SUPPORTING INFORMATION

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1. General Remarks

All reactions requiring exclusion of oxygen and moisture were carried out in dry glassware with dry solvents (SPS MBraun) under a dry and oxygen free argon atmosphere using standard Schlenk technique. The addition of dry solvents or reagents was carried out using argon flushed plastic syringes.

For spectroscopic and analytic characterizations, the following devices were used:

Analytical thin layer chromatography (TLC) was performed on Merck Silica gel 60 F_{254} precoated aluminum sheets. Components were visualized by observation under UV light (254 nm or 365 nm) or dyed by aqueous $KMnO_4$ or anisaldehyde reagent.

Flash column chromatography was carried out using silica gel 60 (230 – 400 mesh), purchased from Merck.

GC chromatograms were recorded using a PerkinElmer Clarus 580 model. As capillary column, an IntertCap 5MS-Sil column was employed with helium as carrier gas. GC conversions were determined based on the ratio of an internal standard (trimethoxybenzene or tetradecane) and the starting material.

^{1}H NMR spectra were recorded in DCM-d_2, DMSO-d_6 and MeOH-d_4 at room temperature on Agilent Mercury spectrometers (400 MHz). The data were interpreted in first order spectra. Chemical shifts δ are reported in parts per million (ppm) downfield from trimethylsilane as reference to residual solvent signal: DCM-d_2 [δ_H = 5.32 ppm], DMSO-d_6 [δ_H = 2.50 ppm], D_2O [δH = 4.79 ppm], and MeOH-d_4 [δ_H = 3.31 ppm]. The following abbreviations are used to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), etc., br. s (broad signal), m (multiplet). Coupling constants (*J*) are given in Hz and refer to H,H-couplings.

^{13}C NMR spectra were recorded at room temperature on Agilent Mercury 101 MHz spectrometers. The spectra were recorded in DCM-d_2, DMSO-d_6 and MeOH-d_4. Chemical shifts are reported in δ units relative to the solvent signal: DCM-d_2 [δ_C = 53.84 ppm], DMSO-d_6 [δ_C = 39.52 ppm] and MeOH-d_4 [δ_C = 49.00 ppm].

High resolution mass spectra (HR-MS) High resolution mass spectroscopy was obtained on AutoSpec Premier spectrometer.

Elemental Analyses were carried out at the Polish Academy of Science, Institute of Organic Chemistry.

IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. Substances were applied as a film, solid or in solution. The obtained data was processed with the software Omni32. Wavenumbers are given in cm^{-1}.

Reagents and Solvents

All reagents were purchased from Sigma-Aldrich, Apeiron Synthesis and POCH and used without further purification unless stated otherwise.

Measurements of N_2 adsorption isotherms

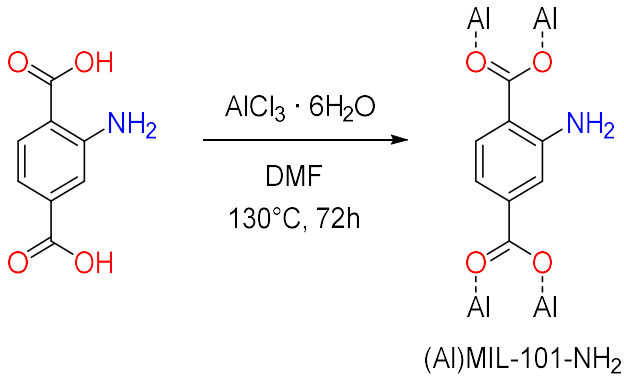
The nitrogen adsorption isotherms were measured at liquid nitrogen temperature (77 K) using Quantachrome Autosorb-IQ-MP sorption analyser. Prior to measurements, all samples were dried for no less than 24 h under vacuum ($2 \cdot 10^{-2}$ mbar) at room temperature. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method. For all isotherm analyses we ensured that the two consistency criteria described by Rouquerol *et al.* and Walton *et al.* were satisfied [1].

Powder X-ray diffraction

All powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover X-ray diffractometer (CuKα radiation), with parallel beam formed by Goebel mirror equipped with a VANTEC 1 position sensitive detector. All measurements were performed in aluminium holder.

2. Synthesis of (Al)MIL-101-NH_2

(Al)MIL-101-NH_2 was synthesized using a modified [2] procedure developed by Gascon and co-workers [3].



(Al)MIL-101-NH_2

Aluminium trichloride hexahydrate (1.53 g, 6.34 mmol, 1.00 equiv.) and a magnetic stir bar were placed in an 150 mL pressure tube followed by DMF (120 ml) and stirred

overnight at room temperature until homogenous solution formed. Next, 2-aminoterephthalic acid (1.68 g, 9.27 mmol, 1.46 equiv.) was added, and after its dissolution the magnetic stir bar was removed, and the pressure tube was sealed and placed in a preheated oven at 130°C for 70 hours. Over this period, a yellow precipitate formed, which was filtered off on a filter funnel (G4) under reduced pressure and washed with DMF (50 mL), acetone (50 mL) and methanol (50 mL). The synthesised MOF was partially formylated, so the crude material was suspended in methanol (60 mL) and placed in an autoclave at 120°C for 20 hours, according to our recently developed deformylation methodology [4]. After cooling down, the solid was collected by filtration (G4), washed with methanol (200 mL) and dried under vacuum ($4 \cdot 10^{-2}$ mbar, room temperature, 24 hours) to yield 1.58 g of a pure product, containing however *ca.* 18-19% MeOH (w/w).

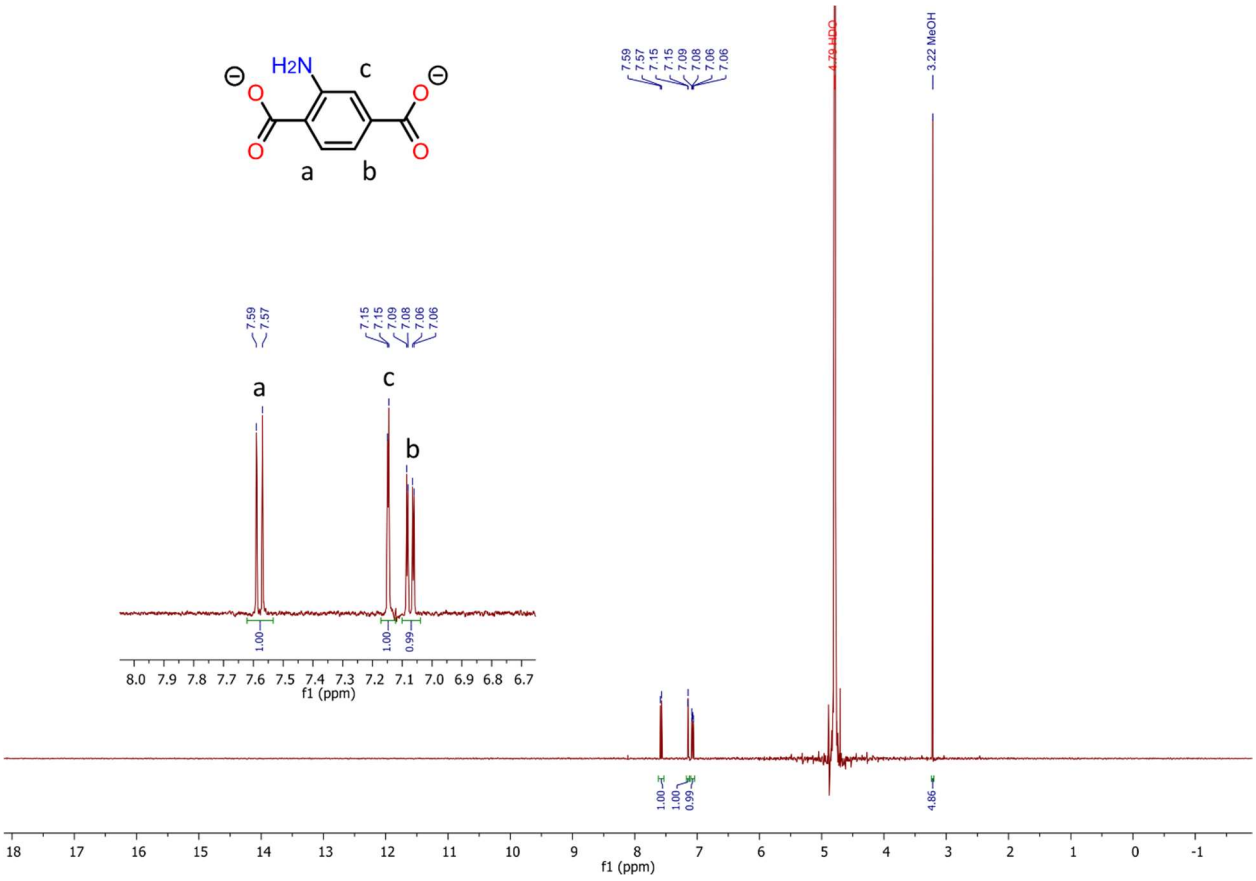


Figure S1.[1]H NMR spectrum of **(Al)MIL-101-NH$_2$** digested in 4 wt. % NaOD/D_2O.

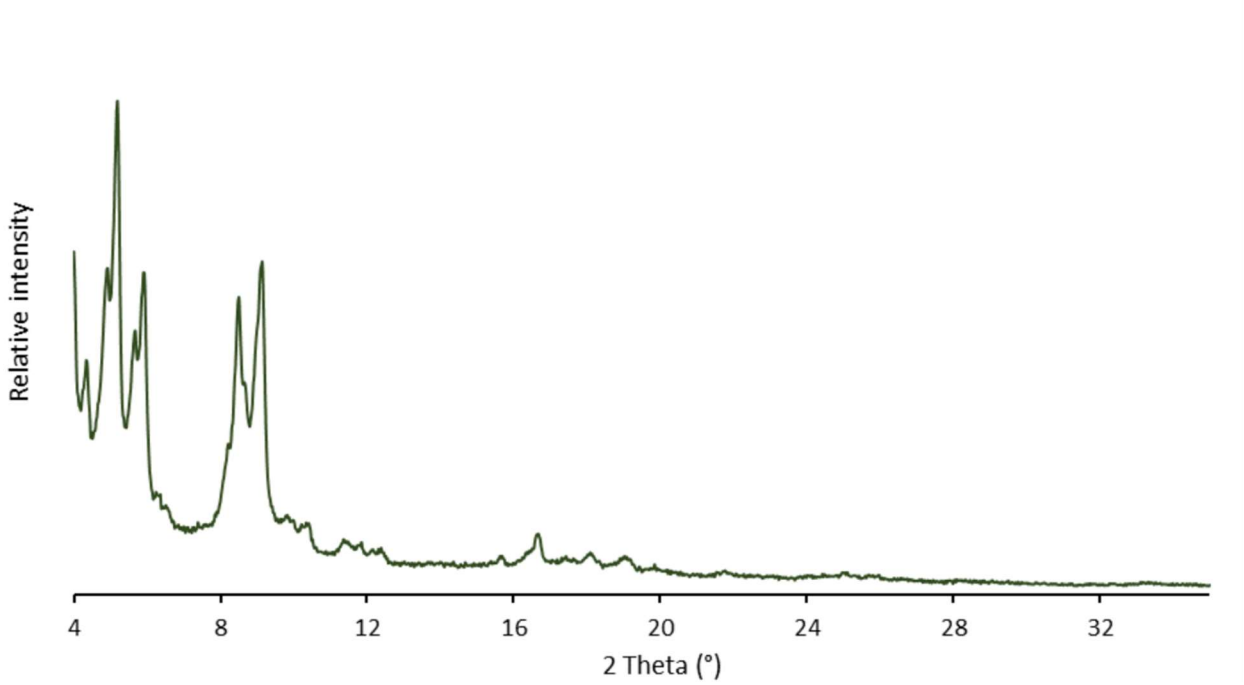


Figure S2. Powder X-ray diffraction (PXRD) pattern of **(Al)MIL-101-NH$_2$**.

