

Supporting information

Preparation of Ruthenium Olefin Metathesis Catalysts Immobilised on MOF, SBA-15 and 13X for Probing Heterogeneous Boomerang Effect

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Materials and Methods

General

Reactions requiring the use of a protective atmosphere were conducted using Schlenk technique in either Schlenk flasks or 4 mL vials, which had been dried at 130 °C for at least 12 h prior to use. All metathesis reactions and sorption of the catalysts were carried out in vials equipped with magnetic stirrers. Purging vials with argon was performed after closing them with a screw cap with septum and piercing it with a needle connected to a Schlenk line.

Solvents

Commercially available (HPLC grade) dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, toluene, and *n*-hexane were purified using solvent purification system MBRAUN SPS-800 and stored in ampules under argon over activated 4 Å molecular sieves for at least 12 h before use, water content was measured with Karl-Fisher apparatus (Titroline® 7500 KF trace) and did not exceed 2 ppm in each case. Anhydrous solvents dimethylformamide (DMF), pyridine, and methanol (MeOH) were purchased from Sigma Aldrich and used as received. *n*-Hexane, EtOAc and DCM for column chromatography were purchased from Avantor Performance Materials Poland S.A. and distilled prior to use.

Reagents

Substrates **12** [1], **14** [2], **18** [3], **20** [4] were prepared according to literature procedures. Substrate **16** was supplied by Sigma Aldrich. All substrates had been freeze/pump/thaw degassed and stored in an argon atmosphere over activated 4 Å molecular sieves for at least 12 h before use. MOF (Al)MIL-101-NH₂ was synthesised according to literature procedure [5], activated at 130 °C under vacuum and stored in a Schlenk flask in an argon atmosphere. Ruthenium catalysts were prepared using either known literature procedure [6] or these stated in paragraph *Synthesis and characterization of newly obtained compounds*, stored in an argon atmosphere and refrigerated at 4 °C. Unless otherwise noted, all common laboratory reagents (NaOH, KOH, Na₂SO₄, MgSO₄, KI, NaCl, NH₄Cl, HCl, H₂SO₄, Na₂CO₃, NaHCO₃) were purchased from Avantor Performance Materials Poland S.A. and used as received. Aluminium oxide (Neutral, Brockmann grade I) was purchased from Sigma Aldrich and activated by heating for at least 3 days at 200 °C prior to use. SnatchCat™ metal scavenger was synthesized according to the known literature procedure [7] and used as a 4.5 mM solution in DCM. Silica gel 60 (230 - 400 mesh) was purchased from Merck and used as received. Sodium hydride (60% in mineral oil) was purchased from TCI Chemicals and used as received. Molecular sieve 13X (powder 2 µm avg. part. size) and mesoporous SBA-15 (<150 µm particle size, pore size 8 nm, hexagonal pore morphology) were purchased from Sigma Aldrich and activated by heating for 24 h at 200 °C under vacuum and stored in an argon atmosphere.

Analytics

GC analyses were performed by means of PerkinElmer Clarus 580 chromatograph with FID detector and GL Sciences InertCap 5MS/Sil Capillary Column (Inner Diameter 0.25 mm, Length 30 m, df 0.50 µm). GC-MS analyses were performed using PerkinElmer Clarus 680 chromatograph with Mass Spectrometer Clarus SQ 8C detector and GL Sciences InertCap 5MS/Sil Capillary Column (Inner Diameter 0.25 mm, Length 30 m, df 0.50 µm).

NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in ppm with a solvent residual peak as a reference (7.26 and 77.16 ppm for ¹H and ¹³C in CDCl₃, 4.87 and 49.00 ppm for ¹H and ¹³C in CD₃OD). Deuterated solvents (chloroform, methanol) were purchased from Euroisotop, stored over molecular sieves and used without further purification. The following abbreviations are used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), sep (septet), m (multiplet), br (broad). ¹H NMR signals are given followed by their multiplicity, coupling constants J in hertz and integration in parentheses.

Elemental Analyses (EA) of carbon, hydrogen, nitrogen, and sulphur were conducted on automatic analyser Elementar Unicube. Chlorine content was examined using a potentio-argonometric method (titration with silver nitrate) on apparatus Mettler Toledo Titrator T50.

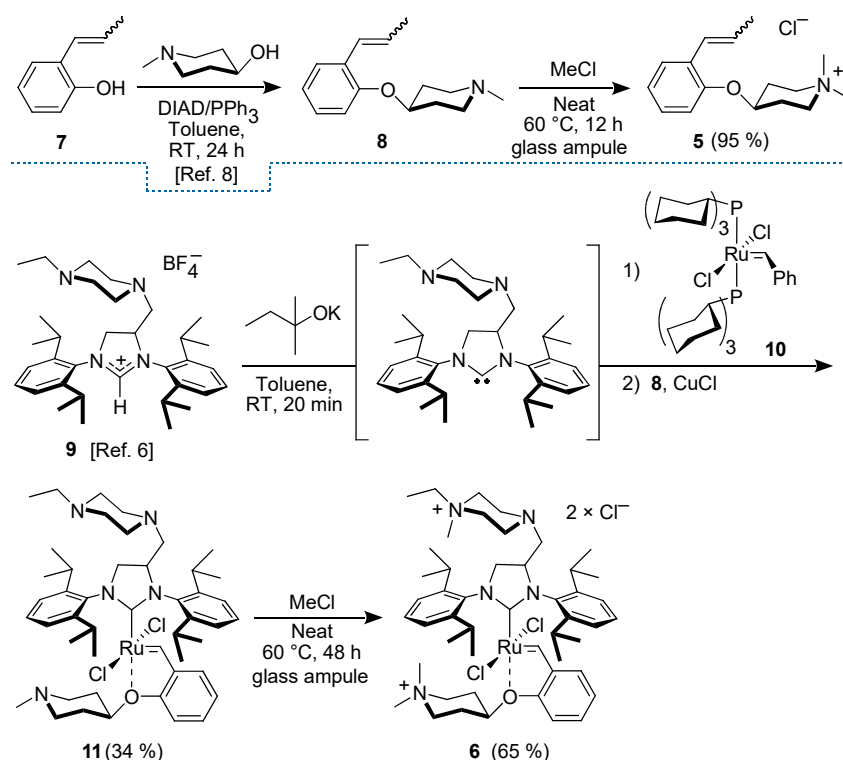
High-Resolution Mass Spectra (HRMS) was performed using Synapt G2-S mass spectrometer (Waters) equipped with the electrospray ion source and quadrupole-Time-of-flight mass analyzer. The measurements were performed in positive ion mode with the resolving power of the TOF analyzer 40000 FWHM. The instrument worked with external calibration on sodium formate in the mass range of $m/z = 50$ -2000. The lock spray spectrum of the leucine-enkephalin was generated by the lock spray source and correction was done for every spectrum. The exact mass measurements for all peaks were performed within 3 mDa mass error.

UV-Vis spectra were collected with Thermo Fisher Scientific Evolution 300 UV-Vis spectrometer in 10.00 mm QS cuvettes with scan speed 600 nm/min., range 300 – 500 nm, bandwidth 1 nm and data interval 1 nm.

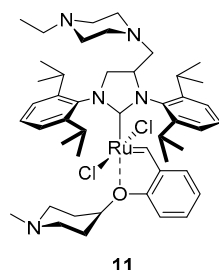
Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover X-ray diffractometer ($\text{CuK}\alpha$ radiation, parallel beam formed by Goebel mirror) equipped with a VANTEC 1 position-sensitive detector. All measurements were performed on standard aluminium holders.

For the measurement of N_2 sorption isotherms, the samples were thermally activated and degassed immediately prior to the N_2 physisorption measurements for at least 12 h at 80 °C. The nitrogen sorption isotherms were determined at liquid nitrogen temperature (77 K) using Micrometrics ASAP 2020 or Quantachrome Autosorb-IQ-MP sorption analyzer. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method using P/P_0 values in the range 0.05-0.2.

Synthesis and characterization of newly obtained compounds



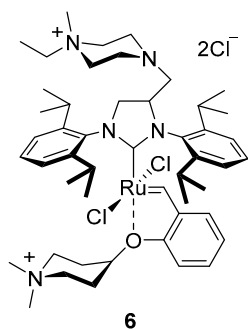
Complex 11



NHC precursor **9** (466 mg, 0.771 mmol, 1.15 equiv.), which had been prepared according to the known literature procedure [6], was dried under vacuum at 60 °C for 1 h, suspended in toluene (2 mL) and treated with potassium *tert*-amylate in toluene (1.7 M, 200 μ L, 0.704 mmol, 1.05 equiv.). A turbid carbene adduct solution was formed over 10 min. at ambient temperature. Then Grubbs 1st generation catalyst (551 mg, 0.67 mmol, 1 equiv.) was added and the mixture was stirred at 80 °C. The solution turned dark red over 20 min. and then **8** (341 mg, 1.47 mmol, 2.2 equiv.) was added in toluene (2 mL) followed by the addition of CuCl (168 mg, 1.68 mmol, 2.5 equiv.). The solution turned dark green over 15 min. with the formation of a brown precipitate. The mixture was then cooled down to RT, filtered through a Celite pad, evaporated, and the product was isolated using column chromatography (silica, 0 – 5 % gradient of NEt₃/EtOAc). The green fractions were evaporated yielding dark green oil, which was again purified by column chromatography (neutral alumina, 5 – 20 % EtOAc/hexane). The pure fractions were combined and evaporated, yielding crude green crystalline product (205 mg, 0.23 mmol, 34%) which was immediately used in the next step without further purification.

