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SUPPORTING INFORMATION

Facile post-synthetic deamination of MOFs and the synthesis of the missing parent compound of the MIL-101 family

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1. General information

All solvents and reagents were commercially available and used as received unless otherwise stated. Toluene and dichloromethane were purified with solvent purification system MBRAUN SPS-800.

Alfa Aesar: diethyl diallylmalonate (DEDAM, 98%).

STREM: ruthenium catalyst AquaMet™

Sigma-Aldrich: terephthalic acid (98%), 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$, 99%), aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, >99.5%), *tert*-butyl nitrite (*t*-Bu-ONO, 90%), hydrogen chloride solution (1.0 M in diethyl ether), hydrofluoric acid (HF_{aq} 47-51%, TraceSELECT), methanol (CH_3OH, CHROMASOLV for HPLC, >99.9%), 4-nitrobenzoyl chloride (≥99%), 4-*tert*-butylbenzoyl chloride (99%).

Fisher Scientific UK: *N,N*-dimethylformamide (DMF anhydrous, synthesis grade, 99.8%).

Euriso-top: DMSO-d_6 + 0.03%TMS v/v (>99.8% D), deuterium oxide (99.90% D), sodium deuteroxide (40% w/w in D_2O, 99.50 %D).

Prior to use, the substrate for olefin metathesis was purified by column chromatography using ALDRICH silica gel 60 (230-400 mesh) followed by passing through neutral anhydrous Al_2O_3 (Aldrich).

Nuclear magnetic resonance experiments

The NMR spectra were recorded using 400 MHz NMR Agilent spectrometer at ambient temperature in 1% NaOD in D_2O using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as a reference standard. The default delay time was elongated to d1 = 10 s. The composition of mixtures obtained after digestion of any analysed MOF material was determined according to the relative quantitation method.[1]

IR spectroscopy

Attenuated total reflection infrared (ATR-IR) spectra were recorded at room temperature on a Thermo Scientific Nicolet iS50 FT-IR Spectrometer, in the range 400-4000cm^{-1}.

Measurement of N_2 sorption isotherms

Prior to the measurements, all samples were heated at 150°C for 24 h under high vacuum and stored in a desiccator. Samples were once again thermally activated and degassed immediately prior to the N_2 physisorption measurements for at least 12 h at 150°C. The nitrogen sorption isotherms were determined at liquid nitrogen temperature (77K) using Micrometrics ASAP 2020 or Quantachrome Autosorb-IQ-MP sorption analyser. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method using P/P_o values in the range 0.05-0.2. For all isotherm analyses we ensured that the two consistency criteria described by Rouquerol *et al.*[2] and Walton *et al.*[3] were satisfied.

Powder X-ray diffraction

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

Scanning Electron Microscopy (SEM)

SEM images were acquired using ZEISS Merlin Gemini II electron microscope operating at 2 kV with Bruker QUANTAX EDS detector operating at 6 kV.

UV-Vis spectroscopy

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.

Gas chromatography

GC measurements were conducted on Shimadzu 2010plus chromatograph equipped with CHIRAMIX column. Retention times of products were compared with those of authentic samples. Conversion values were calculated using calibration curves.

2. The synthesis of MOFs

2.1 (Al)MIL-101-NH_2 by a modified Gascon method

(Al)MIL-101-NH_2 was synthesized using a modified procedure[4] by Gascon and co-workers.[5] Aluminium trichloride hexahydrate (1.53 g, 6.28 mmol) and a magnetic stir bar were placed in an 150 ml Ace Glass pressure tube followed by dry DMF (120 ml) and stirred overnight at room temperature until homogenous solution formed. Next, 2-aminoterephthalic acid (1.68 g, 9.28 mmol) 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 3 days. Over this period a precipitate formed, which was filtered off on a glass frit (G4) under reduced pressure and washed with DMF (40 ml), acetone (50 ml) and methanol (50 ml). The as-synthesised MOF contained *ca.* 18% of formylated amino groups. Next, the as-synthesised material was extracted with methanol for 24 h in a Soxhlet apparatus and then heated in methanol at 120°C in a pressure tube overnight. After cooling down the solid was collected by filtration and activated under vacuum (10 µbar) at 150°C for 24h.