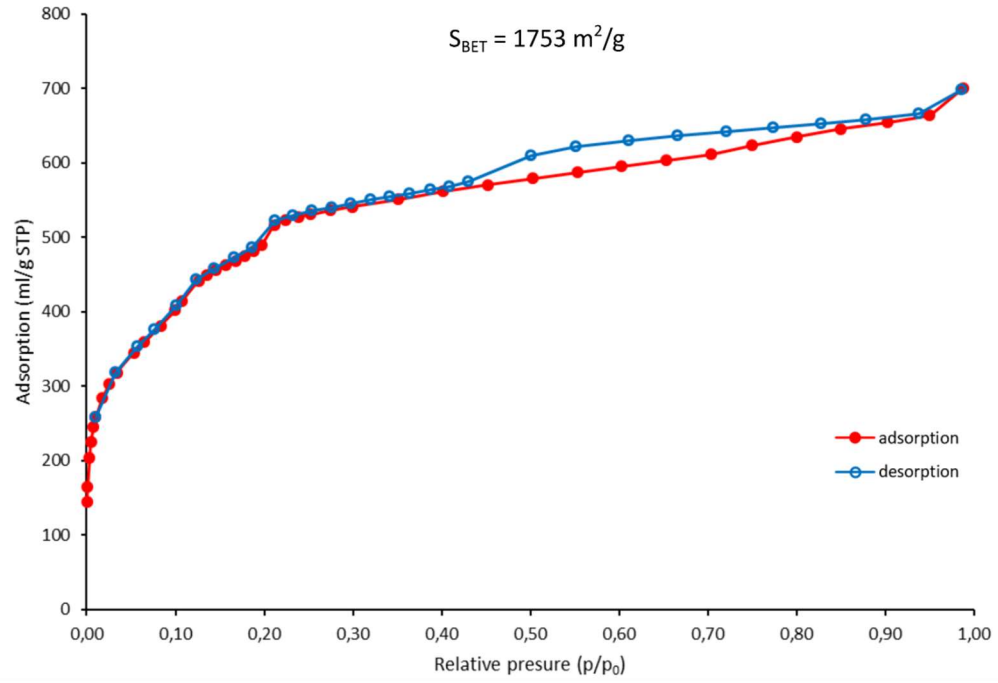
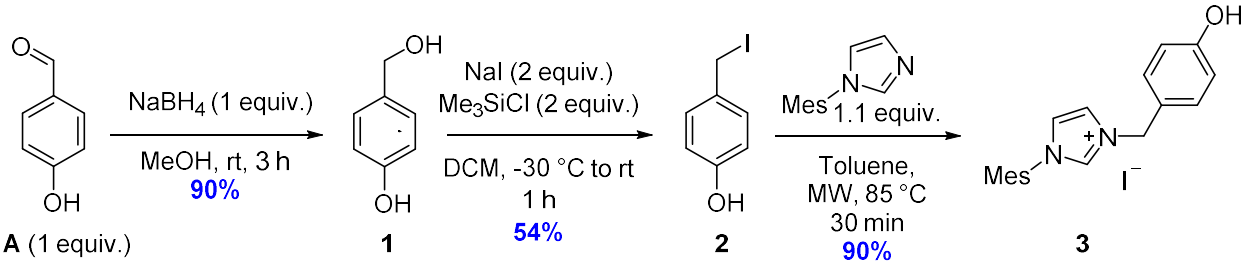


Figure S3. N_2 adsorption/desorption isotherm of **(Al)MIL-101-NH$_2$**. Points in the range p/p_0 = 0.0005-0.21 were used to calculate BET surface area.

3. Synthesis of the uNHC Ligand 3



Procedure for the synthesis of 4-(hydroxymethyl)phenol (1)

In a 250 mL round bottom flask 4-hydroxybenzaldehyde (5 g, 40.1 mmol, 1 equiv.) was dissolved in MeOH (50 mL) at toom temperature. When the solution turned to transparent, sodium borohydride (1.6 g, 40.1 mmol, 1 equiv.) was added portionwise. The resulting mixture was stirred for additional 3 hours at room temperature (TLC control, 30% EtOAc/*n*-hexane). After the reaction time was completed, the mixture was extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the volatiles removed under reduced pressure. The product was obtained without additional purification to give a colourless powder in 90% of yield (4.5 g, 36.2 mmol).

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 9.21 (m, 1H), 7.12 – 7.09 (m, 2H), 6.70 (dd, *J* = 8.5, 2.5 Hz, 2H), 4.94 – 4.91 (m, 1H), 4.36 (dd, *J* = 5.5, 2.1 Hz, 2H).

^{13}C NMR (101 MHz DMSO-d$_6$) δ 156.2, 132.8, 128.1, 114.8, 62.8.

Procedure for the synthesis of 4-(iodomethyl)phenol (2)

In a round-bottom flask provided with a magnetic stirring bar and under an argon atmosphere, 4-hydroxybenzyl alcohol **1** (1.50 g, 12.1 mmol, 1.0 equiv.) and sodium iodide (3.66 g, 24.2 mmol, 2.0 equiv.) were mixed in 20 mL of dry dichloromethane. The reaction mixture was cooled down to -30 ºC and TMSCl (3.1 mL, 24.2 mmol, 2.0 equiv.) was added dropwise avoiding the fuming. After the completion of addition, the reaction was allowed to warm up to room temperature while stirring. Upon reaction completion, brine (20 mL) was added, and the mixture vigorously stirred for 20 minutes. Then, the organic phase was extracted with DCM (3 x 30 mL), dried over anhydrous $MgSO_4$ and the volatiles removed under reduced pressure obtaining the product **2** as a dark orange solid (1.52 g, 6.49 mmol, 54% yield) [5].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.82 (s, 1H), 4.46 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 131.6, 130.3, 115.7, 6.36.

Procedure for the synthesis of Ligand 3

In a microwave tube provided with a magnetic stirring bar and under argon atmosphere, 1-mesityl-1*H*-imidazole (308 mg, 1.65 mmol, 1.05 equiv.) and 4-(iodomethyl)phenol **2** (369 mg, 1.57 mmol, 1.0 equiv.) were suspended in 20 mL of dry toluene, and the mixture was heated up at 85 ºC under 150 W of microwave irradiation for 1 hour. Upon the reaction completion, the formed precipitate was filtered, washed with cold toluene and cold diethylether affording the desired product as a yellow solid (594 mg, 1.41 mmol, 90% yield).

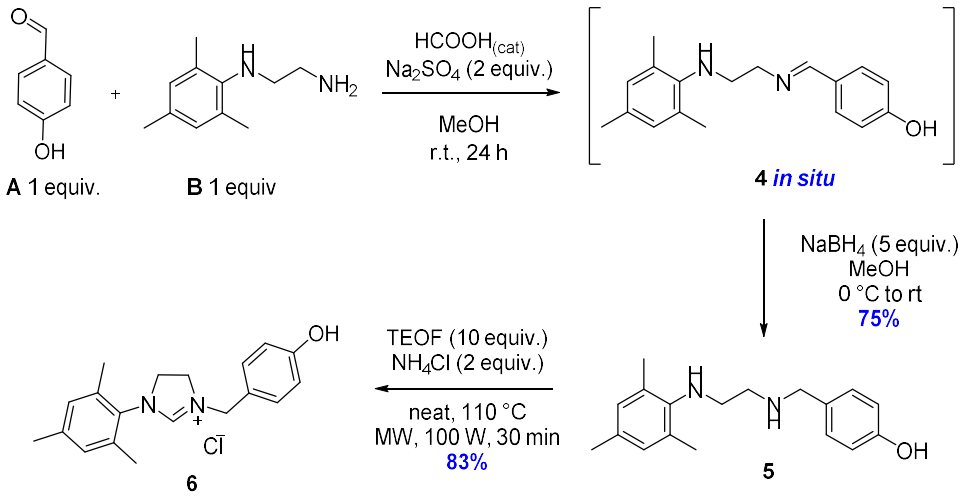
^{1}H NMR (400 MHz, CD_3OD) δ 9.26 (s, 1H), 7.84 (m, 1H), 7.69 (m, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 1.4, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.43 (s, 2H), 2.35 (s, 3H), 2.04 (s, 6H).

^{13}C NMR (101 MHz, CD_3OD) δ 158.4, 141.2, 137.0, 134.3, 129.9, 129.3, 124.4, 122.9, 115.8, 52.9, 19.7, 15.9.

HRMS (ESI TOF *m/z*) calculated for $C_{19}H_{21}N_2O$ $[M\text{-}I]^+$: 293.1654, Found: 293.1657.

IR $\tilde{\nu}$: 3153, 2962, 1747, 1610, 1592, 1529, 1513, 1483, 1441, 1418, 1347, 1258, 1211, 1191, 1170, 1151, 1099, 1061, 859, 822, 787, 745, 690, 583, 546.

4. Synthesis of the NHC Ligand 6



Procedure for the synthesis of 4-(((2-(mesitylamino)ethyl)amino)methyl)phenol (5)

In a round bottom flask provided with a magnetic stirring bar, (4-hydroxy)-benzaldehyde (1.03 g, 8.4 mmol, 1 equiv.) was dissolved in 40 mL of MeOH. Then, 2 drops of formic acid, *N*-mesitylethane-1,2-diamine (1.5 g, 8.4 mmol, 1 equiv.) and sodium sulphate (2.4 g, 16.8 mmol,

2 equiv.) were added. The reaction mixture was stirred at room temperature for 24 hours (TLC control, 50% EtOAc/*n*-hexane). After the reaction time was completed, the desiccant was filtered off and washed with DCM (3 x 10 mL). The organic layers were combined and concentrated under reduced pressure. The product of condensation, imine **4,** was obtained as an orange oil and used in the next step without purification.

In a round bottom flask provided with a magnetic stirring bar, imine **4** was dissolved in 40 mL of MeOH. The mixture was cooled down to -10 ºC, and $NaBH_4$ (1.62 g, 42.1 mmol, 5 equiv.) was added portion-wise to the cooled mixture. After the completion of the addition, the resulting mixture was allowed to warm up to room temperature while stirred for 2 hours (TLC control, 40% EtOAc/*n*-hexane), then, extracted with DCM (3 x 50 mL). The combined organic fractions were collected, dried over anhydrous sodium sulphate. Then, the desiccant was filtered off, and the volatiles were removed under reduced pressure affording a dark orange oil (1.8 g, **75%**). The product was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.06 (s, 2H), 6.82 (s, 2H), 6.63 – 6.60 (m, 2H), 3.74 (s, 2H), 3.09 (dd, *J* = 6.6, 4.7 Hz, 2H), 2.89 (dd, *J* = 6.6, 4.7 Hz, 2H), 2.26 (s, 6H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 143.1, 131.9, 129.8, 129.6, 115.9, 53.3, 49.3, 47.9, 20.7, 18.5.

Procedure for the synthesis of Ligand 6

In a microwave tube provided with a magnetic stirring bar and under an argon atmosphere, 4-(((2-(mesitylamino)ethyl)amino)methyl)phenol **5** (1.5 g, 5.27 mmol, 1 equiv.), triethyl orthoformate (7.98 g, 8.96 mL, 52.7 mmol, 10 equiv.) and NH_4Cl (0.56 g, 10.5 mmol, 2 equiv.) were mixed, and the mixture was heated up at 110 ºC under 100 W of microwave irradiation for 30 minutes. Upon reaction completion, the formed precipitate was filtered, washed with cold toluene and cold diethyl ether affording the desired product **6** as a yellow solid (1.3 g, 4.4 mmol, 83% yield).

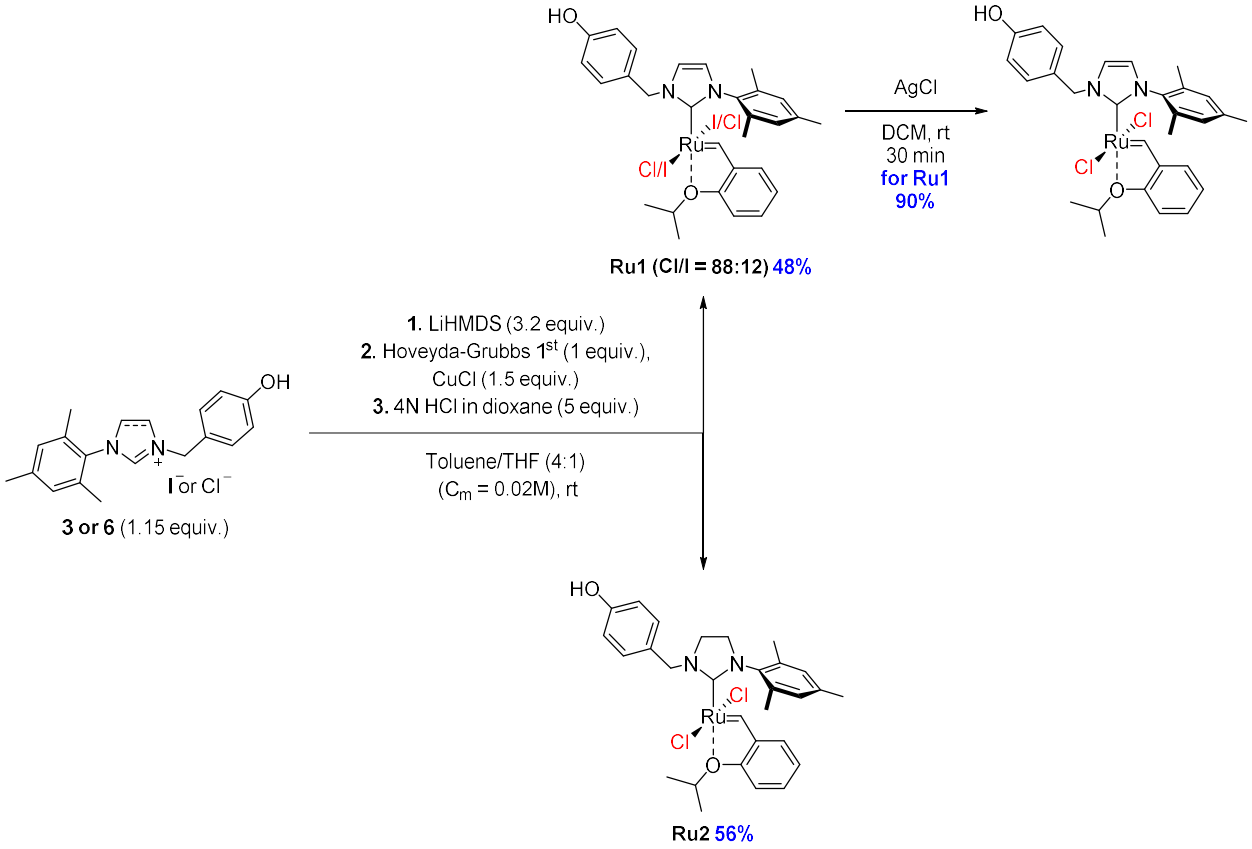
^{1}H NMR (400 MHz, CD_3OD) δ 8.75 (s, 1H), 7.29 (d, *J* = 8.5, 2H), 7.08 – 6.99 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.73 (s, 2H), 4.20 – 4.05 (m, 4H), 2.29 (s, 9H).