HRMS(ESI): m/z calcd for C₄₇H₇₀Cl₂N₅ORu [M+H]⁺ 892.4001, found 892.3985.

Complex 6



At $-78\text{ }^{\circ}\text{C}$ an excess of liquid MeCl was transferred into a glass pressure-resistant ampule previously cooled down to $-78\text{ }^{\circ}\text{C}$. Then complex **11** (205 mg, 0.23 mmol, 1 equiv.) was added and dissolved. The vessel was closed and put in a heated bath at $60\text{ }^{\circ}\text{C}$ for 48 h. During the process, a precipitation was observed. After 48 h the ampule was cooled down to ambient temperature and excess of MeCl was evaporated. The crude product was purified by column chromatography (acid activated alumina, gradient 0 – 5 % MeOH/DCM). The pure fractions were combined, evaporated and dried under vacuum, yielding green hygroscopic product (149 mg, 0.15 mmol, 65%).

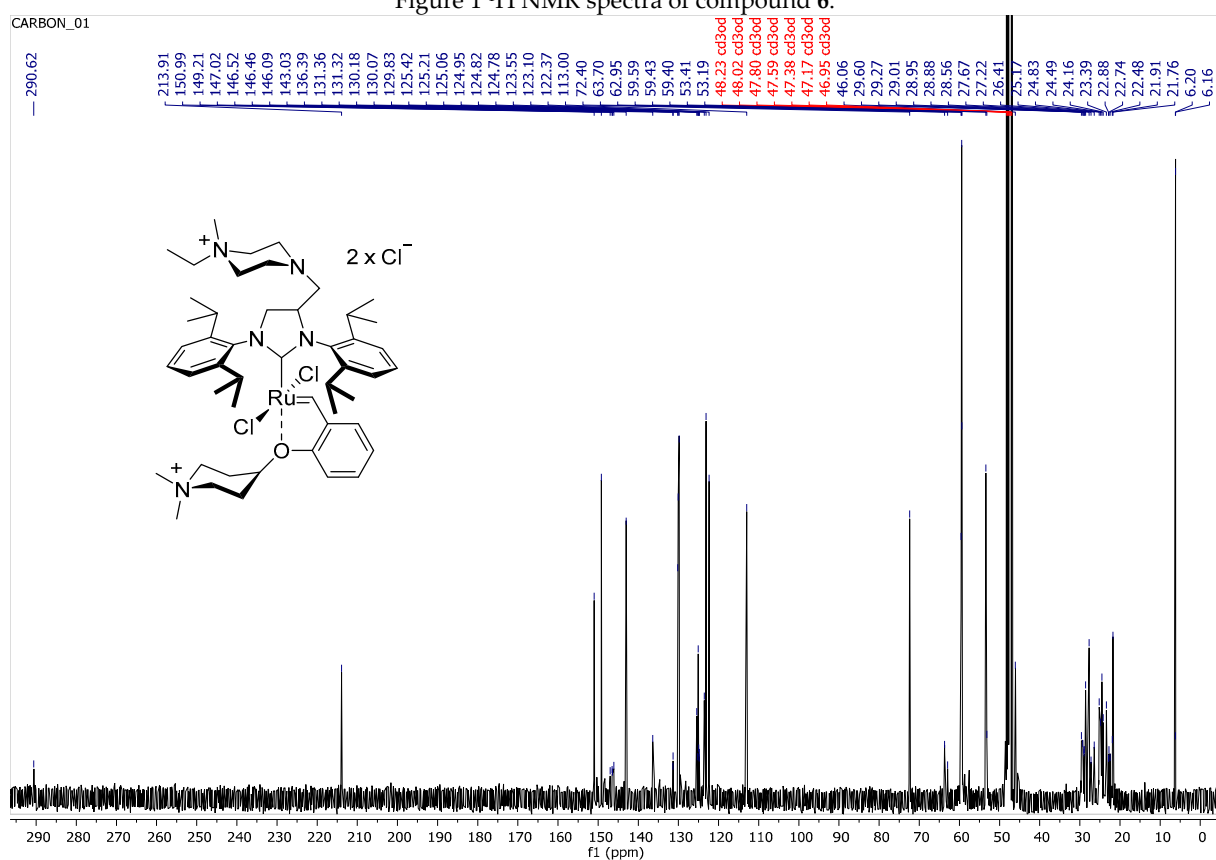
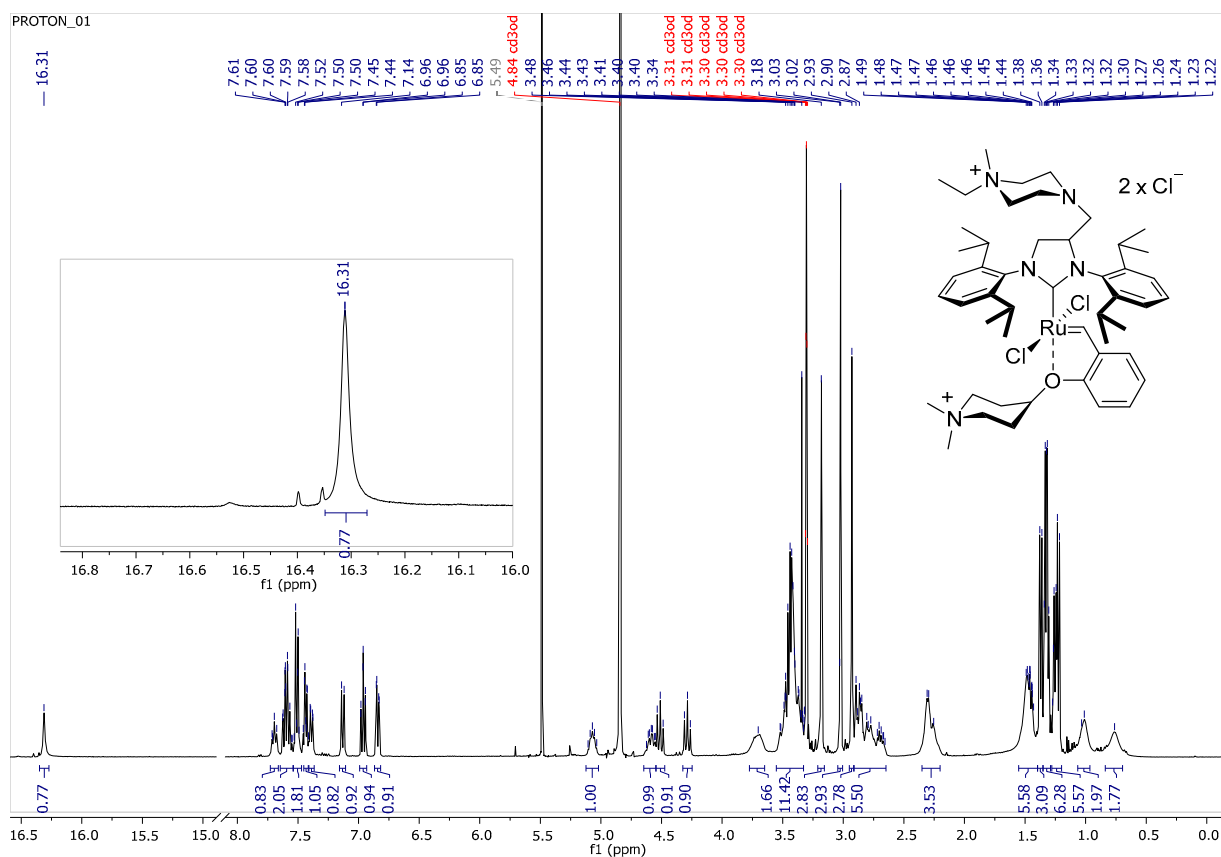
^1H NMR (400 MHz, Methanol- d_4) δ 16.31 (s, 1H), 7.70 (t, $J = 7.7\text{ Hz}$, 1H), 7.64 – 7.54 (m, 2H), 7.51 (d, $J = 8.0\text{ Hz}$, 2H), 7.44 (dd, $J = 7.8, 1.5\text{ Hz}$, 1H), 7.39 (dd, $J = 7.8, 1.5\text{ Hz}$, 1H), 7.13 (d, $J = 8.3\text{ Hz}$, 1H), 6.96 (td, $J = 7.5, 0.7\text{ Hz}$, 1H), 6.84 (dd, $J = 7.6, 1.6\text{ Hz}$, 1H), 5.07 (p, $J = 7.0\text{ Hz}$, 1H), 4.65 – 4.46 (m, 2H), 4.29 (t, $J = 9.7\text{ Hz}$, 1H), 3.70 (s, 2H), 3.57 – 3.29 (m, 10H), 3.18 (s, 3H), 3.02 (s, 3H), 2.93 (s, 3H), 2.91 – 2.63 (m, 3H), 2.28 (d, $J = 21.8\text{ Hz}$, 4H), 1.57 – 1.40 (m, 2H), 1.40 – 1.19 (m, 15H), 1.01 (s, 2H), 0.76 (s, 2H) ppm.

