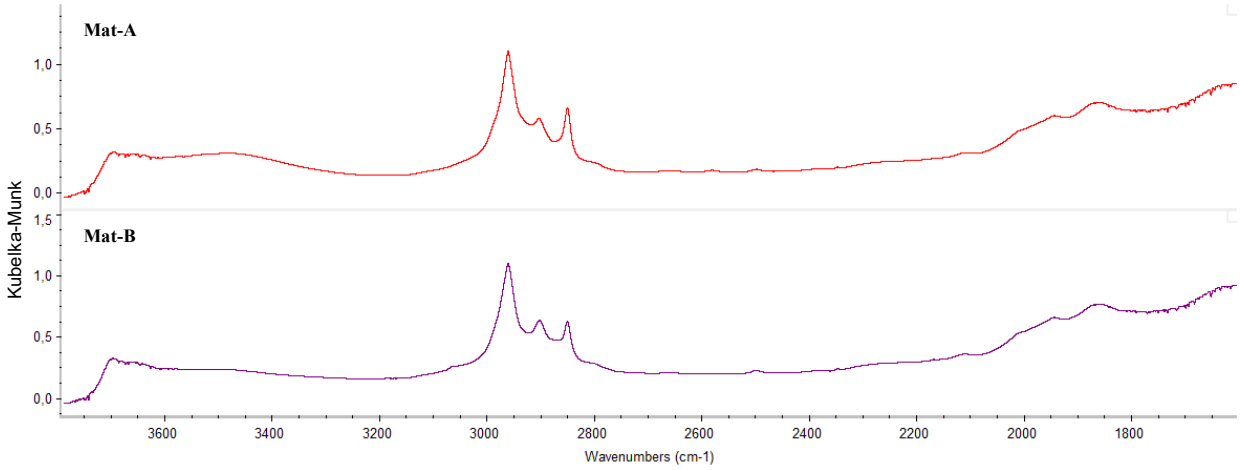


Procedure for the catalyst physisorption in the absence of base

A solution of **HG-II** (125 mg, mmol) in toluene (8 mL) was added to material **Mat-PhSh** (400 mg). The mixture was stirred for 20 h at room temperature. Subsequently, the solvent was filtered off and the material washed with dry DCM (3 x 10 mL). The material was dried under high vacuum for 20 h.

General procedure for catalytic tests

For **Mat-A** and **Mat-B**: The immobilized catalyst (≈ 10 mg) was weighed in a 2 mL vial with a stirring magnet inside the glovebox. Then, the dodecane (internal standard, ≈ 50 mg) and the substrate (≈ 500 mg) were added, the vial was capped and the reaction was stirred at the desired temperature. Samples were directly injected into a GC-FID, and yields and *Z*-selectivity were calculated against the internal standard.

[The catalytic test with the physisorbed material was carried out in the exact same way as described for **Mat-A** and **Mat-B**]

For **A, B** and **HG-II**: Inside the glovebox, the catalyst (≈ 10 mg) was dissolved in 0.5 mL of dry and degassed DCM and an aliquot of 20 µl was added into a 2 mL vial containing the dodecane (internal standard, ≈ 50 mg), the substrate (≈ 500 mg) and a stirring magnet. Then, the vial was capped and the reaction was stirred at the desired temperature. Samples were directly injected into a GC-FID, and yields and *Z*-selectivity were calculated against the internal standard.

Analytical methods:

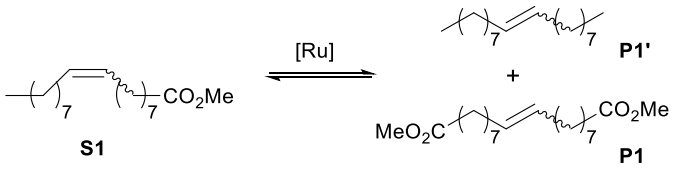
1-Hexene: column: DB-23, 0.25 µm x 0.25 mm x 50 m; carrier: hydrogen; oven temperature: 50 °C (5 min), 5 °C/min, 105 °C: hexene = 5.0 min; (*E*)-5-decene = 9.3 min, (*Z*)-5-decene = 9.6 min, dodecane = 14.0 min.