^{13}C NMR (101 MHz, CD_3OD) δ 158.6, 158.1, 140.2, 135.4, 130.0, 129.44, 123.4, 115.7, 51.4, 50.7, 19.7, 16.3.

HRMS (ESI TOF *m/z*) calculated for $C_{19}H_{23}N_2O$ $[M\text{-}Cl]^+$: 295.1810, Found: 295.1814.

IR $\tilde{\nu}$: 3088, 3006, 2802, 1659, 1637, 1618, 1596, 1515, 1497, 1457, 1449, 1361, 1287, 1263, 1235, 1213, 1136, 851, 701.

5. General Procedure for synthesis of Ru Complexes



In a dried 50 mL Schleck flask, the corresponding NHC ligand **3** or **6** (1.15 equiv.) was suspended in dry toluene (12 mL). To the resulting suspension LiHDMS (3.2 equiv.) was added and the mixture was stirred for 1 hour at room temperature in an atmosphere of argon. To this suspension, 3 mL of dry THF was added and the reaction was stirred until the solution became clear and homogeneous. To this clear solution **Hov I** was added (124 mg, 0.206 mmol, 1.0 equiv.). The resulting solution was stirred at room temperature for 2 hours (the reaction was monitored by TLC, 50% AcOEt/*n*-hexane). After the complete disappearance of **Hov I** on TLC, CuCl (31 mg, 0.31 mmol, 1.5 equiv.) was added to the reaction and stirred for additional 30 min followed by dropwise addition of 4N HCl in dioxane (0.258 mL). The reaction mixture was stirred for another 30 minutes, transferred to a round bottom flask and volatiles were evaporated to dryness. The crude mixture was purified by column chromatography (20% to 50% AcOEt/*n*-hexane).

Synthesis of Ruthenium Complex Ru1

Following the general procedure, using NHC ligand **3** (100 mg, 0.238 mmol, 1.15 equiv.), LiHDMS (110 mg, 0.66 mmol, 3.2 equiv.), **Hov I** (124 mg, 0.206 mmol, 1.0 equiv.), CuCl (31 mg, 0.31 mmol, 1.5 equiv.) and 4N HCl in dioxane (0.258 mL, 1.03 mmol). The desired product was crystallised from the mixture of DCM/MeOH (3:1) to give a fine dark green powder (60 mg, 0.1 mmol, **48%**).

The ratio of Cl/I at the ruthenium coordination centre was established based on integration of benzylidene signals by ^{1}H NMR as **88:12**.

An oven-dried vial was charged with AgCl (1.1 equiv. per iodide) and Ru-complex (30 mg). The vial was evacuated and three times flushed with argon, dry DCM (1 mL) was added, and the resulting mixture was stirred for 30 minutes at room temperature. The resulting solution was centrifuged, filtered through Celite® pad and washed with MeOH (20 mL). Solvents were evaporated and the residue was crystallised from the mixture of DCM/MeOH and dried under vacuum overnight to provide pure product as a fine dark green powder (90%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.38 (s, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.9 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.17 (m, 2H), 7.11 – 6.98 (m, 3H), 6.93 (dd, *J* = 5.4, 3.2 Hz, 3H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.08 (s, 2H), 5.45 (s, 1H), 5.21 (hept, *J* = 6.2 Hz, 1H), 2.53 (s, 3H), 2.04 (d, *J* = 0.7 Hz, 6H), 1.76 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 287.5, 172.3, 156.2, 152.4, 144.1, 139.8, 137.2, 131.1, 129.1, 129.0, 127.9, 124.4, 122.6, 121.7, 121.2, 115.6, 112.9, 75.3, 54.8, 21.8, 21.0, 17.6.

EA: calculated for $C_{29}H_{32}Cl_2N_2O_2Ru$: C, 56.86; H, 5.27; N, 4.57; Found C, 56.59; H, 5.48; N, 4.34.

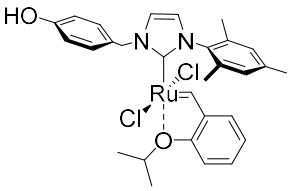
Synthesis of Ruthenium Complex Ru2

Following the general procedure, using NHC ligand **6** (100 mg, 0.3 mmol, 1.15 equiv.), LiHDMS (110 mg, 0.66 mmol, 3.2 equiv.), **Hov I** (158 mg, 0.263 mmol, 1.0 equiv.), CuCl (39.4 mg, 0.39 mmol, 1.5 equiv.) and 4N HCl in dioxane (0.118 mL, 1.31 mmol). The desired product was crystallised from the mixture of DCM/MeOH (3:1) to give a fine dark green powder (72 mg, 0.12 mmol, **56%**).

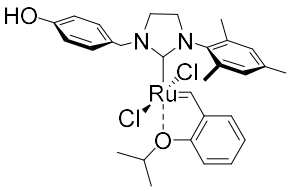
^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.22 (s, 1H), 7.67 – 7.54 (m, 3H), 7.11 (s, 2H), 7.04 – 6.95 (m, 3H), 6.90 (d, *J* = 7.8 Hz, 2H), 5.53 (s, 2H), 5.18 (hept, *J* = 6.1 Hz, 1H), 3.92 (t, *J* = 10.0 Hz, 2H), 3.64 (d, *J* = 10.0 Hz, 2H), 2.48 (s, 3H), 2.24 (s, 6H), 2.01 (s, 1H), 1.71 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 152.2, 138.9, 138.0, 137.7, 130.6, 129.5, 129.5, 122.5, 122.1, 115.3, 112.86, 75.2, 47.7, 21.8, 20.9, 17.7.

6. Stability Studies of Ru1 and Ru2 in Toluene-d_8 and DCM-d_2



Ru1



Ru2

Experimental Procedure

In an NMR tube under an argon atmosphere, a corresponding ruthenium complex (10.8 µmol, 1.0 equiv.) dissolved in CD_2Cl_2 (0.5 mL) and 1,3,5-trimethoxybenzene (1.82 mg, 10.8 µmol, 1.0 equiv.) dissolved in CD_2Cl_2 (0.2 mL) were mixed and let stabilise at 30 ºC. NMR was recorded at room temperature at selected time to establish the decomposition of the complexes.

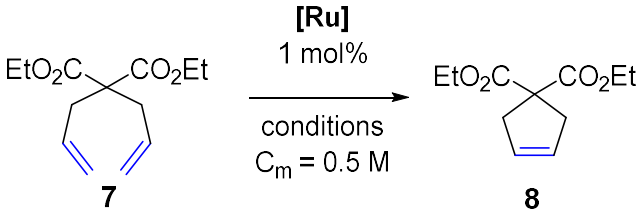
The same protocol was followed to establish the decomposition of obtained ruthenium complexes **Ru1** and **Ru2** in Toluene-d_8. However, after 24 hours, formation of a precipitate in the samples at 50 ºC was observed which made it impossible to record reliable NMR spectra and finish the experiment in Toluene-d_8.

Table S1. Stability studies of **Ru1** and **Ru2** in CD_2Cl_2.

[Ru1] – saturated version		**[Ru2] – unsaturated version**	
Time, [days]	**Remained catalyst, [%]**	**Time, [days]**	**Remained catalyst, [%]**
0	100	0	100
1	100	1	100
2	98.1	2	100
3	98.1	3	97.1
7	96.2	7	94.1

8	96.2	8	94.1
9	96.2	9	94.1

7. Ring-Closing Metathesis reaction of DEDAM



Experimental Procedure

To the solution of diethyl diallylmalonate **7** (38.7 mg, 0.158 mmol, 1.0 equiv.) and mesitylene (19.0 mg 0.158 mmol,1.0 equiv., used as an internal standard) in a dry solvent (DCM or Toluene, 9.5 mL) 1 mol% of a corresponding ruthenium complex (**Ru1** or **Ru2**) was added in one portion in argon flow. The resulting mixture was stirred under given conditions (see Table S2) for 24 hours. Aliquot (0.5 mL) was taken at selected times and quenched with SnatchCat (4.4 equiv. vs Ru). Conversion of the substrate **7** was determined by GC.

Table S2. Conditions of the RCM reaction and conversion of diethyl diallylmalonate (**7**) in the presence of 1 mol% **Ru1** or **Ru2**.

[Ru]	Conditions	Time, h	Conversion, %
Ru1	DCM, rt	3	36
		24	79
Ru1	Toluene, 50 °C	3	95
		24	>99
Ru2	DCM, rt	3	15
		24	49
Ru2	$B(OEt)_3$ (1 mol%), DCM, rt	3	16
		24	56
Ru2	Toluene, 50 °C	3	84
		24	**>99**

8. **Sorption Experiment**

Solutions of precisely known concentrations of catalysts **Ru1** and **Ru2** were prepared, and their UV-Vis spectra measured. Molar absorption coefficients were determined by linear regression.

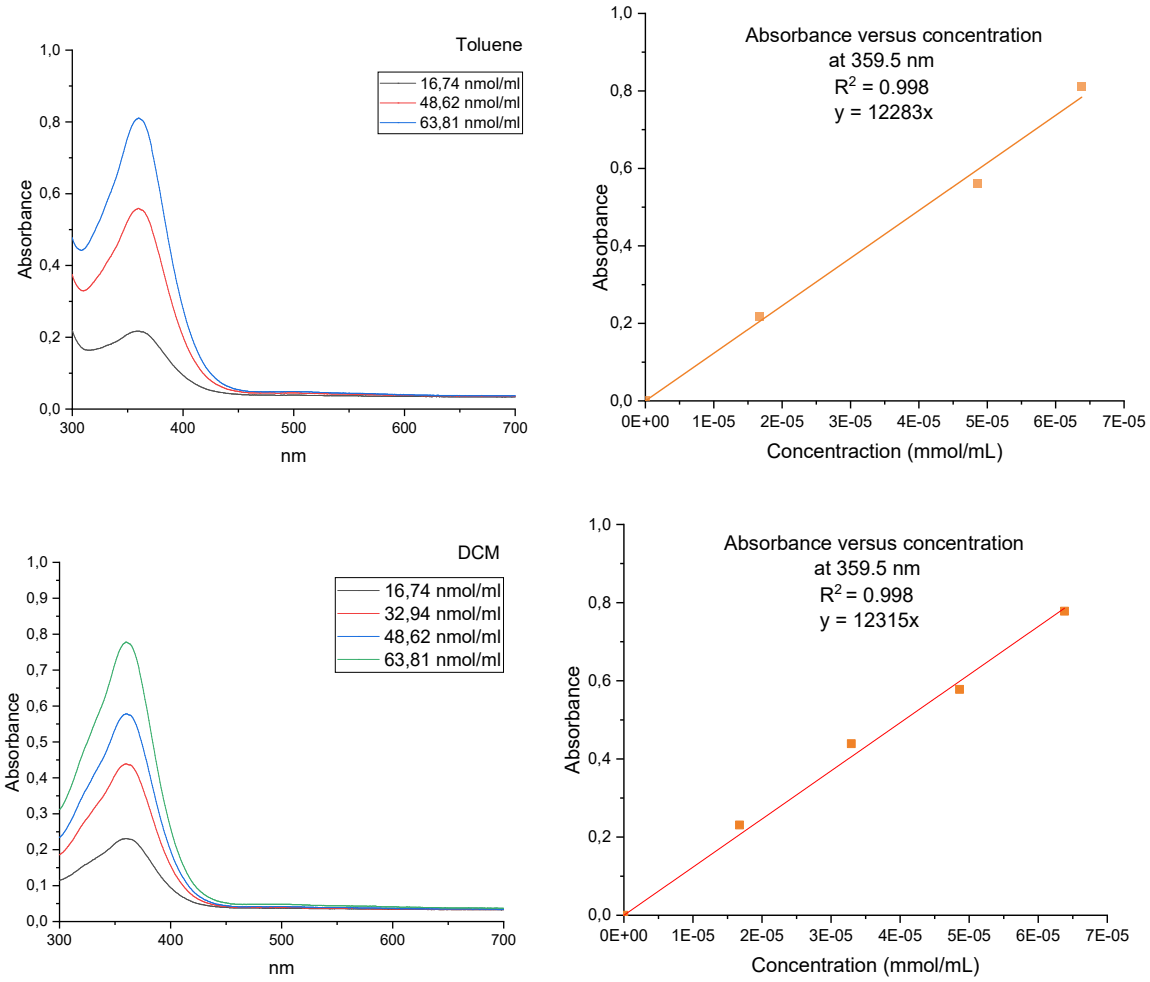


Figure S4. UV-Vis spectra of catalysts **Ru1** and **Ru2** and determination of their molar absorption coefficients ε.