^{13}C NMR (101 MHz, Methanol- d_4): δ 290.6, 213.9, 151.0, 149.2, 147.0, 146.5, 146.5, 146.1, 143.0, 136.4, 131.7, 131.3, 130.2, 130.1, 129.8, 125.4, 125.2, 125.1, 125.0, 124.8, 124.8, 123.6, 123.1, 122.4, 113.0, 72.4, 63.7, 63.0, 59.6, 59.4, 59.4, 53.4, 53.2, 46.1, 29.6, 29.3, 29.0, 29.0, 28.9, 28.6, 27.7, 27.2, 26.4, 25.2, 24.8, 24.5, 24.2, 23.4, 22.9, 22.7, 22.5, 21.9, 21.8, 6.2, 6.7.

IR (solid phase): 3380, 2967, 2928, 2869, 1705, 1624, 1589, 1474, 1386, 1325, 1302, 1262, 1183, 1158, 1110, 1047, 1032, 990, 955, 926, 873, 808, 757, 640 cm^{-1} .

Elemental analysis calcd for $\text{C}_{49}\text{H}_{75}\text{Cl}_4\text{N}_5\text{ORu} \cdot 2\text{ MeOH} \cdot \text{H}_2\text{O}$: C, 57.03; H, 7.88; N, 6.52; Cl, 13.20; found: C, 56.99; H, 7.87; N, 6.22; Cl, 12.92.

HRMS(ESI): m/z calcd. for $\text{C}_{49}\text{H}_{75}\text{Cl}_4\text{N}_5\text{ORu} [\text{M}]^{2+}$ 460.7191; found 460.7186.



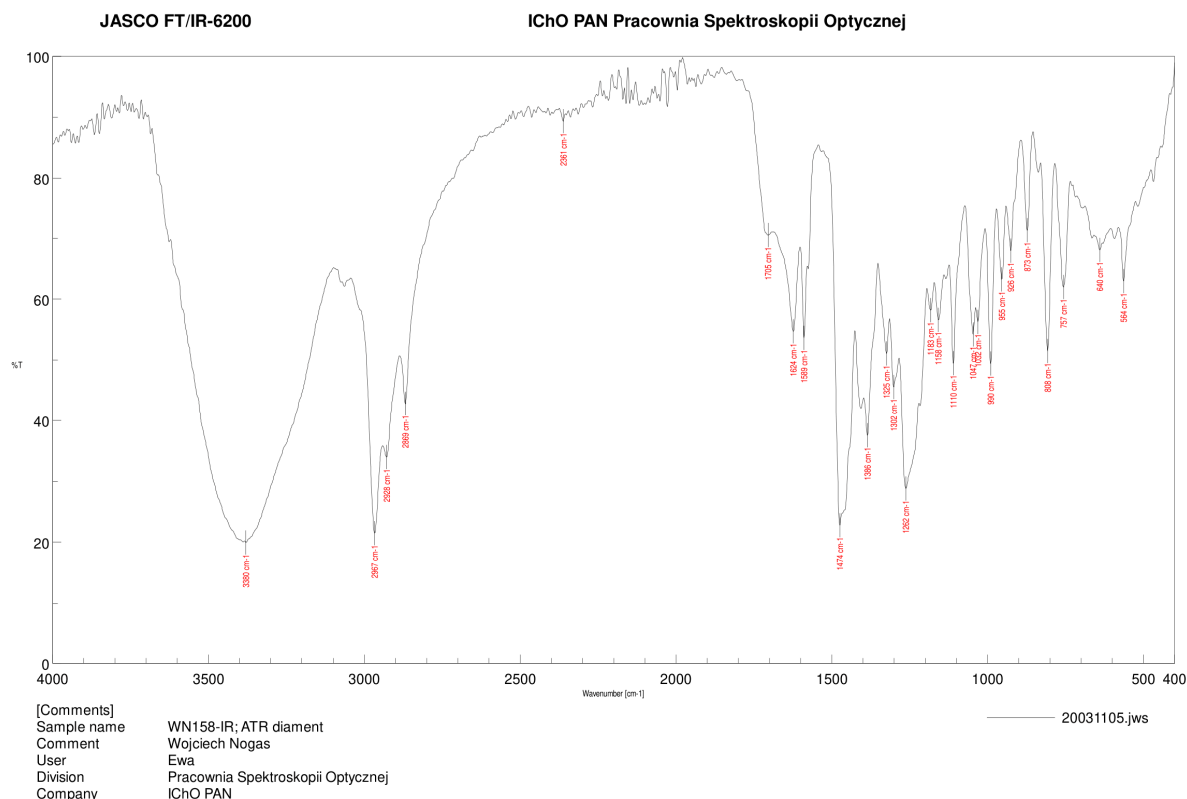
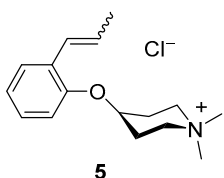


Figure 3 IR spectra of compound 6.

1,1-dimethyl-4-(2-(prop-1-en-1-yl)phenoxy)piperidinium chloride (5)



A pressure vessel containing propenylbenzene derivative **8** [8] (310 mg, 1.35 mmol, 1 equiv) was cooled in a acetone/dry ice bath and MeCl (1.3 g, 27 mmol, 20 equiv) was condensed in the vessel. Then the flask was tightly closed and heated for 12 h at 60 °C. After that time, MeCl was evaporated and the white residue was dissolved in a mixture of DCM/hexane (1:1, 10 mL). Then the solution was evaporated in a rotary evaporator until it turned turbid. At this point the evaporation was stopped, hexane (5 mL) was added and the suspension was kept in a fridge for 12 h until white product precipitated. Then it was decanted, washed with EtOAc, hexane and dried, yielding off white hygroscopic product (360 mg, 1.28 mmol, 95 %). *E/Z* ratio (¹H NMR): 5.0.

¹H NMR(400 MHz, CDCl₃): δ 7.38 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.25 – 7.11 (m, 1H), 7.00 – 6.83 (m, 2H), 6.59 (dq, *J* = 15.8, 1.8 Hz, 1H), 6.45 (dd, *J* = 11.5, 2.0 Hz, 0H), 6.17 (dq, *J* = 15.8, 6.6 Hz, 1H), 5.83 (dq, *J* = 11.5, 7.0 Hz, 0H), 4.70 (qt, *J* = 4.7, 2.5 Hz, 1H), 4.07 – 3.93 (m, 2H), 3.70 (s, 3H), 3.68 (s, 1H), 3.59 – 3.46 (m, 7H), 2.42 (ddt, *J* = 14.7, 10.7, 3.6 Hz, 2H), 2.16 – 2.04 (m, 3H), 1.88 (dd, *J* = 6.6, 1.8 Hz, 3H), 1.77 (dd, *J* = 7.0, 1.8 Hz, 1H).

¹³C NMR(101 MHz, CDCl₃): δ 153.2, 152.3, 130.9, 128.6, 128.2, 128.1, 128.0, 127.8, 127.5, 127.1, 125.0, 122.4, 121.9, 115.0, 114.7, 67.3, 67.1, 58.8, 58.51, 54.6, 49.3, 25.3, 25.1, 19.1, 14.8.

IR (solid phase): 3402, 3033, 2957, 2877, 1706, 1597, 1486, 1454, 1403, 1326, 1237, 1168, 1115, 1057, 978, 928, 848, 758, 701, 622, 534, 482, 402 cm⁻¹.

Elemental analysis calcd for C₁₆H₂₄ClNO*½H₂O: C, 66.08; H, 8.66; N, 4.82; Cl, 12.19. Found: C, 66.12; H, 8.60; N, 5.06; Cl, 12.05.

HRMS(ESI): *m/z* calcd. for C₁₆H₂₄NO [M]⁺ 246.1858, found 246.1857.