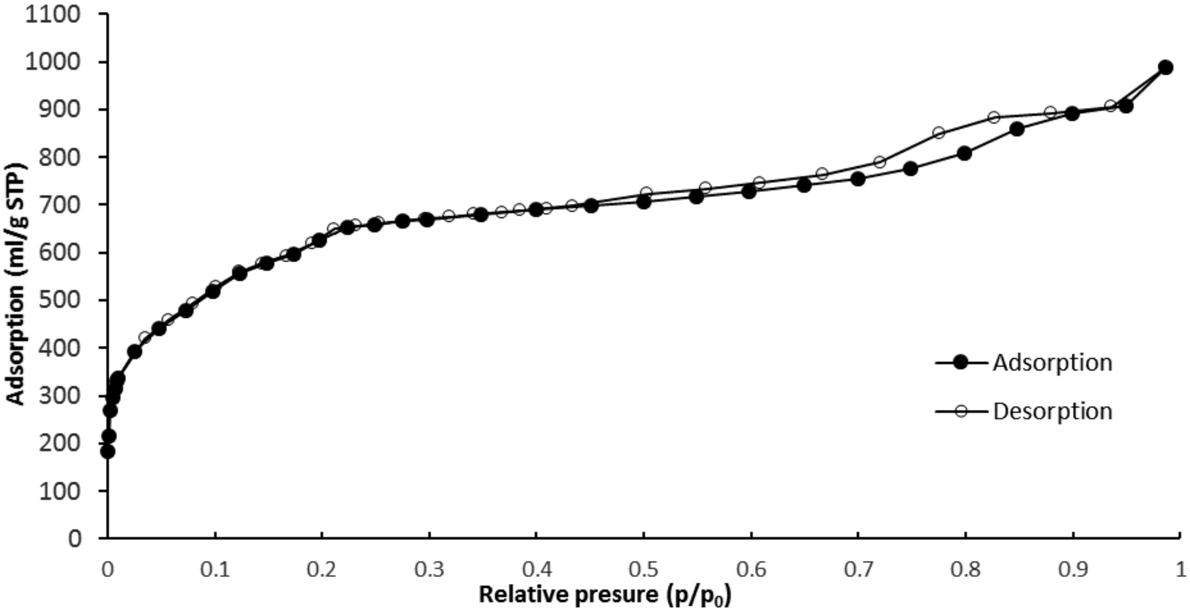

Figure S1. The N_2 adsorption isotherm of (Al)MIL-101-NH_2 obtained by the Gascon method. S_{BET} = 2303 m^2/g.