Sorption of Ru1 Complex on (Al)MIL-101-NH_2

First, 1.00 mM solutions of catalyst Ru1 was prepared. To a 4 ml vial with a screw cap a sample of **(Al)MIL-101-NH_2** was weighed (12 mg), and 1mM solution of the complex in a given solvent was added (2.0 mL, 2 µmol). The resulting suspension was stirred at room temperature for 1 h. Then, the reaction mixture was centrifuged, the supernatant was removed off through a syringe filter (PTFE, 0.2 µm) and analyzed by UV-Vis spectroscopy to determine the amount of the adsorbed catalyst. The solid residue was dried under vacuum (at least 2 hrs in 8 µbar) at room temperature.

Table S3. Results of absorption experiments of **Ru1** in DCM and toluene.

Catalyst/ Solvent	The amount of catalyst adsorbed from solution, [%]
Ru1/ Toluene	99.4
Ru1/ DCM	99.2

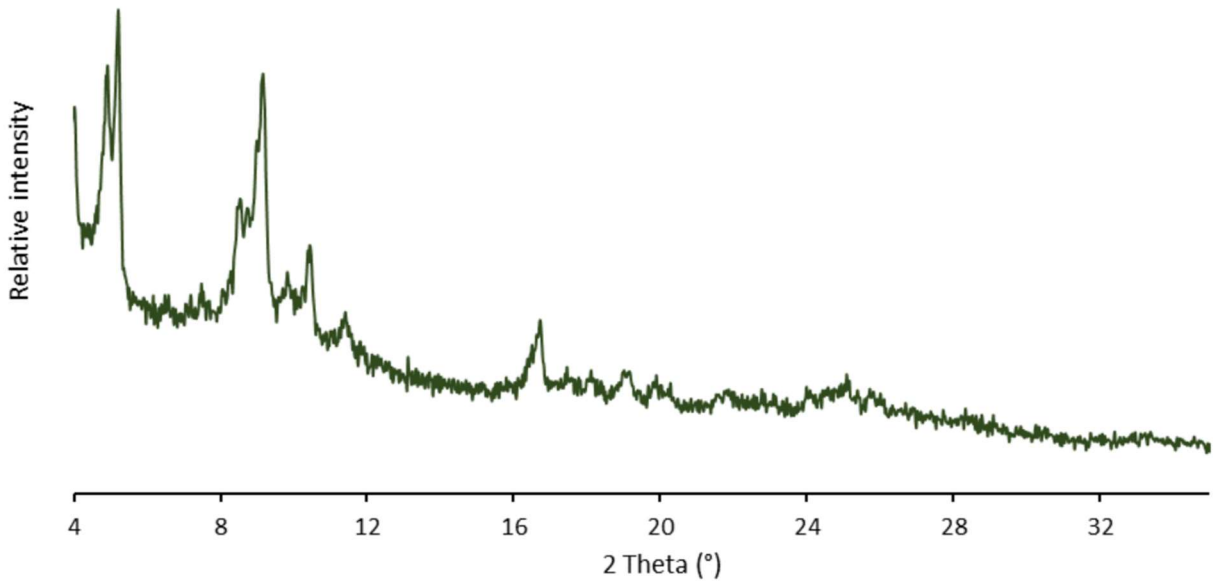


Figure S5. Powder X-ray diffraction (PXRD) pattern of **Ru1@(Al)MIL-101-NH$_2$**.

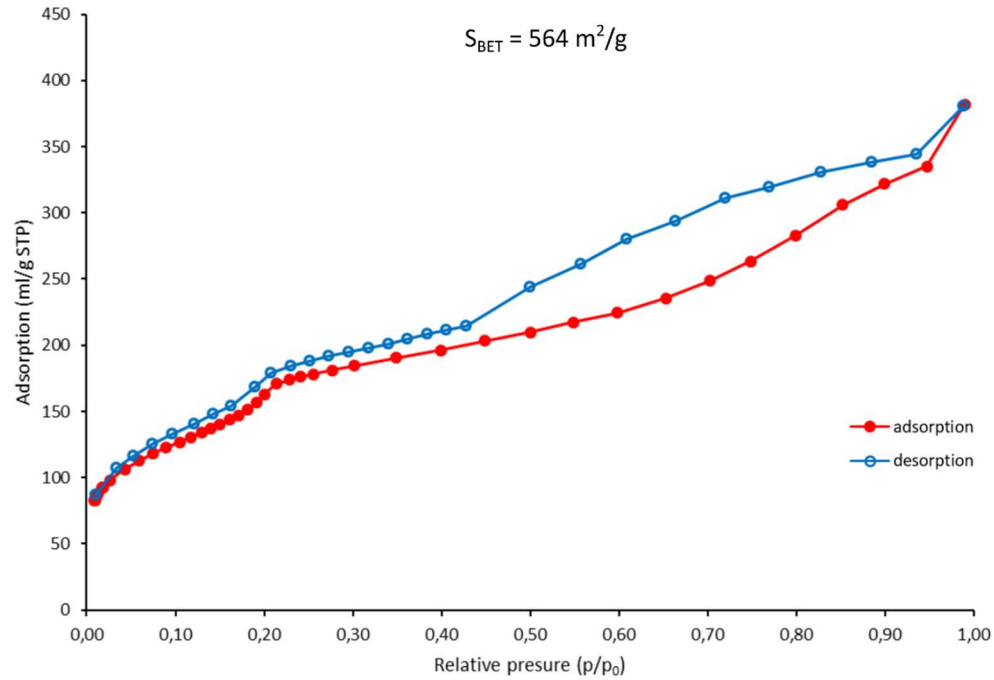


Figure S6. N_2 adsorption/desorption of **Ru1@(Al)MIL-101-NH$_2$**. Points in the range p/p_0 = 0.0005-0.21 were used to calculate BET surface area.

9. **Desorption (Leaching) Experiments**

Dried overnight corresponding [Ru]@MOF complex was suspended in 3 mL (out of 20 mL) of toluene with short sonication and placed in a G4 filtering funnel with side argon inlet. The rest of 20 mL of toluene followed by 20 mL of DCM were slowly passed through the sample and were collected in vials. The experiment was conducted in argon flow. The concentration of catalysts in each extract was analysed by UV-Vis spectroscopy [2].

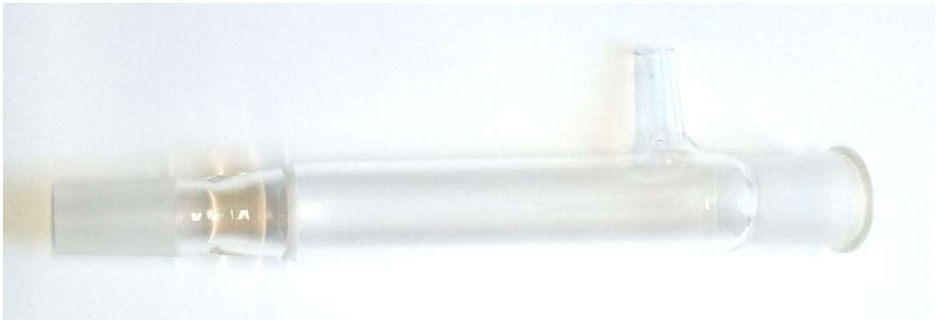
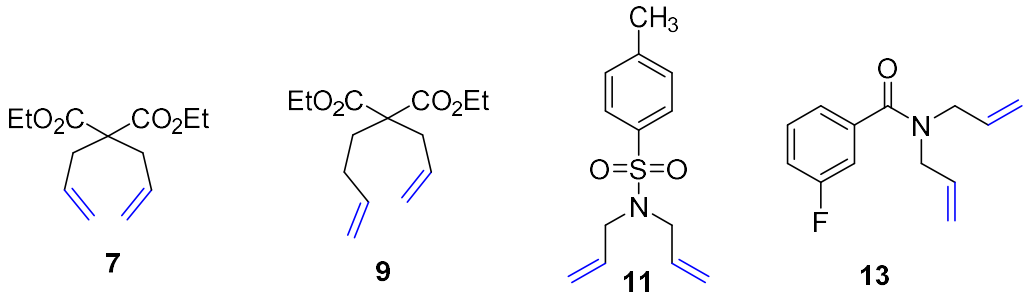


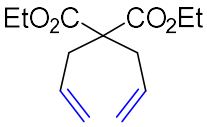
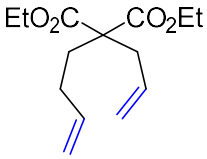
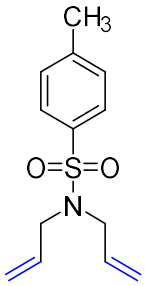
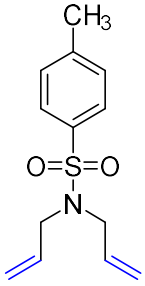
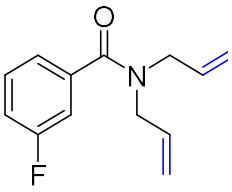
Figure S7. Glassware used in the desorption (leaching) experiments.

10. **Activity Assessment of Ru1@MOF Complex in Ring-Closing Metathesis Reaction**



A 4 mL vial with a septum cap was charged with a magnetic stirring bar, **[Ru]@MOF** (1 mol% of [Ru] *vs.* a substrate), toluene (2 mL) and a corresponding substrate (0.95 mmol). The suspension was stirred for 3 hours in a vial with perforated septum at 80 °C (0.4 mm needle was stuck in the septum, to release ethylene). After this time the vial was taken from the stirring plate and 1 mL of the supernatant was withdrawn and filtered through a syringe filter. 0.1 mL of the filtrate was added to a vial containing 10 mg of Apeiron SnatchCat™ to quench the reaction, whereas the remaining 0.9 mL was added to another vial with septum cap to perform split test. After 24 h both heterogeneous and homogeneous reaction were quenched with 0.1 mL of 1M SnatchCat™ solution in DCM and subjected to GC analysis to determine the conversion of the substrate [2-3]. The

product of the RCM reaction of DATA was isolated by column chromatography (20% to 50% EtOAc/*n*-hexane).

[Ru]@MOF	Substrate	At split	In filtrate (24 h)	In suspension (24 h)
Ru1@(Al)MIL-101-NH_2		52 (3 h)	53	53
Ru1@(Al)MIL-101-NH_2		26 (3 h)	26	31
Ru1@(Al)MIL-101-NH_2		65 (3 h)	65	91*
Ru1@(Al)MIL-101-NH_2·HCl		78 (15 min)	78	78
Ru1@(Al)MIL-101-NH_2		13 (3 h)	14	30

*The isolated yield of the product **12** is 79%.