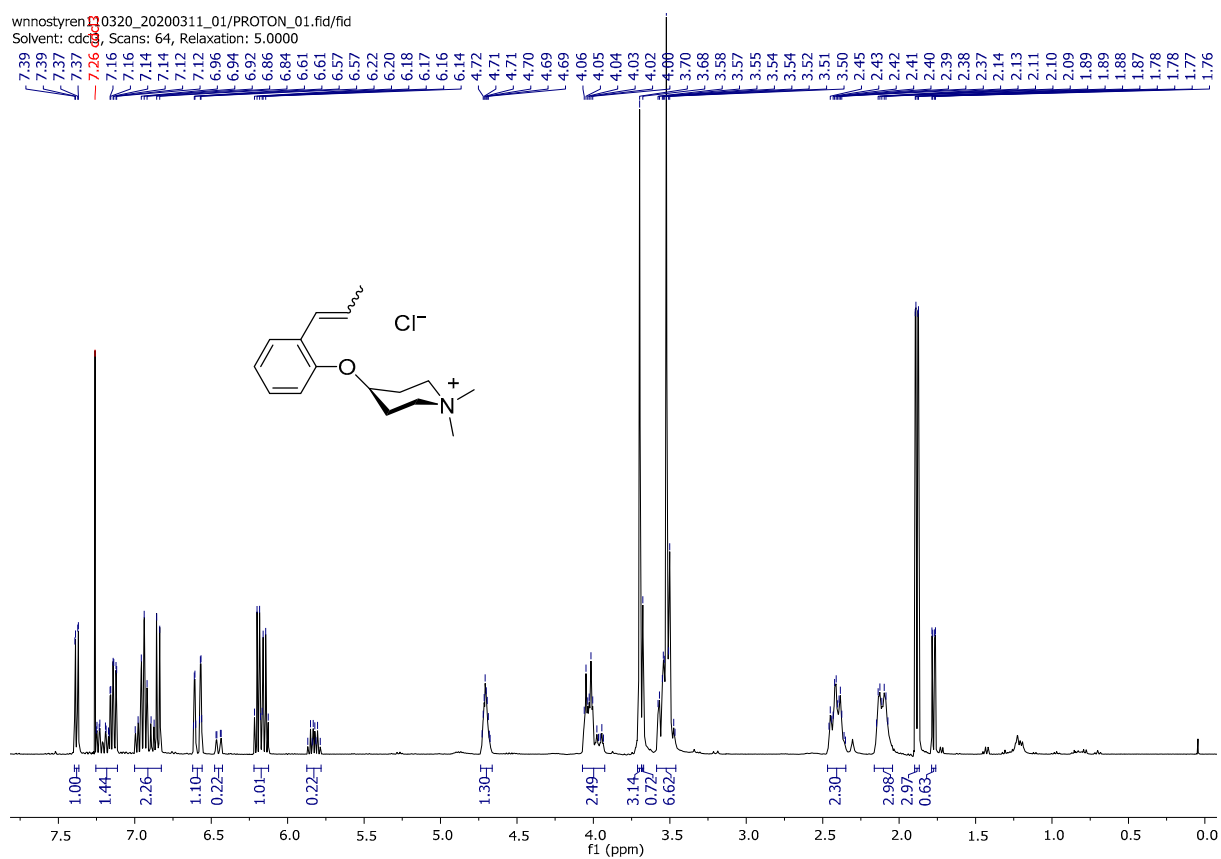


Figure 4 Figure 5 ¹H NMR spectra of compound 5.

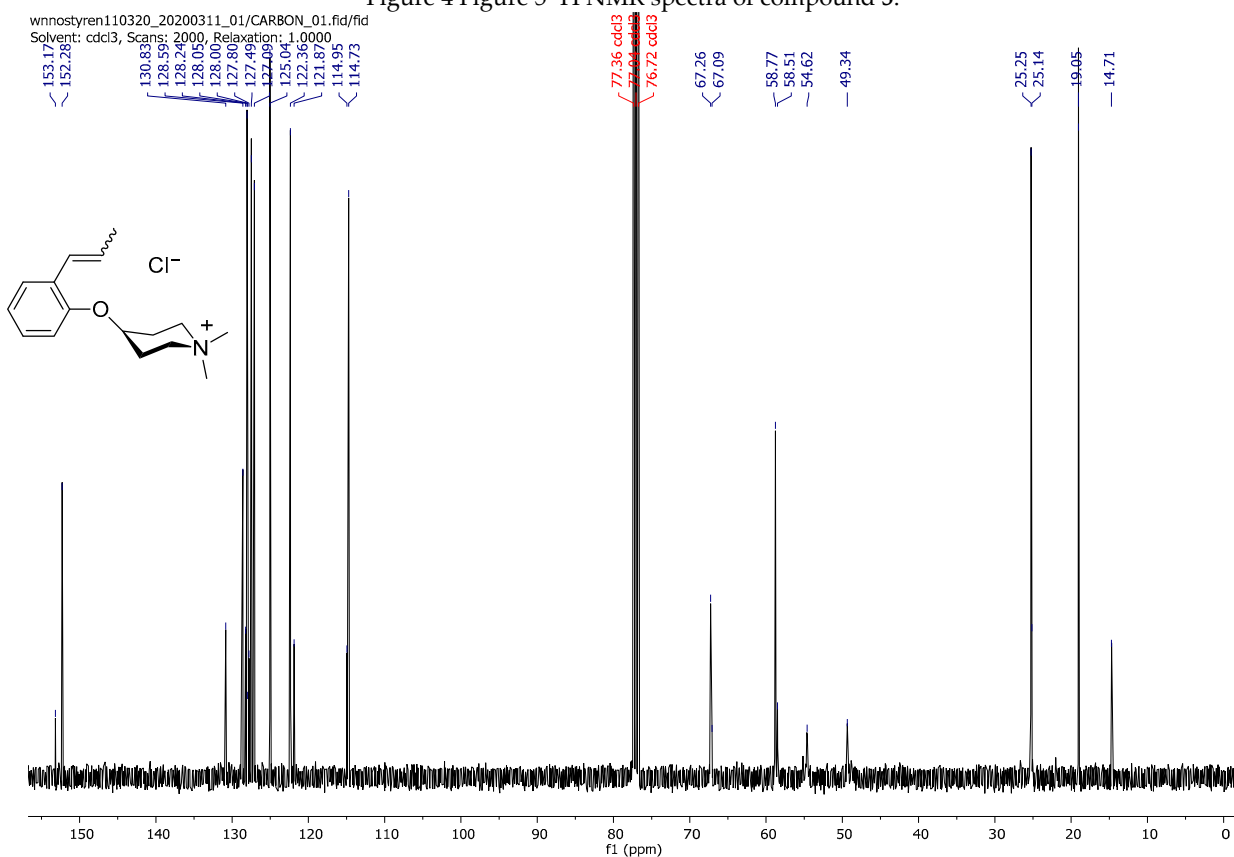


Figure 6 ¹³C NMR spectra of compound 5.

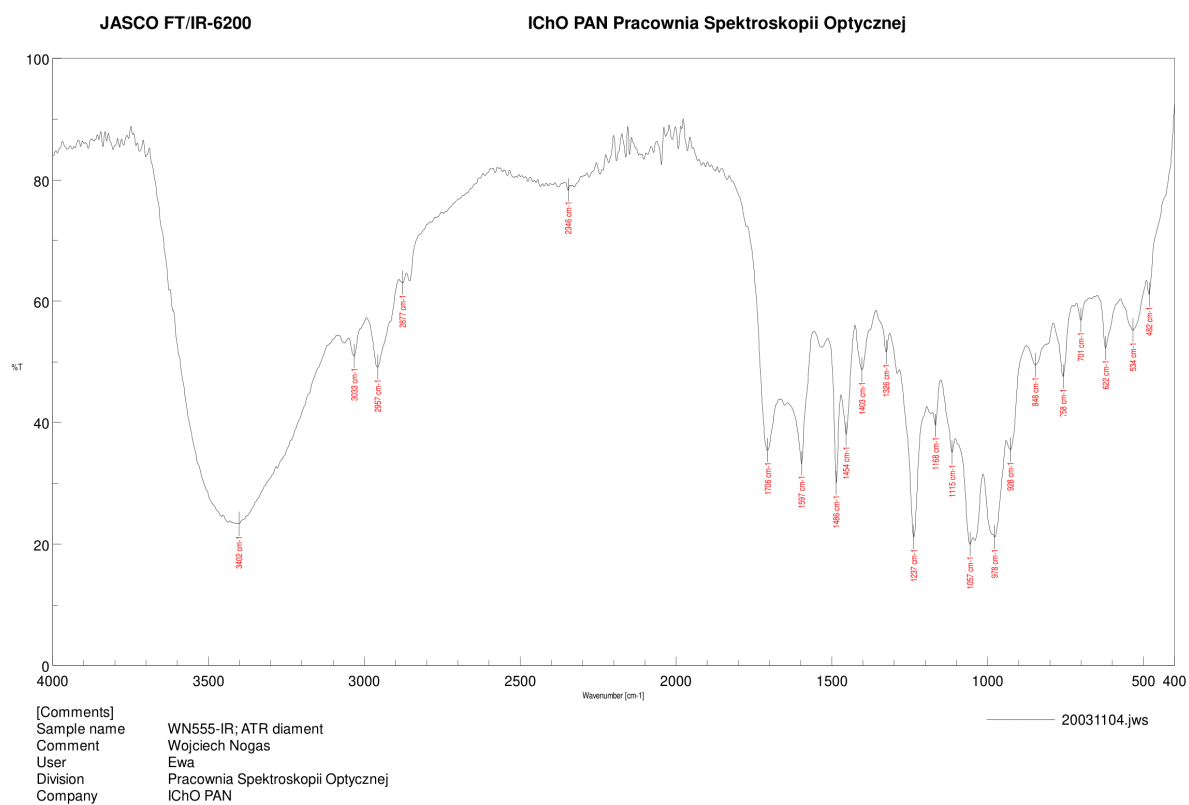


Figure 7 IR spectra of compound 6.

Catalysts and ligand immobilization

The immobilization of ruthenium-based catalysts on MOF (Al)MIL-101-NH₃Cl has been previously reported in the literature, and the below procedure is optimal as based on the reference. Similarly, all the specific porous material characterization data (BET surface area, SEM images, EDS analysis, PXRD patterns) are available there [5].