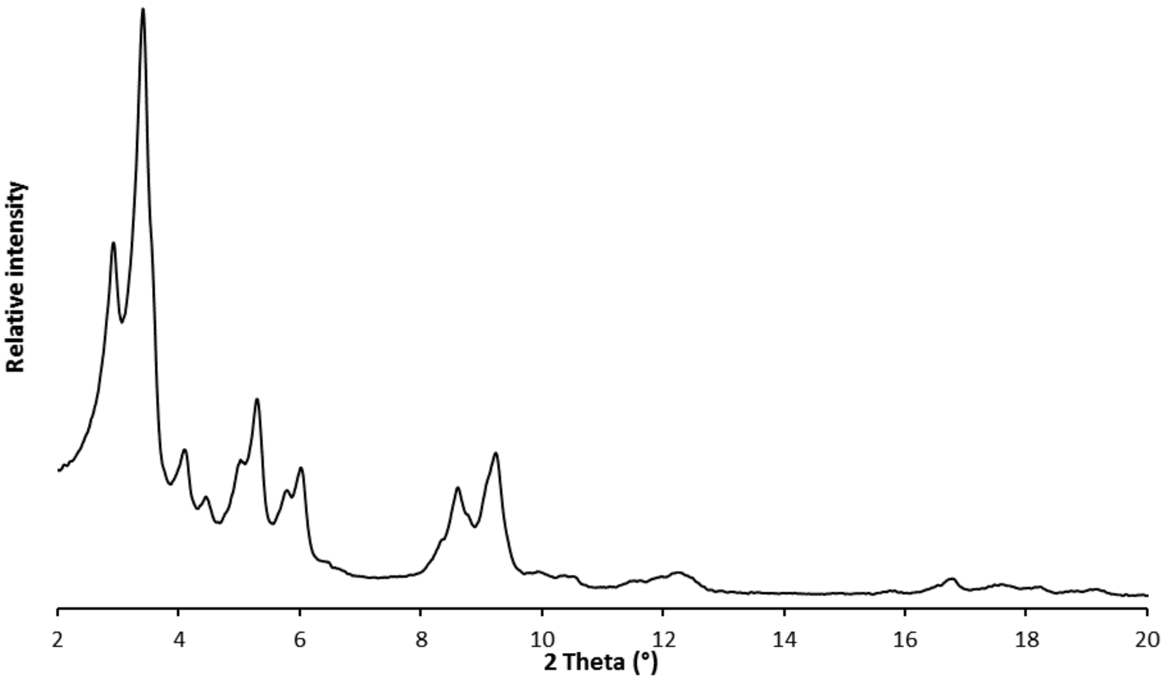

Figure S2. Powder X-ray diffraction pattern (PXRD) of activated (Al)MIL-101-NH_2 obtained by the Gascon method.

2.2 (Al)MIL-101-NH_2 by a modified Hartmann method

(Al)MIL-101-NH_2 was synthesized using a modified procedure by Hartmann and co-workers.[6] DMF (90 ml) and 2-aminoterephtalic acid (1.22 g, 6.80 mmol) was placed in a 250 ml round-bottom flask and heated in an oil bath to 110 °C until complete dissolution (15 min). Then aluminum chloride hexahydrate (1.10 g, 4.56 mmol) was added with stirring in 7 equal portions every 15 min, and then was further stirred for 3 h. After this time the stirring bar was removed and the mixture was heated further for 18h. The obtained MOF was filtered off on a G4 glass frit, washed with DMF (50 ml), ethanol (50 ml) and finally extracted with ethanol in a Soxhlet extractor overnight. *Ca.* 12% of ligands of the thus-obtained MOF was formylated, so it was further heated in MeOH at 120°C overnight, filtered off, washed with methanol (50 ml) and activated under high vacuum at 150°C overnight.