11. NMR Spectra

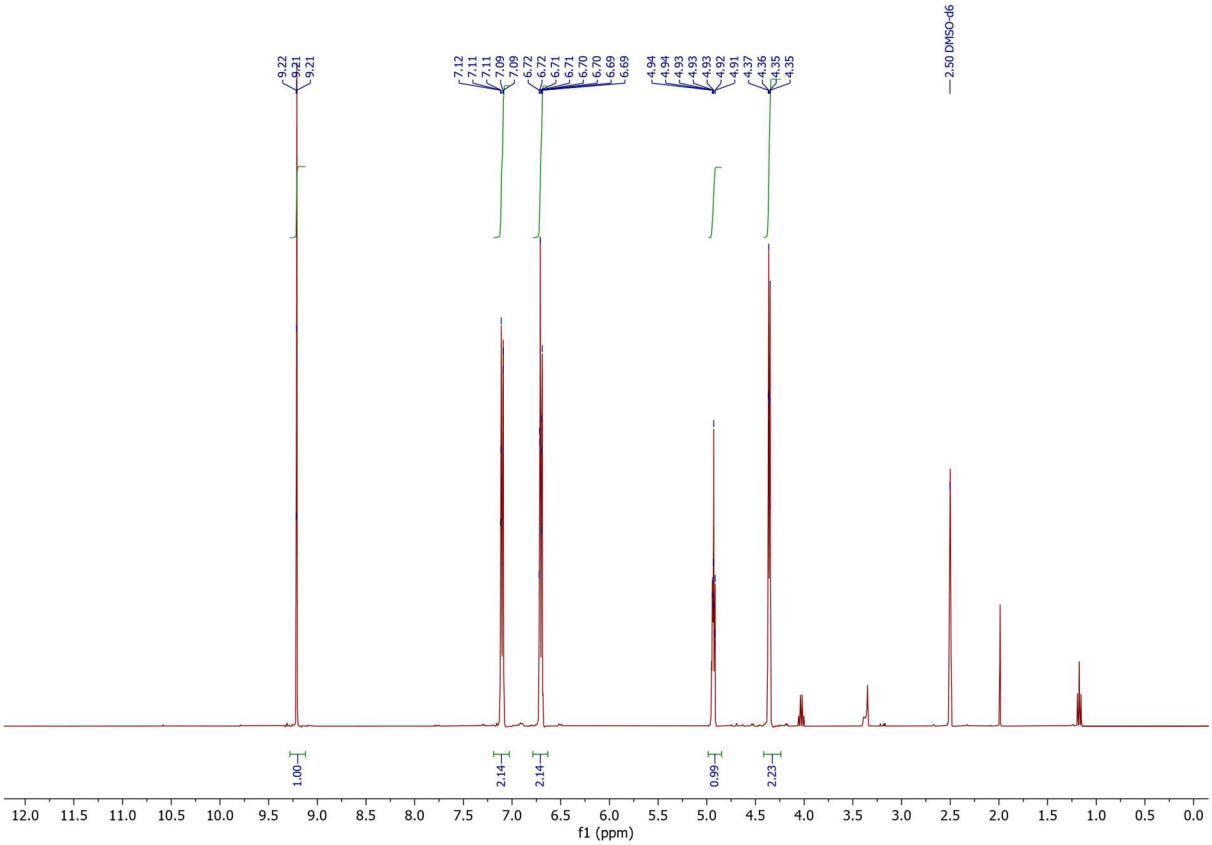


Figure S8. ^{1}H NMR of compound **1.**

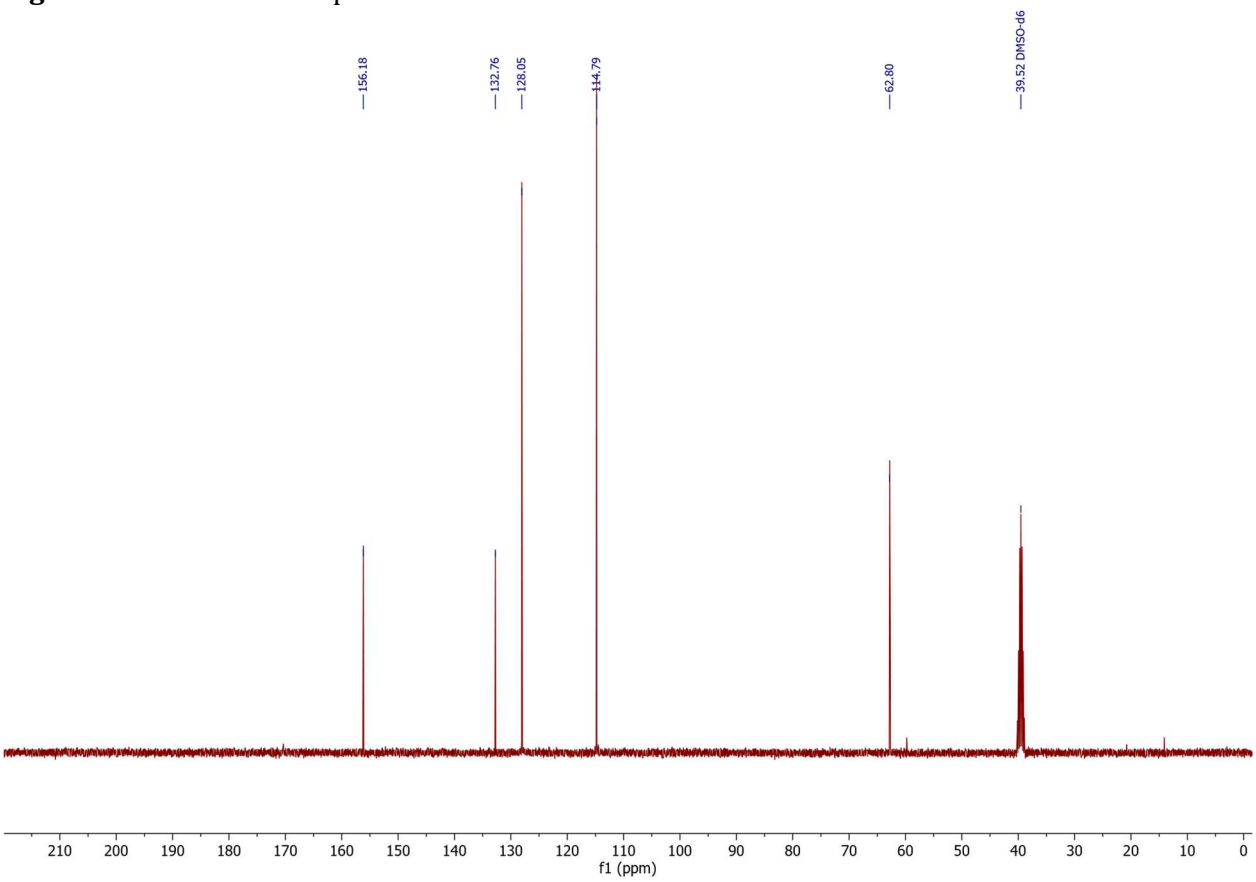


Figure S9. ^{13}C NMR of compound **1.**

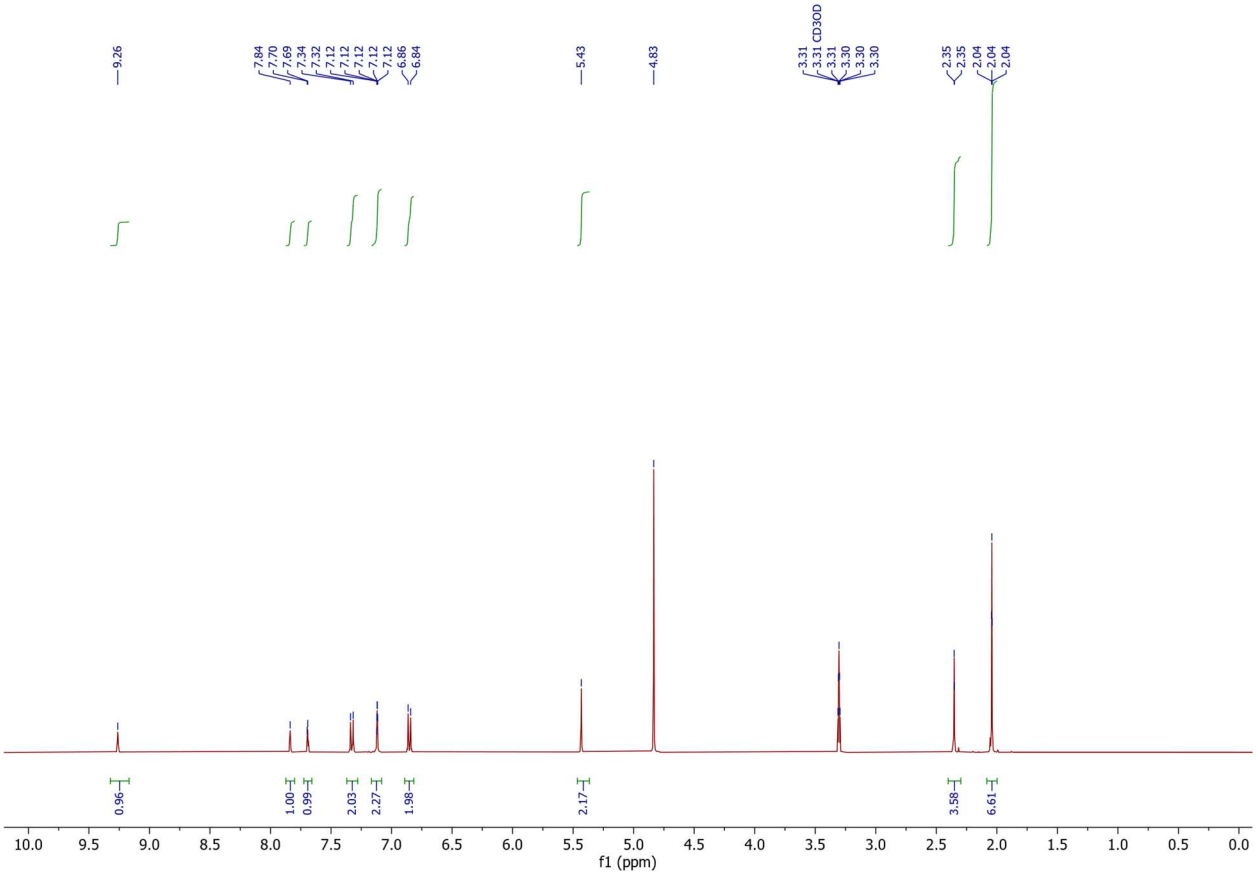


Figure S10. ^{1}H NMR of compound **3.**

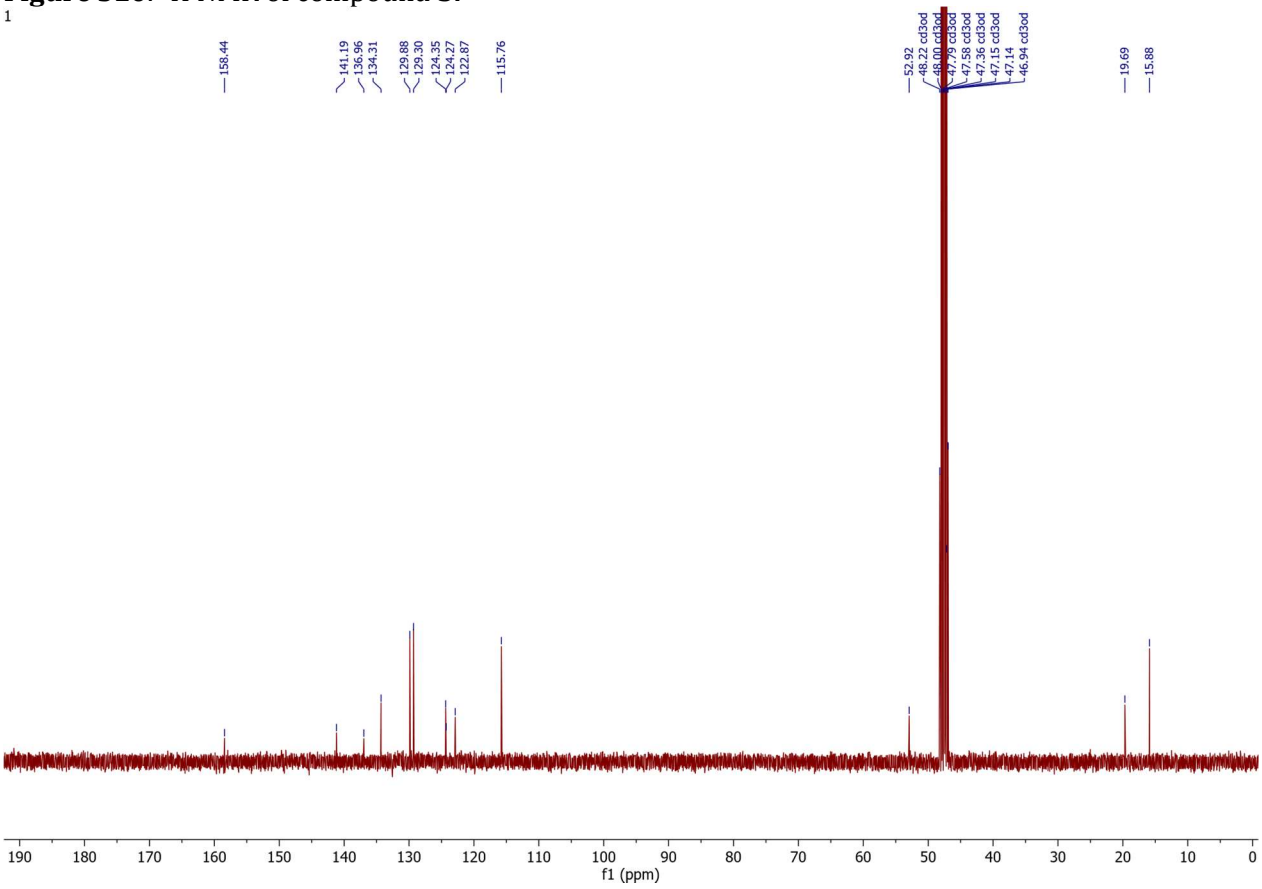


Figure S11. ^{13}C NMR of compound **3.**