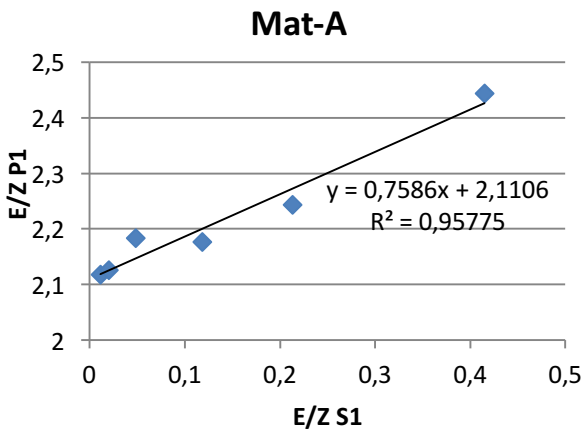
4-Phenyl-1-butene: column: HP-5, 0.25 µm x 0.32 mm x 30 m; carrier: hydrogen; oven temperature: 50 °C (5 min), 10 °C/min, 205 °C: 4-phenyl-1-butene = 12.1 min; (*E*)-1,6-diphenylhex-3-ene = 23.5 min, (*Z*)-1,6-diphenylhex-3-ene = 23.4 min, dodecane = 14.5 min.

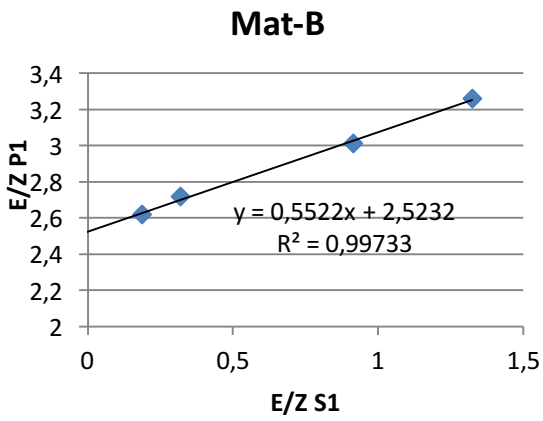
Methyl oleate: column: DB-23, 0.25 µm x 0.25 mm x 50 m; carrier: hydrogen; oven temperature: 80 °C (5 min), 10 °C/min, 150 °C (5 min), 10 °C/min, 250 °C (11 min): *E*-9-octadecene = 18.2 min, *Z*-9-octadecene = 18.3 min, methyl heptadecanoate = 25.3 min, methyl elaidate = 26.4 min, methyl oleate = 26.5 min, dimethyl *E*-9-octadecene-1,18-dioate = 33.3 min, dimethyl *Z*-9-octadecene-1,18-dioate = 33.5 min.

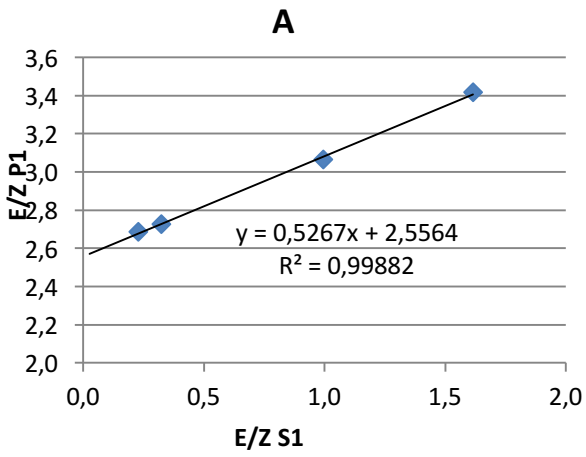
Plotted E/Z ratios in the self-metathesis of methyl oleate

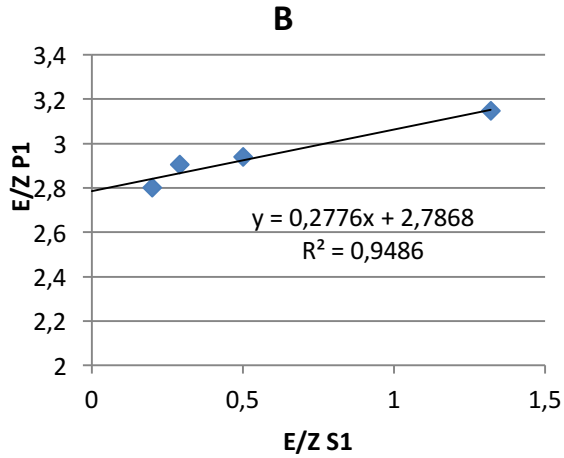
1 mg of homogeneous catalyst (**A** or **B**) were mixed with 300 mg of methyl oleate or 10 mg of heterogeneous catalyst (**Mat-A** or **Mat-B**) were mixed with 100 mg of methyl oleate. The reaction was stirred at room temperature. Samples were taken at different times during the first minutes of reaction and injected in the GC-FID. The *E*/*Z* ratios between the starting material (**S1**) and the diester (**P1**) of each sampling were plotted, and the *E*/*Z* value at 0% conversion was obtained by extrapolation of the trendline.