In an oven-dried and purged with argon vial closed with a screw cap containing a magnetic stirrer, MOF (Al)MIL-101-NH₂ was weighed (100 mg). Then 1 M solution of HCl in anhydrous diethyl ether was added (2 mL). The suspension was sonicated and then stirred at RT for 0.5 h. After that, the vial was centrifuged, the solvent was removed and the MOF was left to dry for several min. under vacuum. Mass of the MOF increased to 120 mg because of HCl accumulation. After that, the stock solution of a catalyst in DCM was added (0.59 mg of the catalyst, concentration 1 mg/mL). In the case of the experiments with the addition of **5**, the previous was followed by the addition of a stock solution of **5** (concentration 10 mg/mL, quantity dependent on the catalyst/**5** ratio). The vial was sonicated and stirred for 1 h. Then it was centrifuged, the solvent was removed and the catalytic material was left to dry under vacuum overnight. Catalyst@MOF was obtained as a yellow powder (ca. 120 mg, 0.5 wt. % of the catalyst).

The same procedure was used for SBA-15 and 13X supports omitting the HCl treatment. For smaller volumes of ruthenium complex solution used for immobilisation (≤ 0.5 mL) the centrifugation step was skipped and all the solvent was removed in vacuum. Prepared materials with a catalyst can be stored refrigerated in an argon atmosphere for at least a month without a significant decrease in catalytic activity.

Proving the possibility of **6** diffusing inside pores of MOF

Using the protocol described above, the immobilization in 10 wt. % of complex **6** inside the support was attempted. In an oven-dried and purged with argon vial closed with a screw cap containing a magnetic stirrer, MOF (Al)MIL-101-NH₂ was weighed (42 mg). Then 1 M solution of HCl in anhydrous diethyl ether was added (0.84 mL). The suspension was sonicated and then stirred at RT for 30 min. After that, the vial was centrifuged, the solvent was removed and the MOF was left to dry for several minutes under reduced pressure of an oil pump. Mass of the MOF increased to 50 mg because of HCl accumulation. After that, the stock solution of the catalyst in DCM was added (5.5 mg of the catalyst, concentration 2 mg/mL). The vial was sonicated and stirred for 1 h. Then it was centrifuged, the supernatant solvent was removed and analysed by UV-VIS spectroscopy. The immobilization was complete – only 0.3 % of catalyst remained in supernatant solution.

Calculating the external surface of the crystallites of MOF can give approximate number how much of the catalyst can be immobilized on the surface. Using cuboid shape for the MOF ($0.2 \times 0.2 \times 0.5$ μm) and density (0.71 g/mL) [9] external surface can be calculated as ca. 34 m²/g. When that surface is covered with **6** (1.7×1.2 nm) the maximal loading on the external surface is 2.7 wt. %.

This experiment shows that the ruthenium complex **6** can enter the inside pores of MOF.

Characterization of porous materials

13X

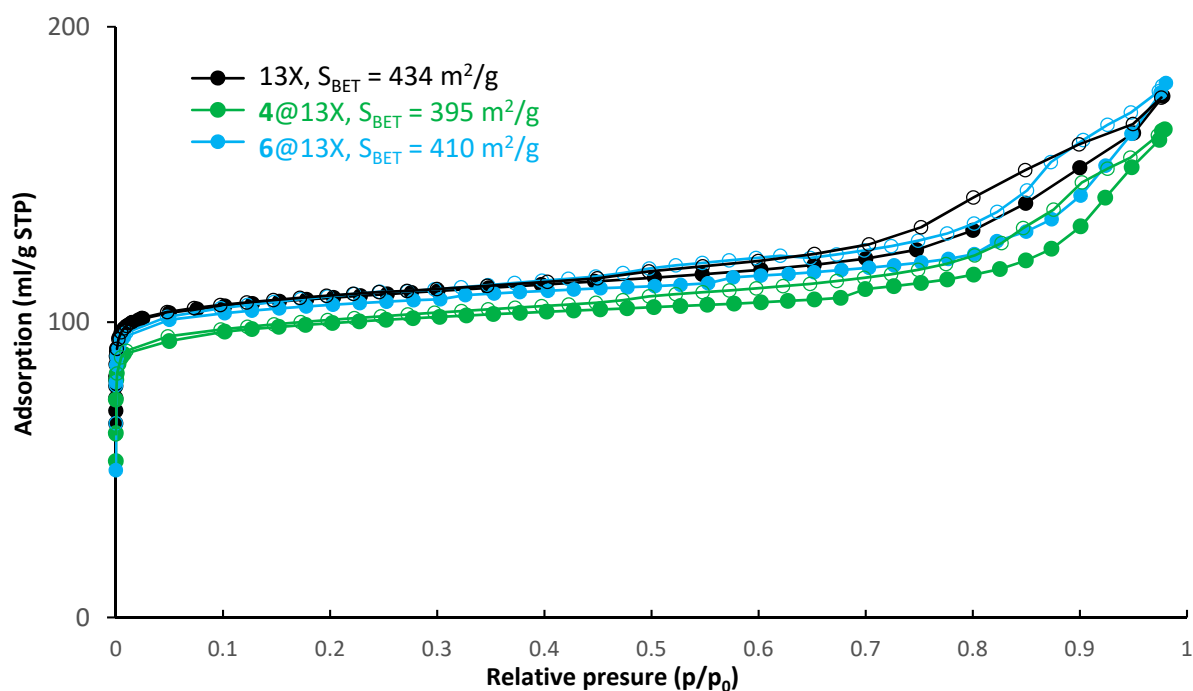


Figure 8 N₂ adsorption isotherm of 13X, 0.5 wt. % of 4@13X and 0.5 wt. % of 6@13X. Full marks represent adsorption, empty desorption curve.

SBA-15

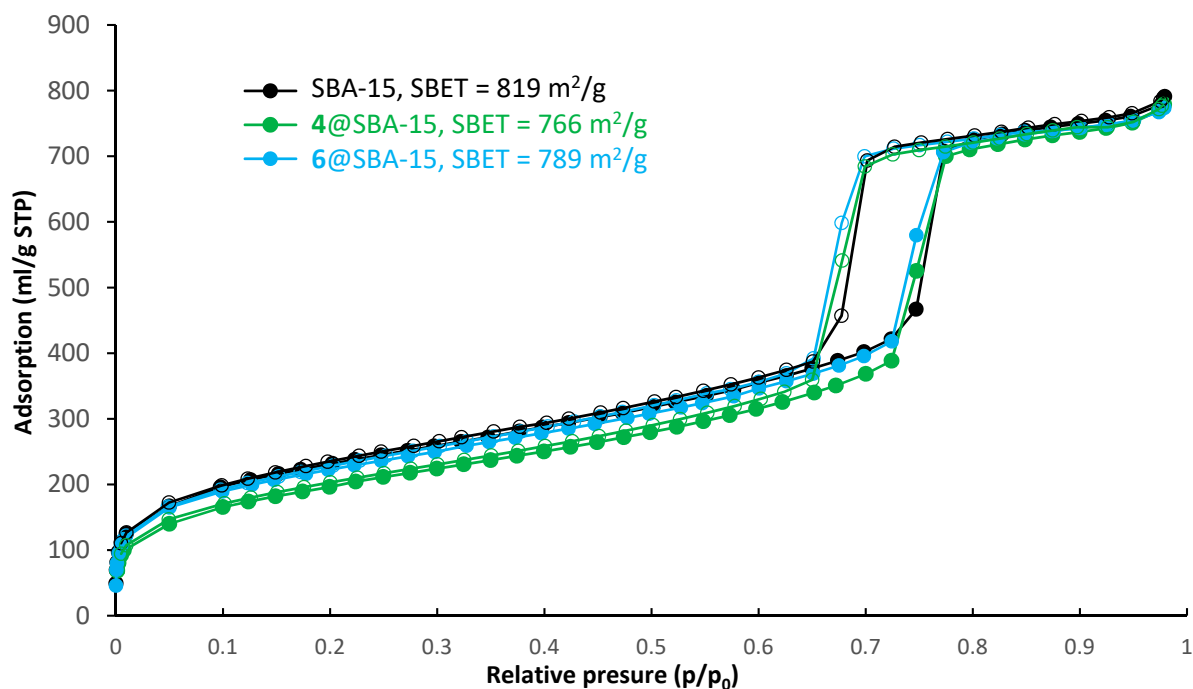


Figure 9 N₂ adsorption isotherm of SBA-15, 0.5 wt. % of 4@SBA-15 and 0.5 wt. % of 6@SBA-15. Full marks represent adsorption, empty desorption curve.