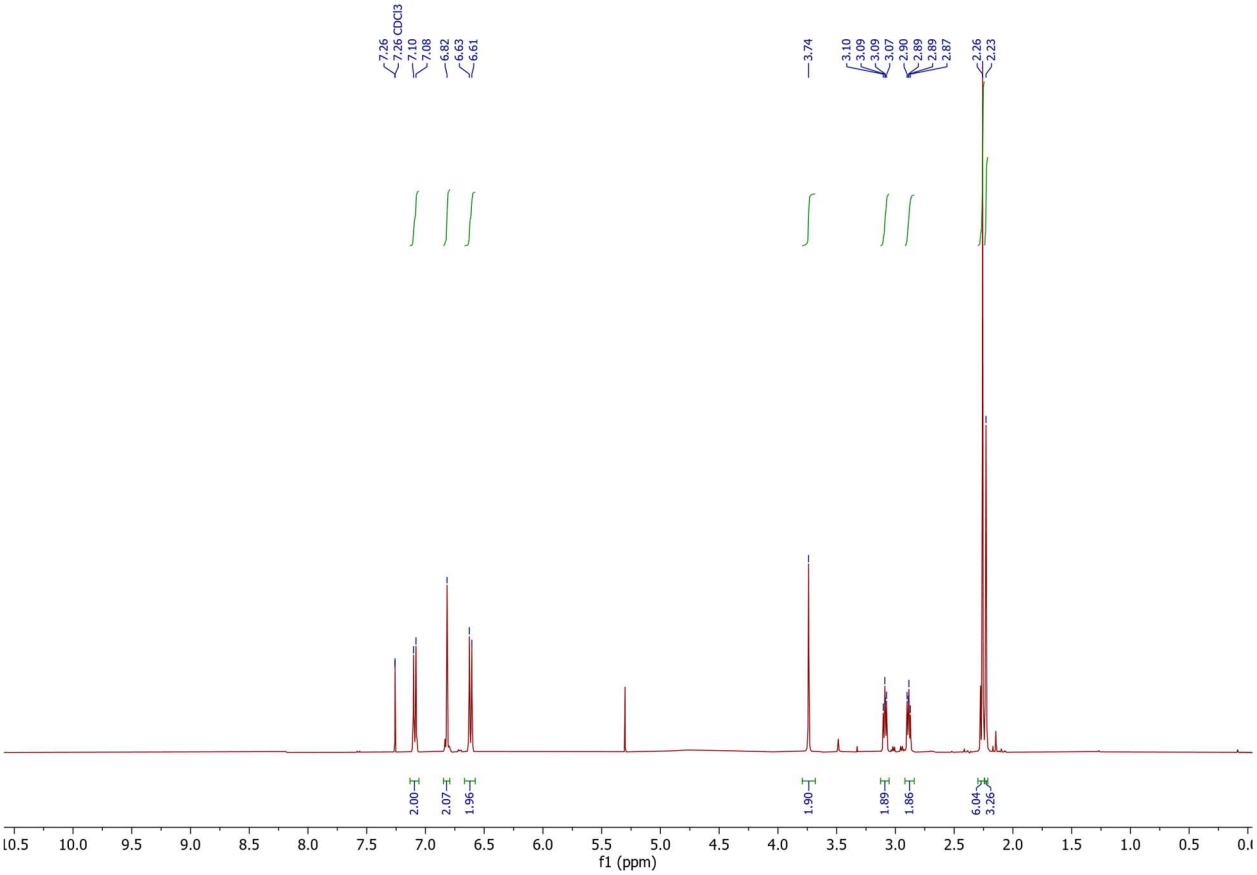


Figure S12. ^{1}H NMR of compound **5.**

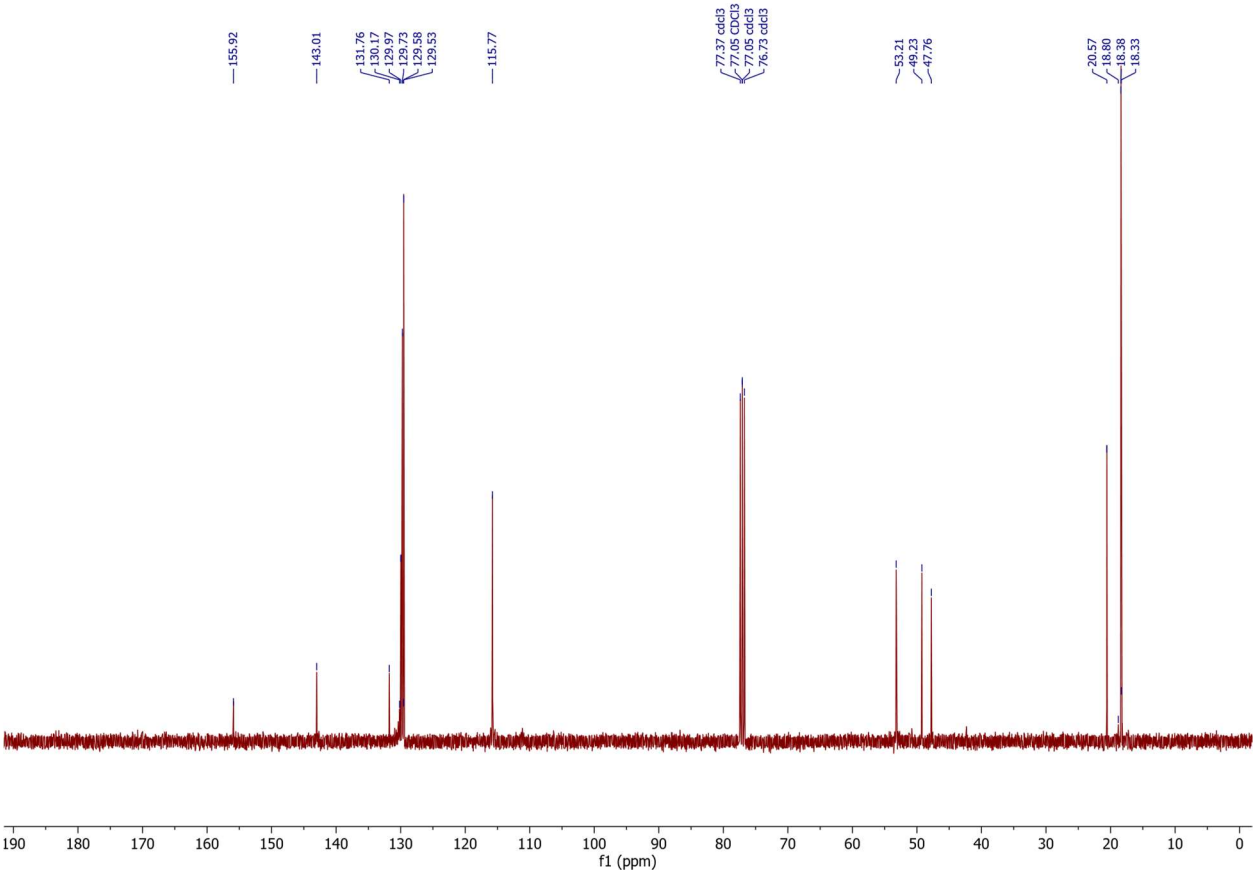


Figure S13. ^{13}C NMR of compound **5.**

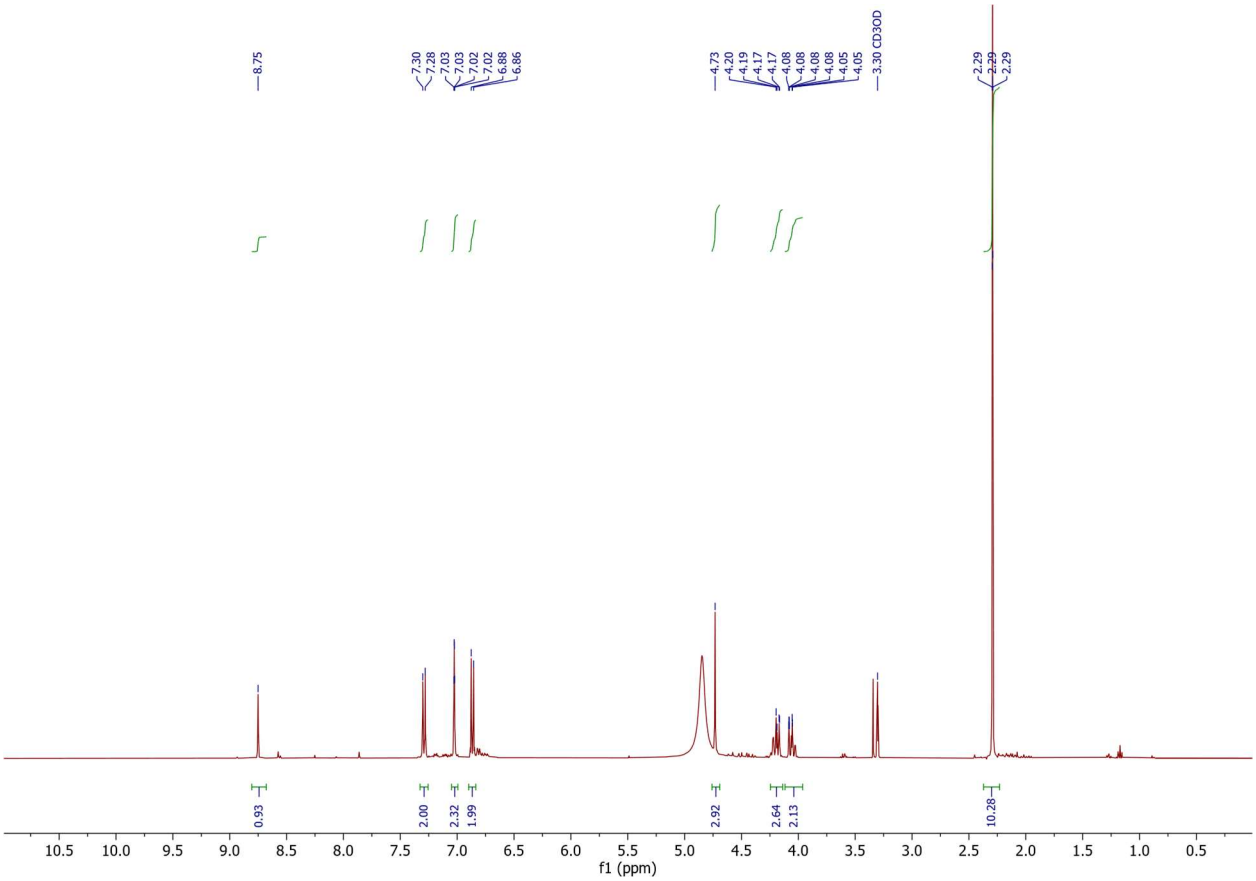


Figure S14. ^{1}H NMR of compound **6.**

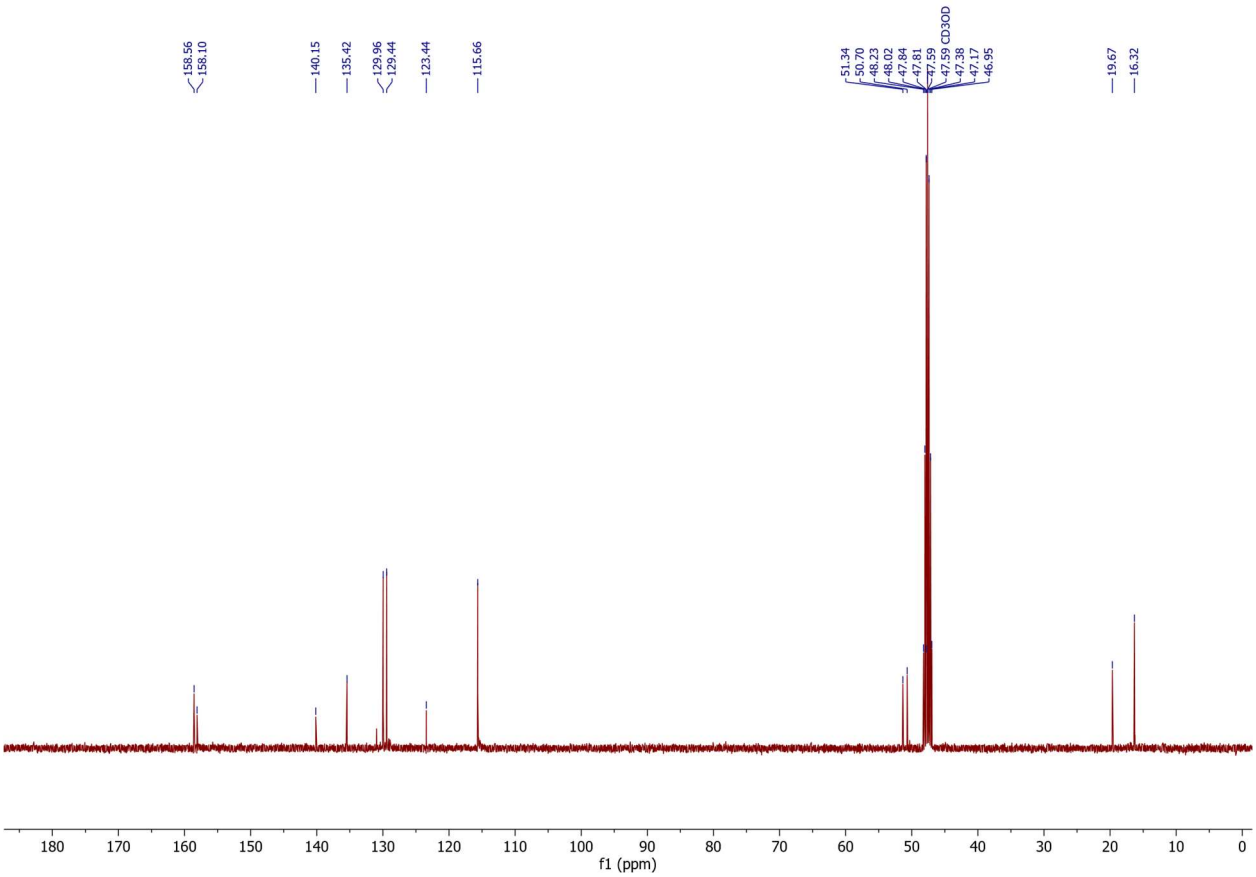


Figure S15. ^{13}C NMR of compound **6.**