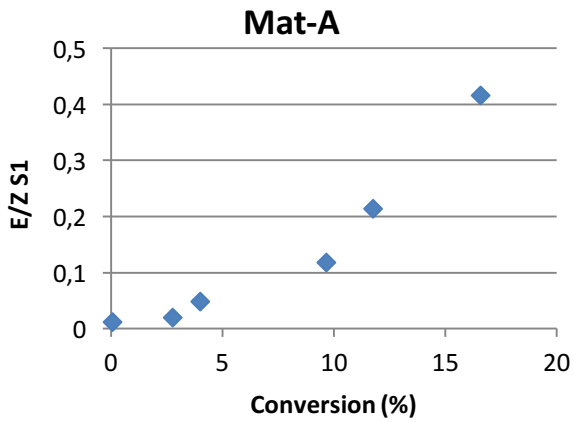


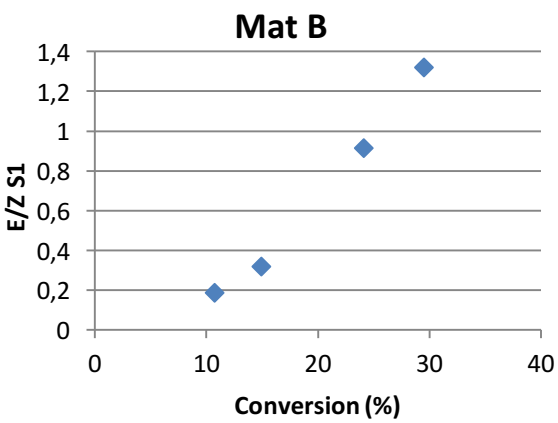


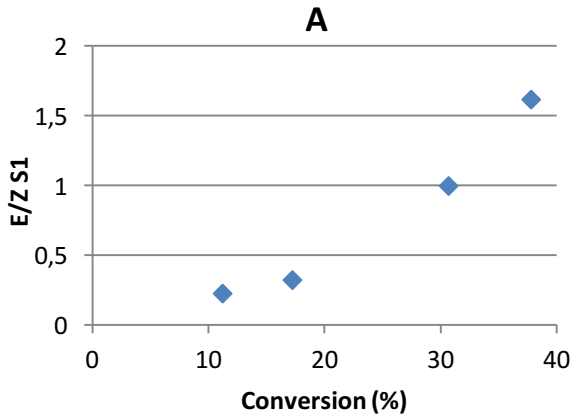


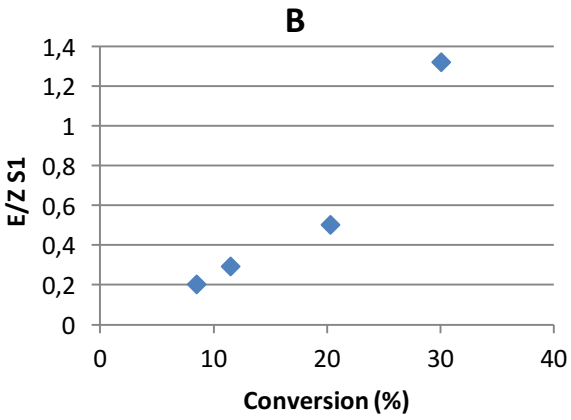


Conversion *vs* E/Z ratio of the starting material (**S1**)









Quantification of the initiated Ru-centers

111.9 mg of **Mat-A** were dissolved in 2 mL of ethyl vinyl ether and the slurry was stirred for 5 h. Then, the solution was filtered with a syringe filter and the solid washed with DCM. The obtained solution was gently concentrated at room temperature under a flow of Ar. 4.7 mg of mesitylene were added as internal standard and everything was dissolved in CD_2Cl_2. ^1H NMR quantification of 1-isopropoxy-2-vinylbenzene gave a 16% of the total Ru quantified by elemental analysis.