(Al)MIL-101-NH₃Cl

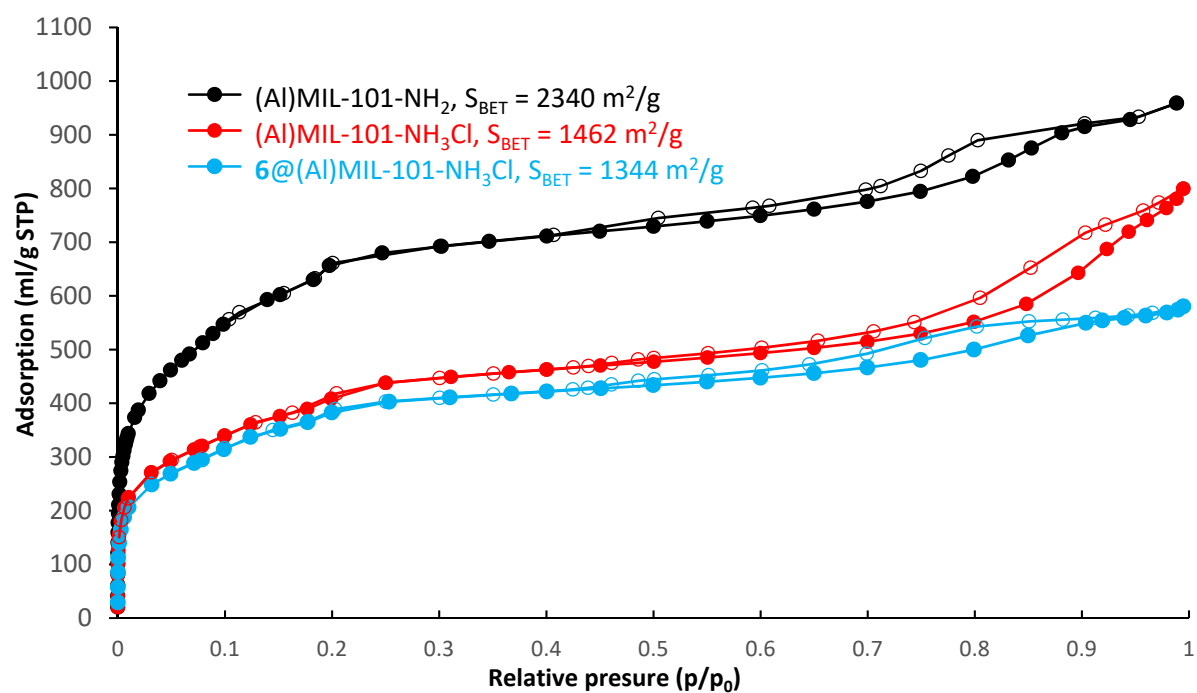


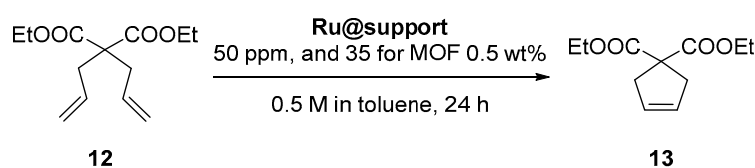
Figure 10 N₂ adsorption isotherm of (Al)MIL-101-NH₂, 4@(Al)MIL-101-NH₂ and 6@(Al)MIL-101-NH₂. Full marks represent adsorption, empty desorption curve.

Catalysis

Homogeneous metathesis

In a 4 mL vial covered with a septum cap and purged with argon (3 x), 0.5 M solution of the substrate with internal standard (0.05 M durene) in toluene or DCE (1 mL) was placed followed by the addition of a stock solution of the catalyst (concentration 1 mg/mL, ca. 50 μ L, the amount corresponding to 50 ppm loading of the catalyst). The reaction was stirred at 50 $^{\circ}$ C for 24 h. After that, 1 mL of 4.5 mM solution of SnatchCatTM in DCM was added and the conversion was measured by GC.

Temperature scope for catalysts

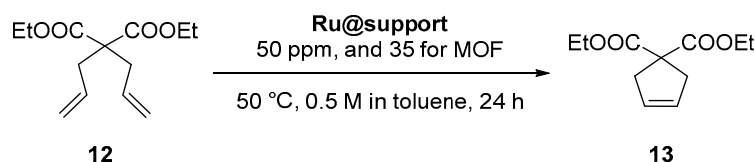


In a 4 mL vial covered with a septum cap, equipped with a magnetic stirrer, catalytic material (50 ppm for SBA, 13X and 35 ppm for MOF, relative to the substrate) was weighted (in the air). The vial was purged with argon (3 x). Then 2 mL of 0.5 M substrate (DEDAM) solution in toluene (2 mmol) with an internal standard (0.05 M durene) was added and stirred at the desired temperature for 24 h. The catalytic material was then filtered off and the conversion was determined by GC analysis.

Table 1 Effect of reaction temperature on the productivity of the heterogeneous system

Catalyst/support	Reaction temperature results in conversion [%] (TON)			
	30 $^{\circ}$ C	50 $^{\circ}$ C	70 $^{\circ}$ C	105 $^{\circ}$ C
4	35 (7000)	52 (10 400)	52 (10 400)	52 (10 400)
4@13X	52 (10 400)	50 (10 000)	50 (10 000)	34 (6 800)
4@SBA-15	42 (8 400)	64 (12 800)	66 (13 200)	60 (12 000)
4@MOF	39 (11 200)	59 (16 800)	55 (15 700)	36 (10 400)
6@MOF	17 (4 750)	28 (8 000)	29 (8 200)	22 (6 400)

Loading scope for catalysts (see Table 1 in manuscript)



Supports with different catalyst loadings (1, 0.5, 0.1, 0.05 wt. %) were prepared according to the procedure from paragraph *Catalysts and ligand immobilization*. Then they were tested in metathesis reaction according to the procedure *Temperature scope for catalysts* except that the temperature was fixed at 50 $^{\circ}$ C.

Metathesis with the addition of 5 (see Table 2 in manuscript)

Preparing the catalytic materials was parallel as in paragraph *Catalysts and ligand immobilization*.

The procedure for a metathesis reaction was identical as in paragraph *Temperature scope for catalysts*, with 50 ppm catalyst loading and temperature 50 °C.

Reuse of heterogeneous catalyst

In a 4 mL vial covered with a septum cap, equipped with a magnetic stirrer, catalytic material (500 ppm relative to the substrate amount) was weighted (in the air). The vial was purged with Ar (3 x). Then 1 mL of 1 M substrate (DEDAM) solution in toluene (1 mmol) with an internal standard (0.1 M) was added and stirred at 50 °C for 1 h. The supported catalyst was then centrifuged and the clear solution decanted from above the solid to determine the conversion by GC analysis. Then the catalytic material was washed with anhydrous toluene (4 x) by repeating the sonication-centrifugation-decantation procedure. Then a new portion of the substrate was added and all the activities were repeated until the final cycle.

Table 2 Effect of ligand precursor 5 co-immobilized on a support on the productivity of the resulted heterogeneous system

Catalyst	4@SBA-15				6@SBA-15		4@MOF			6@MOF		
Equiv. of 5 per catalyst /cycle	5	10	20	-	10	-	20	70	-	20	70	-
1	73	53	40	98	42	91	100	99	99	16	3	60
2	48	37	22	80	23	66	93	93	95	10	2	38
3	40	25	16	69	14	54	91	86	92	7	2	26
4	33	21	14	58	17	42	80	78	77	7	2	20
5	28	16	11	36	14	34	67	62	68	6	1	18
6	29	18	10	27	15	36	44	43	44	7	2	17
7	22	14	9	21	14	27	38	36	40	6	1	14
8	21	12	8	14	15	30	35	33	36	5	2	13
9	19	10	7	11	13	18	29	27	31	5	1	12
10	13	8	25	17	8	14	25	25	26	5	1	10
11	14	9	5	8	16	14	23	22	21			
12	15	8	5	0	13	12	20	20	21			
13	11	7	4	0	8	10						
summary TON	7329	4773	3490	8762	4250	8934	12880	12458	12994	1480	340	4560

Results in conversion [%]

Scope of substrates (see Table 3 in manuscript)

To a 4 mL vial covered with a septum cap, equipped with a magnetic stirrer, catalytic material (catalyst loading was different for each substrate) was weighted (in the air). The vial was purged with Ar (3 x). Then 1 mL of 1 M substrate solution in toluene (1 mmol) with internal standard (0.1 M durene) was added and stirred at 50 °C for 24 h. The catalytic material was then filtered off and the conversion was determined by GC analysis.

Probing the boomerang existence (excluding a false-positive result)

To be sure that benzylidene ligands do not spontaneously exchange, without the catalyst carrying out olefin metathesis, the following experiments were conducted:

1. Catalyst **4** (1 equiv.) and styrene **5** (10 equiv.) were dissolved in MeOH and stirred at room temperature for 3 h. The progress of reaction was monitored by TLC. After 3 h no traces of catalysts **6** were observed (see Table 3).
2. Catalyst **4** (1 equiv.) and styrene **5** (10 equiv.) were immobilised either on MOF or SBA-15 (DCM, room temperature, 30 min). Heterogeneous complex was suspended in MeOH, the mixture was sonicated at room temperature for a few minutes, centrifuged, and the content of supernatant was checked on TLC. Again, no traces of catalysts **6** were observed (see Table 3).
3. Catalyst **4** (1 equiv.) and styrene **5** (10 equiv.) were immobilised either on MOF or SBA-15 (DCM, room temperature, 30 min). Heterogeneous complex was suspended in toluene and stirred at 50 °C for 3 h (to mimic standard reaction conditions). Toluene was evaporated, catalyst was suspended in MeOH, the mixture was sonicated at room temperature for a few minutes, centrifuged, and the content of supernatant was checked on TLC. Also here no traces of catalyst **6** were observed (see Table 3).