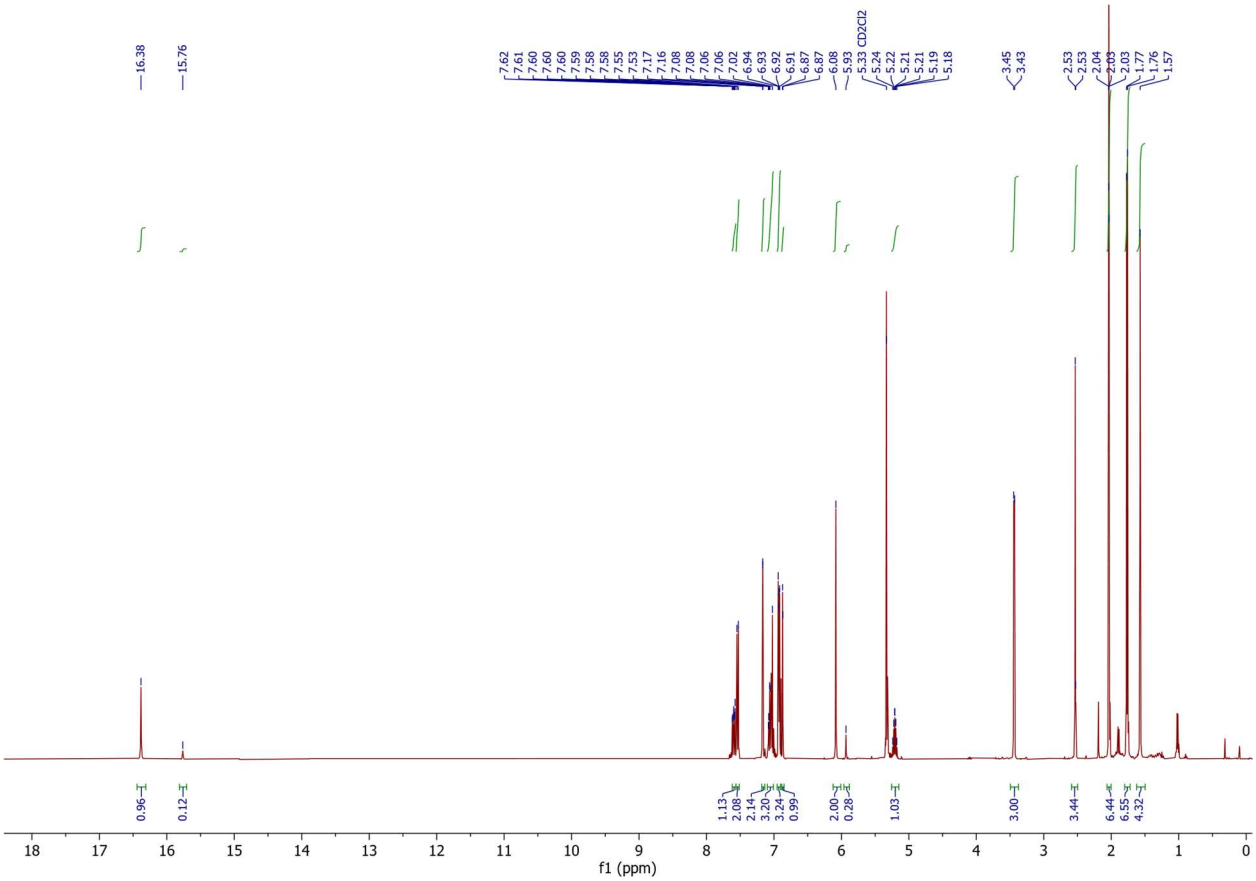


Figure S16. ^{1}H NMR of **Ru1** after the crystallization from DCM/MeOH.

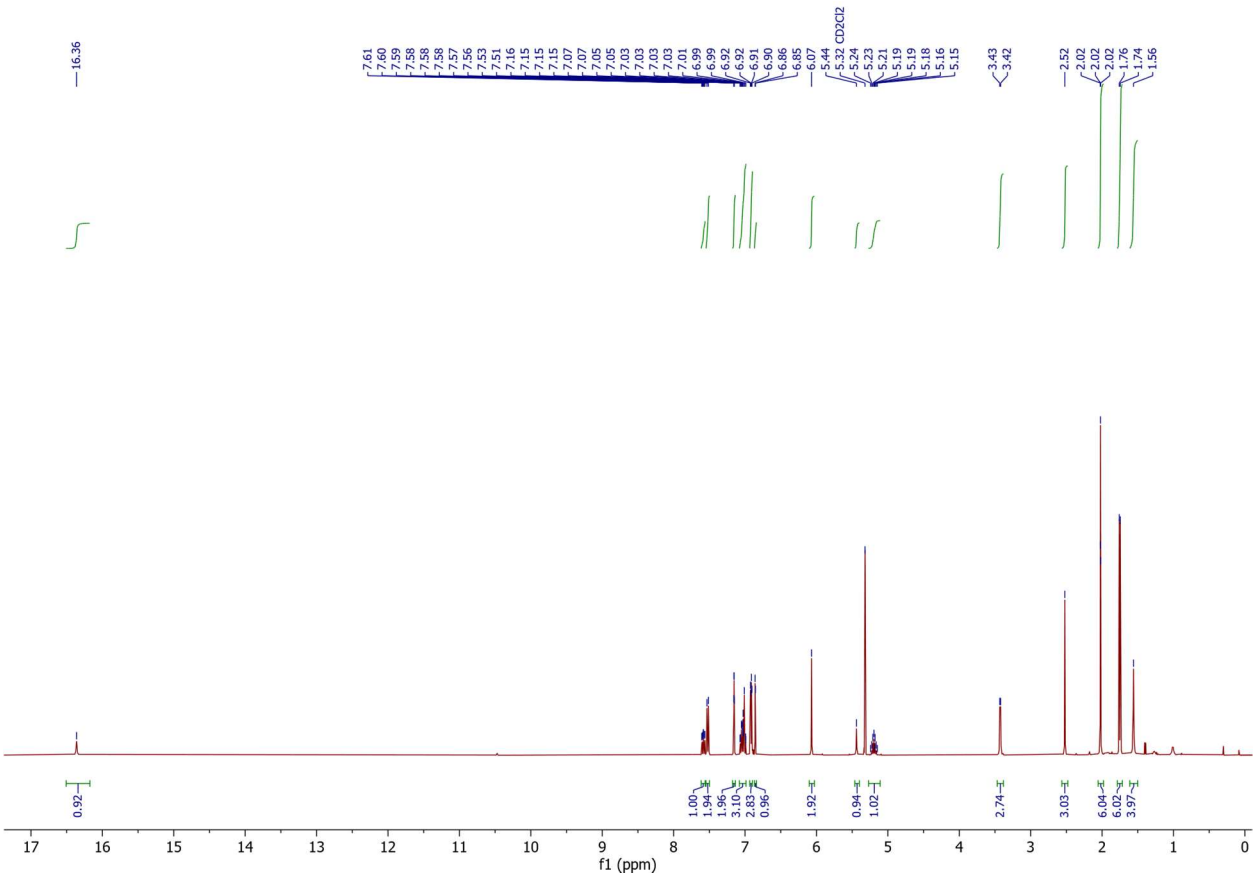


Figure S17. ^{1}H NMR of **Ru1** after stirring it with AgCl.

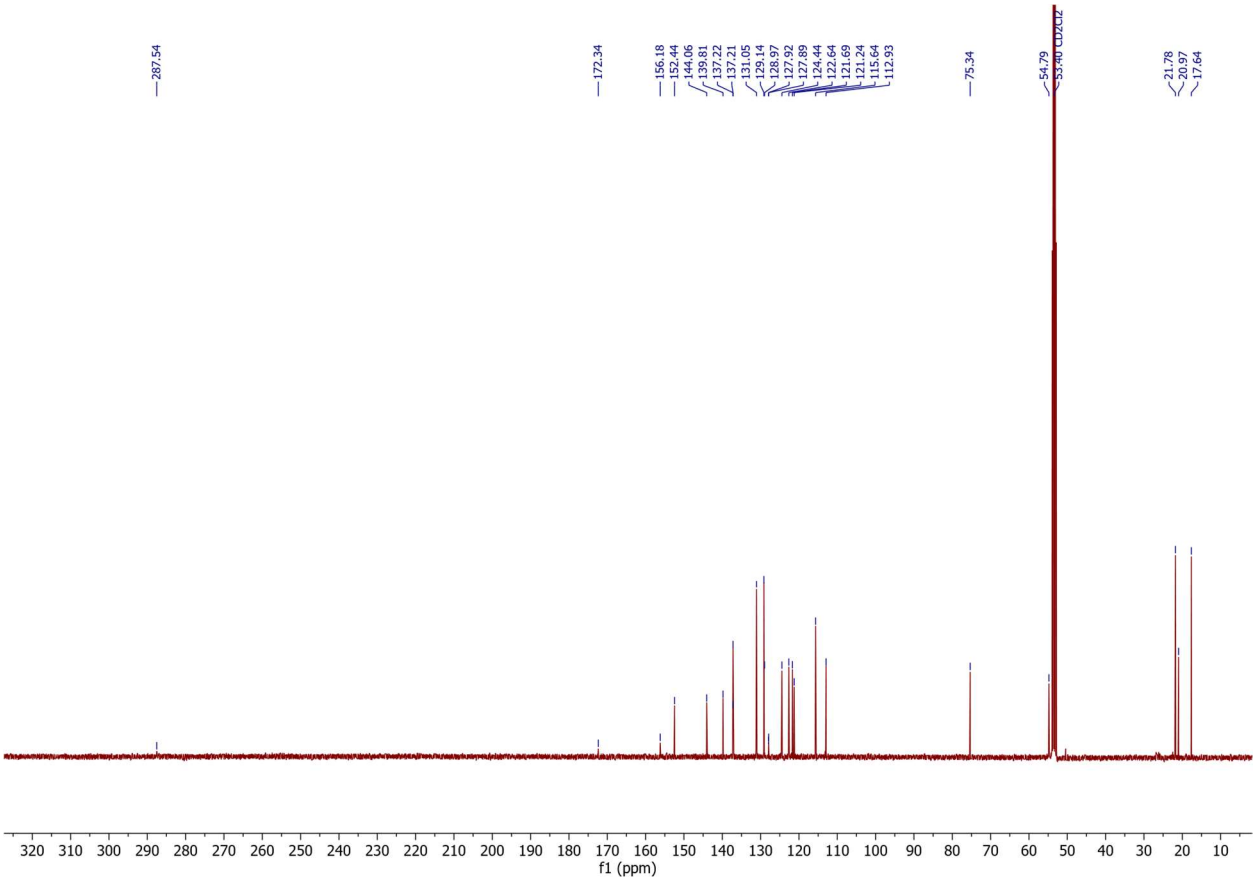


Figure S18. ^{13}C NMR of **Ru1** after stirring it with of AgCl.