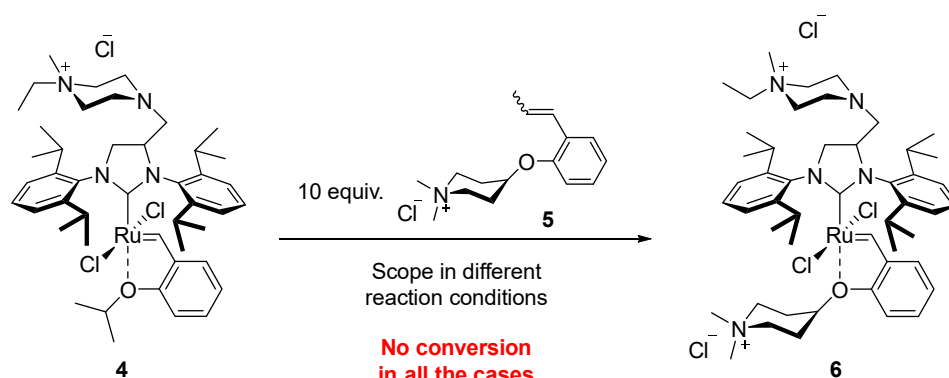


Table 3 Results of the benzylidene exchange confirmed by TLC.

Support	None	SBA-15	MOF	SBA-15	MOF
Reaction conditions	MeOH, rt, 3 h, c _{cat} = 10 mM	1. Immobilization of 4 in DCM, rt, 30 min. 2. Desorption in MeOH, rt, ca. 30 min.		1. Immobilization of 4 in DCM, rt, 30 min. 2. Toluene, 50 °C, 3 h. 3. Desorption in MeOH, rt, ca. 30 min.	
TLC (silica gel, eluent 10 % MeOH in DCM)					

Experimental procedures

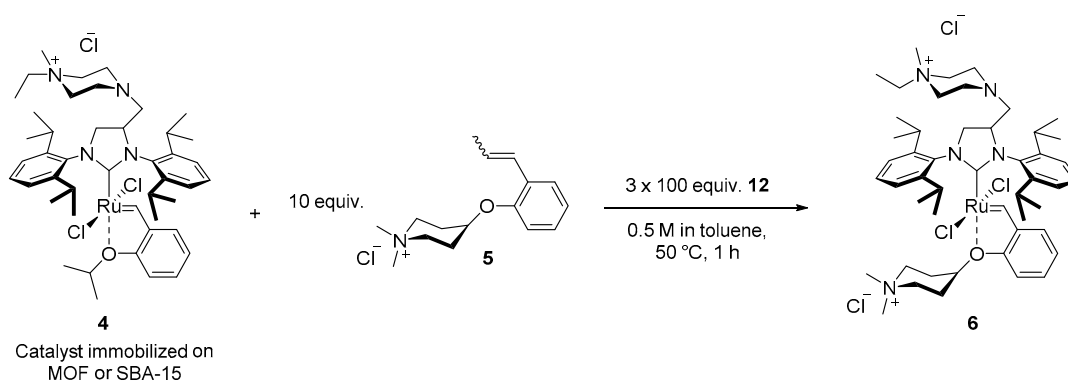
- Homogeneous

In a 4 mL vial covered with a septum cap that had been equipped with a magnetic stirrer, 29 mg (0.1 mmol, 20 equiv.) of **5** was weighted. The vial was purged with Ar (3 x). Then **4** (4.5 mg, 5 μ mol, 1 equiv.) dissolved in anhydrous MeOH (0.5 mL) was added and the suspension was stirred for 3 h. TLC analysis showed no conversion after this time.

- On supports

In a 4 mL vial covered with a septum cap that had been equipped with a magnetic stirrer, MOF or SBA-15 material (50 mg of 5 wt. % with respect to **4**, 1 equiv. of **4** with 10 equiv. of **5**) was weighted (in the air). The vial was purged with Ar (3 x). Then anhydrous toluene (2 mL) was added. The vial was sonicated and suspensions were stirred at 50 °C for 3 h. The MOF/SBA-15 material was then centrifuged and the clear solution decanted from above the solid. Then the materials were washed with anhydrous MeOH (3 x 2 mL) by repeating the sonication-centrifugation-decantation procedure. The MeOH solutions were combined and the TLC of it performed.

The benzylidene exchange experiments



In a 4 mL vial covered with a septum cap that had been equipped with a magnetic stirrer, MOF or SBA-15 material (180 mg of 5 wt. % with respect to **4**, 1 equiv. of **4**, 10 μ mol with 10 equiv. of **5**, 0.1 mmol) was weighted (in the air). The vial was purged with Ar (3 x). Then 2 mL of 0.5 M substrate **12** solution (100 equiv., 1 mmol) was added. The vial was sonicated and the suspension was stirred at 50 °C for 1 h. The MOF/SBA-15 material was then centrifuged and the clear solution decanted from above the solid. Then the catalytic material was washed with anhydrous toluene (3 x 1 mL) by repeating the sonication-centrifugation-decantation procedure. Then a new portion of the substrate was added and all the activities repeated until the third cycle. In the end, the material was washed with anhydrous methanol (5 x 2 mL), (this led to a catalyst, styrene, and other compounds desorption), filtered with a 1 μ m syringe filter and the solvent evaporated using a rotary evaporator. The mixture was analysed by HPLC for a **4/6** ratio.

Calculation of 4 to 6 conversion and yield of complex recovered from supports

HPLC calibration

HPLC was calibrated using a mixture of **4** and **6** at molar ratio 3:1, 1:1 and 1:3 respectively. Calibration was performed by injecting different volumes of these samples (1 to 10 μ l). The response factor of **6** is higher than that of complex **4**.

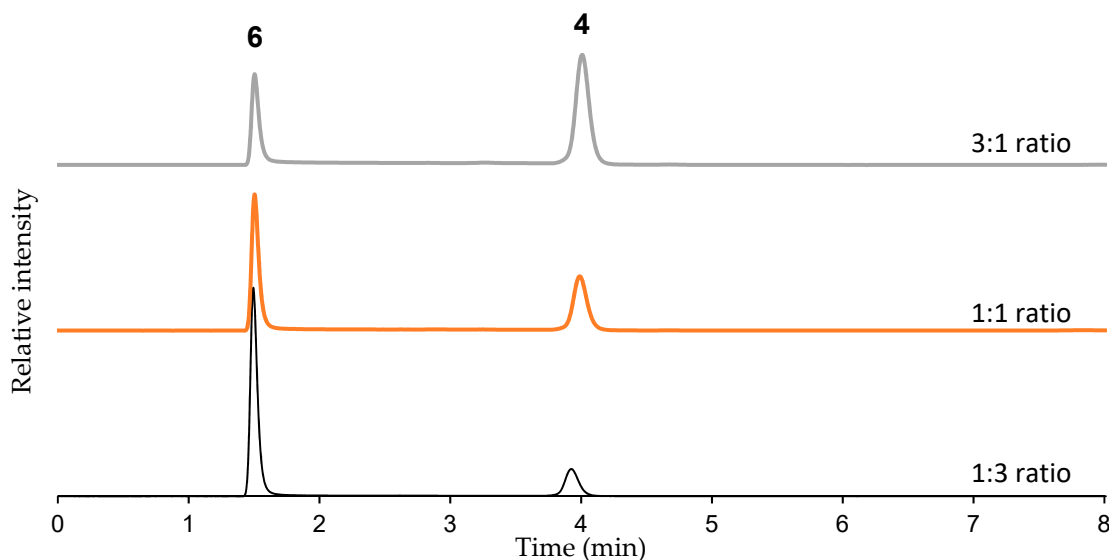


Figure 11 HPLC calibration on a mixture of **4** and **6**.

Analysis of eluate from SBA-15

The eluate from the experiment was diluted with DCM and analysed. 84% of ruthenium complexes were recovered from the starting material. Conversion **4** to **6** was measured as 98% which makes the total yield of **6** 82%:

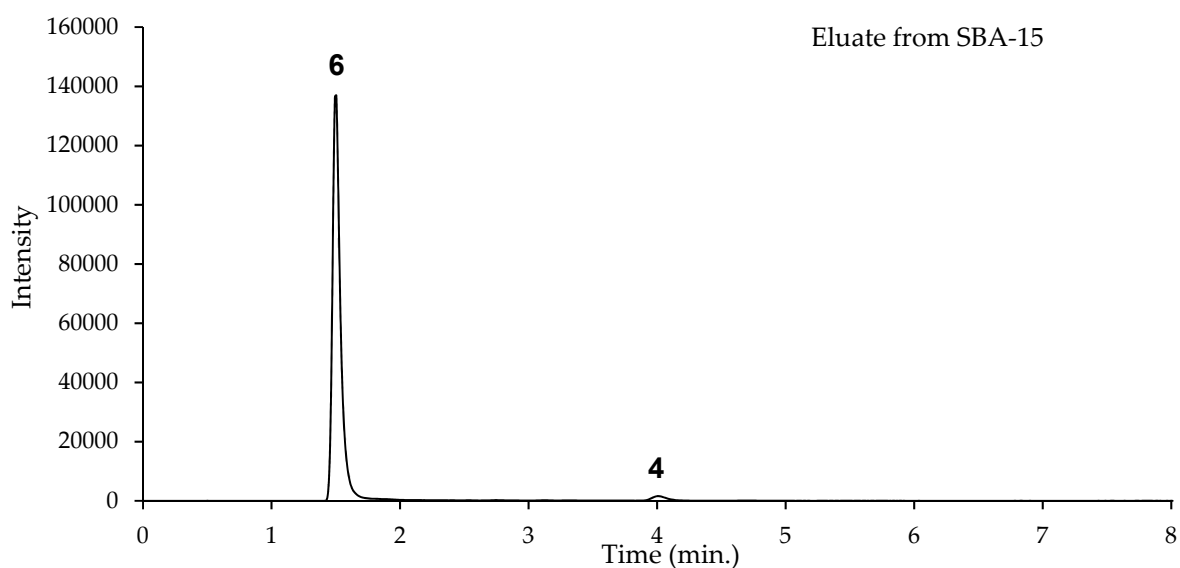


Figure 12 **4** to **6** conversion in SBA-15 pores through the boomerang mechanism.

Analysis of eluate from MOF

The eluate from the experiment was diluted with DCM and analysed. 92% of ruthenium complexes were recovered from the starting material. Conversion **4** to **6** was measured as 37% which makes the total yield of **6** 34%. We found that the 2-aminoterephthalate linker of the MOF is leaching out to methanol and is observed as additional signals in the chromatogram:

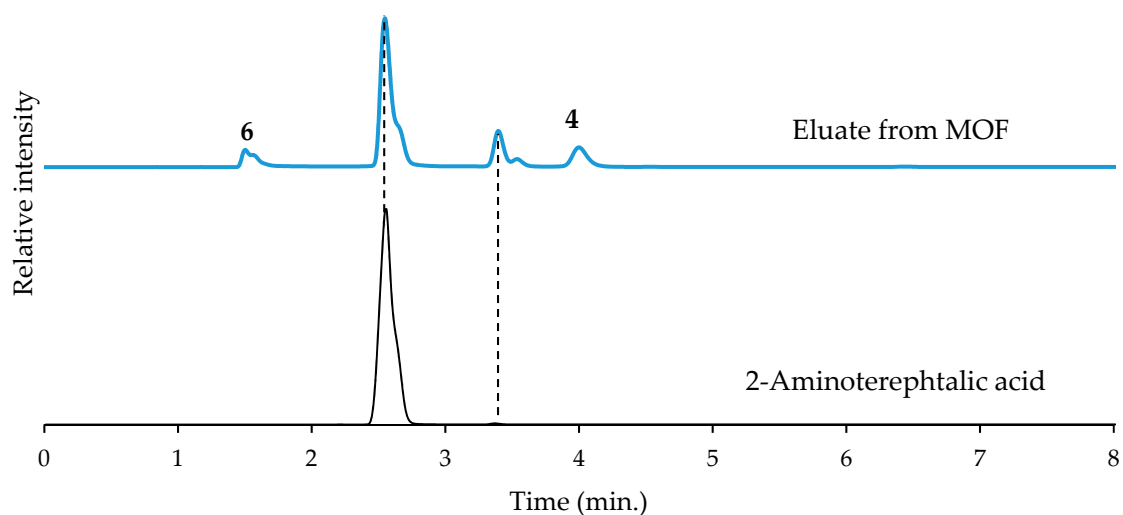


Figure 13 MOF ligand (2-aminoterephthalic acid) compared to the eluted mixture.

Crystal structure data

High-quality crystals of **6** were obtained by layering a MeOH/MeCN solution of the complex with an Et₂O/MTBE solvent mixture and allowing the precipitated oil to recrystallize over 2 weeks. Remarkably, thus formed needle-like crystals were stable for several months in the non-gassed, non-dried mother liquor in a closed flask. To our knowledge, this is the first XRD measured crystal structure of a double ammonium tagged olefin metathesis catalyst.

Table 3 **6** XRD measurement data and refinement parameters.

Crystal data	
Chemical formula	2(C ₄₉ H ₇₅ Cl ₂ N ₅ ORu)·3(Cl)
Mr	1950.56
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.0619 (10), 16.6327 (6), 27.9379 (12)
β (°)	95.991 (6)
<i>V</i> (Å ³)	6036.5 (6)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	3.78
Crystal size (mm)	0.40 × 0.24 × 0.14
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas Analytical
Absorption correction	<i>CrysAlis PRO</i> 1.171.38.43d (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). <i>Acta Cryst.</i> A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
<i>T</i> _{min} , <i>T</i> _{max}	0.456, 0.693
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	23875, 10769, 8030
<i>R</i> _{int}	0.041
(sin θ / λ) _{max} (Å ⁻¹)	0.597
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.087, 0.227, 1.03
No. of reflections	10769
No. of parameters	550
No. of restraints	278
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 19.7526P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.43, -0.71

In order to assess the effect of the ammonium tags on the ruthenium coordination sphere, we compared **6**, **4** [6] and SiPr-Hoveyda 2nd generation [10] catalysts' structural features to investigate whether the introduction of the quaternary ammonium groups influences the geometry of the complexes.

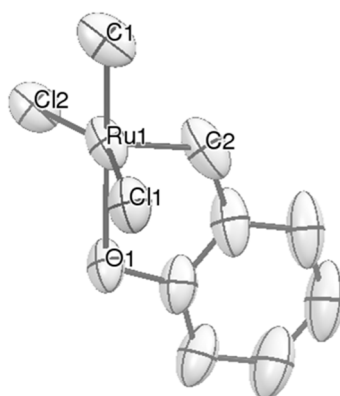


Figure 14 Ruthenium coordination sphere in **6** atom labelling.

Table 4. Comparison of coordination sphere geometry of **6**, **4** and SiPr-Hov2.

Structural features of catalysts	6	4	SiPr-Hov2
Bond lengths, Å			
Ru1-Cl1	2.3209(19)	2.3275(18)	2.3283(2)
Ru1-Cl2	2.3395(19)	2.3290(18)	2.3480(2)
Ru1-C1	1.963(8)	1.987(7)	1.9789(8)
Ru1-C2	1.839(7)	1.840(7)	1.8322(8)
Ru1-O1	2.247(5)	2.256(5)	2.2357(6)
Bond angles, °			
Cl1-Ru1-Cl2	156.56(6)	154.04(8)	156.858(9)
Cl1-Ru1-C1	90.3(2)	87.84(19)	85.99(2)
Cl2-Ru1-C1	97.9(3)	98.24(19)	101.65(2)
Cl1-Ru1-C2	100.0(3)	101.6(2)	99.45(3)
Cl2-Ru1-C2	99.4(2)	101.8(2)	100.32(3)
Cl1-Ru1-O1	85.34(13)	87.42(14)	85.621(17)
Cl2-Ru1-O1	85.73(13)	86.12(14)	86.373(17)
C1-Ru1-C2	103.0(4)	101.7(3)	101.57(3)
C2-Ru1-O1	78.9(3)	79.1(3)	79.24(3)
C1-Ru1-O1	175.5(2)	175.3(2)	171.58(3)

In all the three complexes, the ruthenium centre has a distorted tetragonal pyramid shape with chloride anions positioned *trans* to each other. The bond lengths within the ruthenium coordination sphere are the same in all the compared catalysts (differences around 1 % or less). However, the distortion of the coordination sphere seems to depend on the presence of the ammonium-bearing groups, as evidenced by differences in bond angles reaching up to 4 ° for the Cl1-Ru-C1 angle (Figure 16, Table 5). Stemming from the addition of bulky ammonium bearing groups, increasing steric congestion results also in the distortion of the molecules, as evidenced by differences in torsion angles and bond angles beyond the immediate ruthenium coordination sphere (Figure 15, Table 4). Especially, the NHC and benzyldiene ligands change their spatial orientation as much as 15 ° (C2-Ru1-C1-N2 torsion angle).

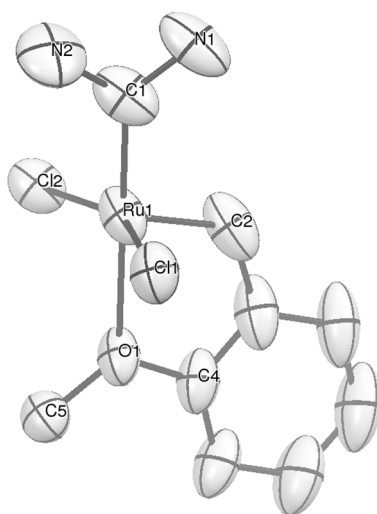


Figure 15 Schematic of the atom labelling in the extended geometry of the ruthenium coordination sphere.

Table 5. Comparison of ligand spatial alignment parameters of **6**, **4** and SiPr-Hov2.

Structural features of catalysts extended	6	4	SiPr-Hov2
Bond angles, °			
N1-C1-N2	106.3(7)	107.4(6)	106.74(6)
N1-C1-Ru1	131.0(8)	131.1(5)	130.91(6)
N2-C1-Ru1	121.5(6)	119.9(5)	120.82(6)
C4-O1-C5	119.3(6)	121.0(6)	119.82(6)
C4-O1-Ru1	111.2(4)	110.5(4)	110.87(5)
C5-O1-Ru1	129.1(4)	128.1(4)	129.23(5)
Torsion angles, °			
C2-Ru1-C1-N1	-26.5(8)	-13.6(7)	-13.88(9)
C2-Ru1-C1-N2	167.5(7)	-177.1(6)	-175.96(7)
C2-Ru1-O1-C4	2.7(5)	3.1(5)	3.29(6)
C2-Ru1-O1-C5	-169.6(6)	-169.4(6)	-167.21(7)

In conclusion, crystallographic data of the no-, mono- and bis- ammonium tagged SiPr-Hoveyda type catalysts prove that in solid state there are no differences in the coordination bond lengths in the ruthenium centres, but their tetragonal pyramid shape and both benzylidene and NHC ligands' positions undergo irregular distortions as the bulky ammonium-bearing groups are introduced.

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