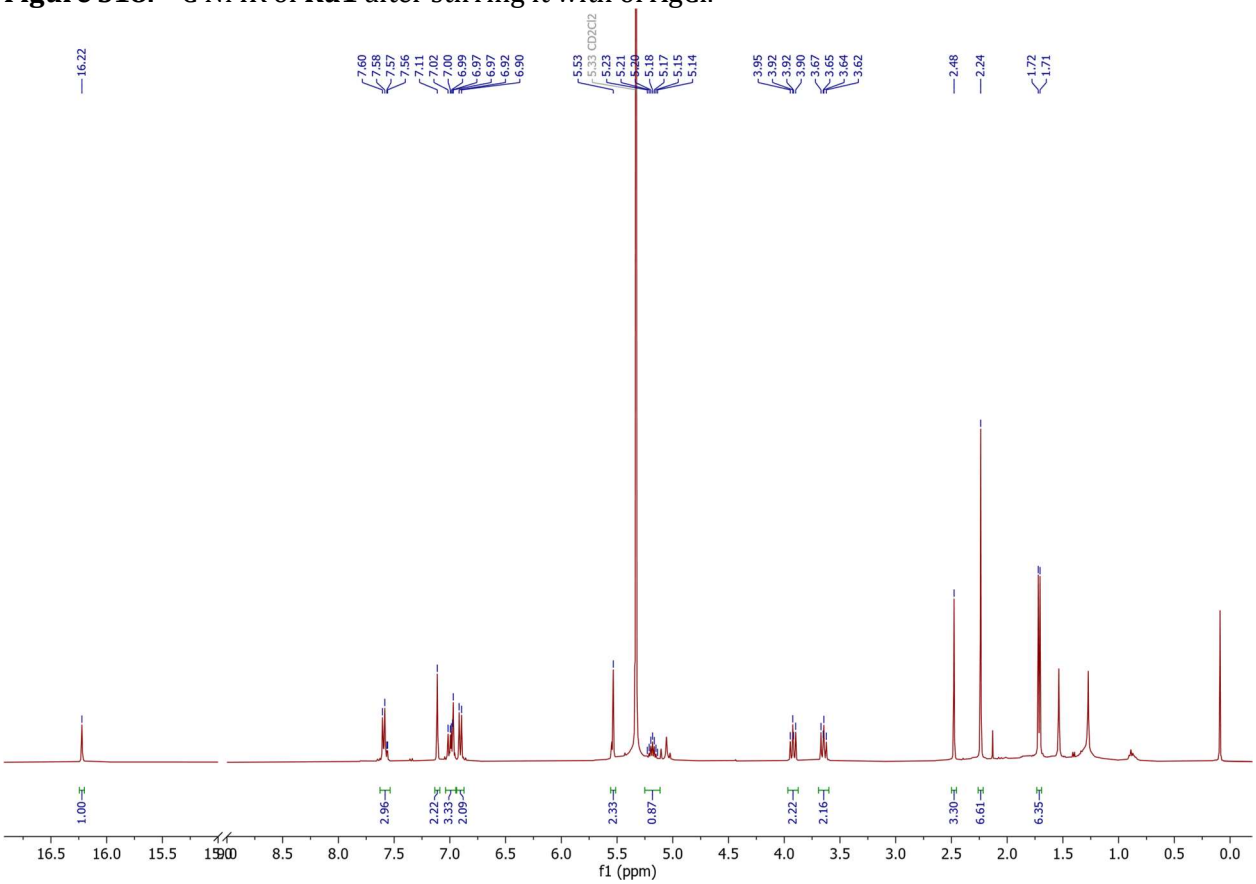


Figure S19. ^{1}H NMR of **Ru2**.

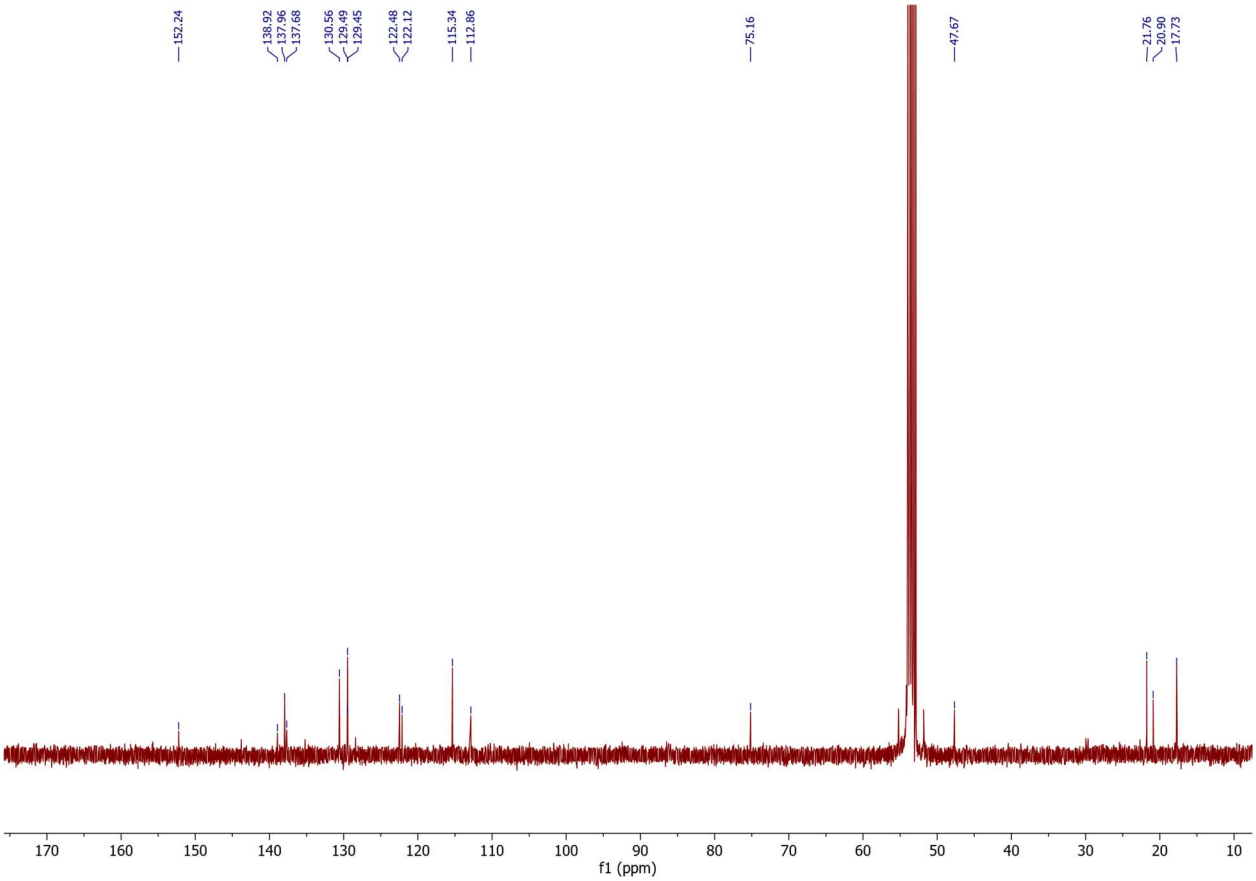


Figure S20. ^{13}C NMR of **Ru2**.

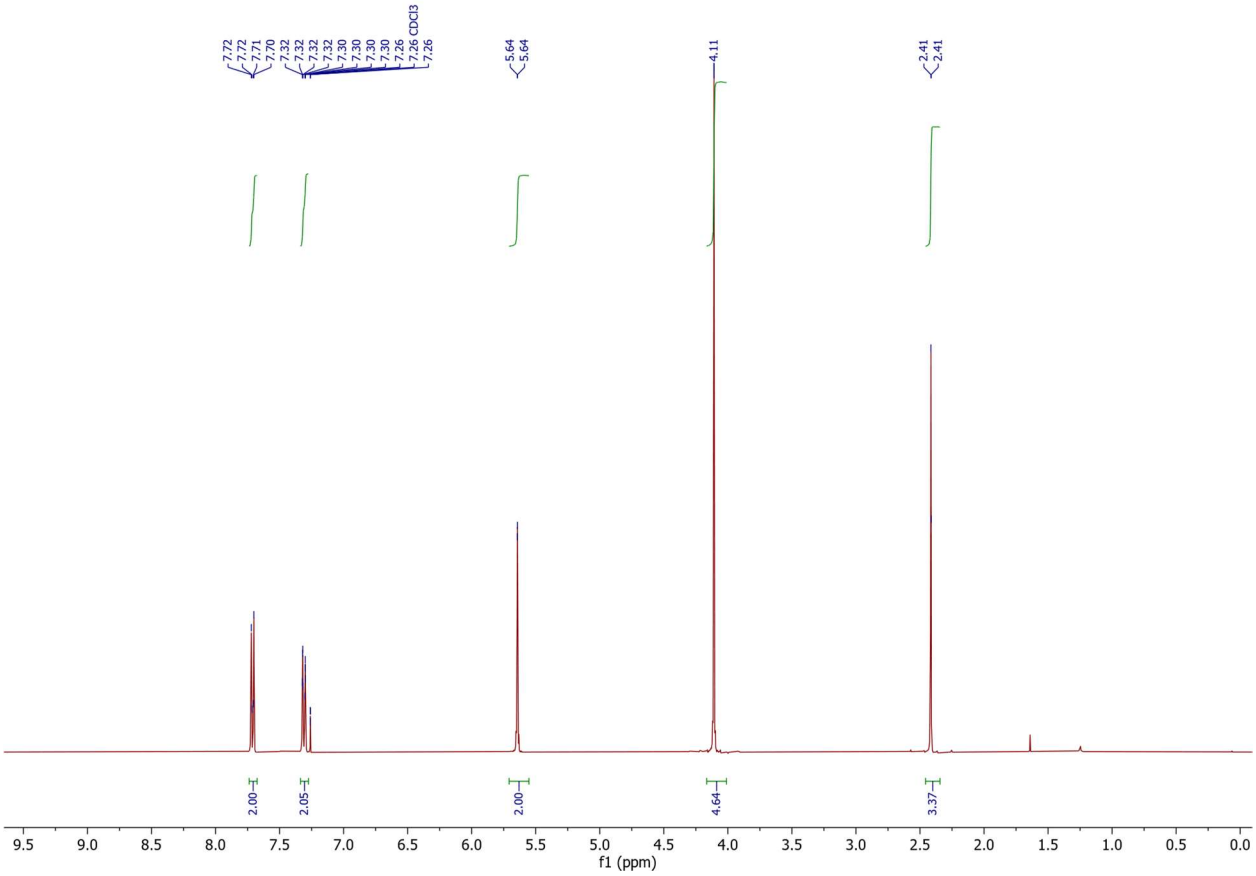


Figure S21. ^{1}H NMR of compound **15**.

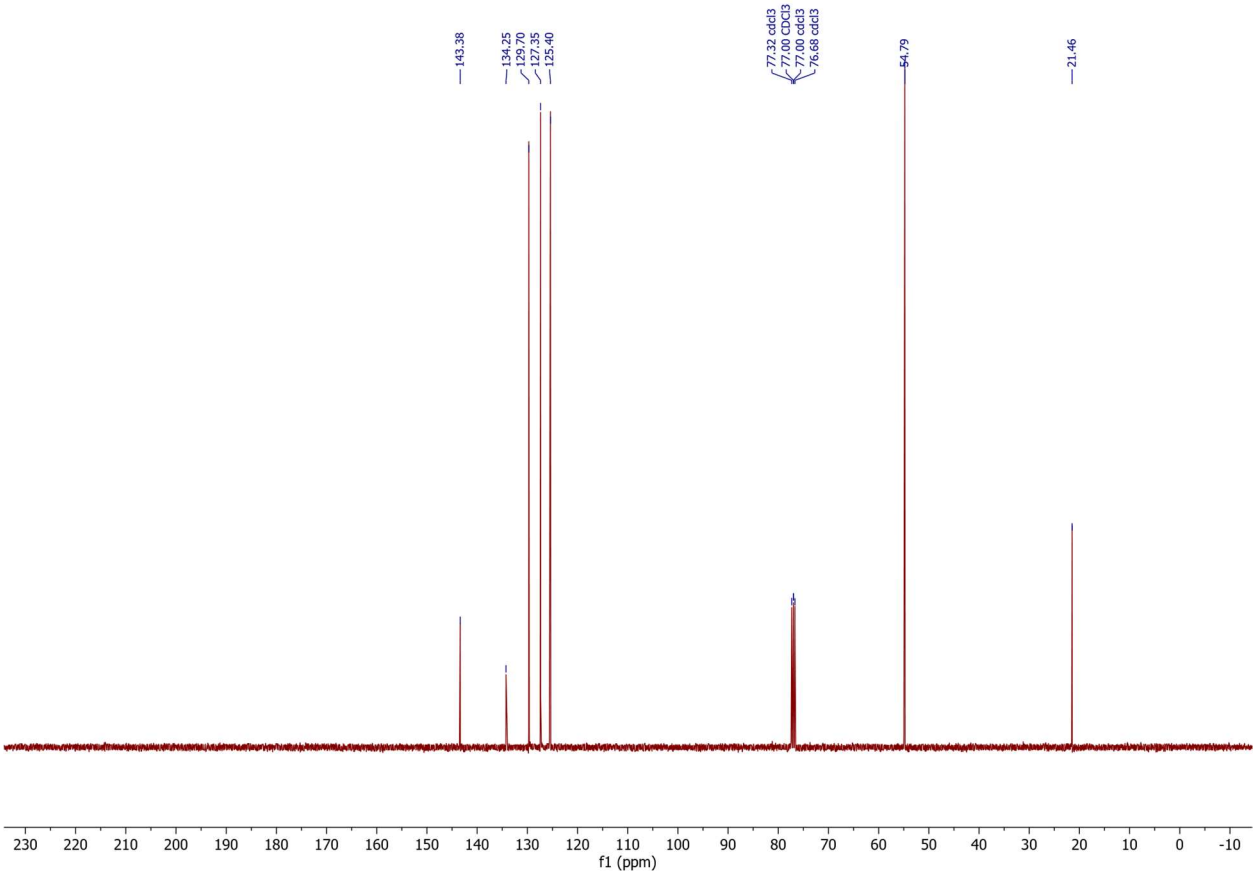


Figure S22. ^{13}C NMR of compound **15**.

12. **References**

[1] (a) J. Rouquerol, P. Llewellyn, F. Rouquerol, *Stud. Surf. Sci. Catal.* **2007**, *160*, 49-56. (b) K. S. Walton, R. Q. Snurr, *J. Am. Chem. Soc.* **2007**, *129*, 8552-8556.

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