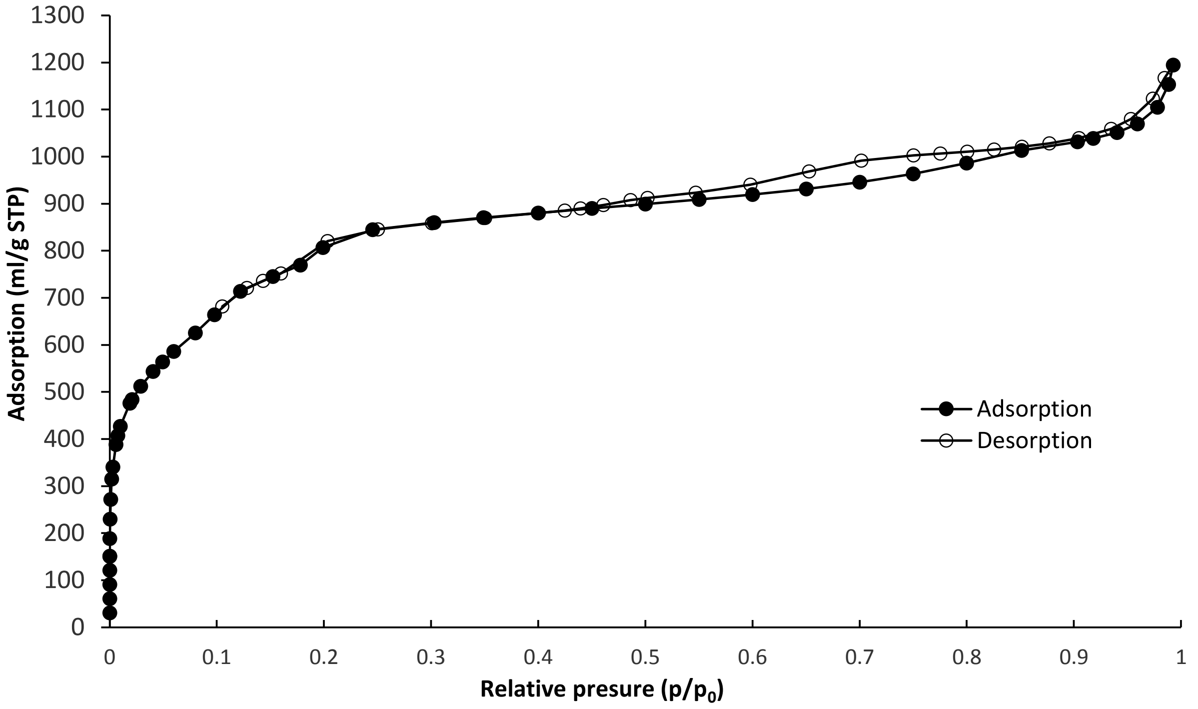

Figure S3. The N_2 adsorption isotherm of (Al)MIL-101-NH_2 obtained by the Hartmann method. S_{BET} = 2970 m^2/g

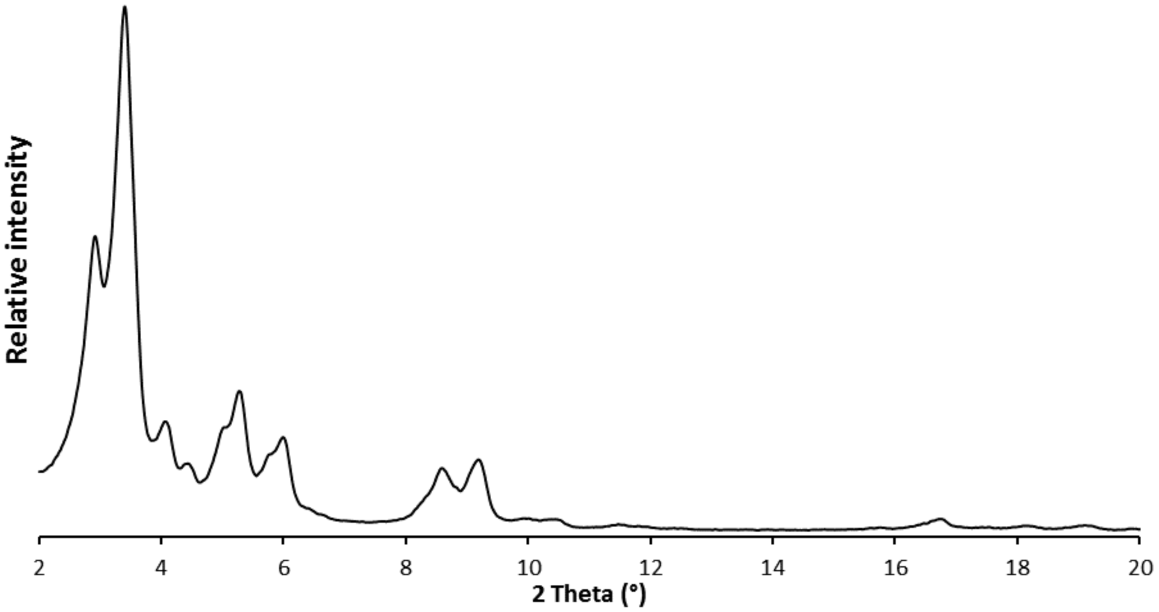

Figure S4. Powder X-ray diffraction pattern (PXRD) of activated (Al)MIL-101-NH_2 obtained by the Hartmann method.

2.3 (Cr)MIL-101

(Cr)MIL-101 was synthesized according to the literature method.[7] H_2BDC (1.660 g, 10.0 mmol), chromium(III) nitrate (4.000 g, 10.0 mmol), deionized water (48.00 ml) and HF_{aq} (0.4125 ml) were transferred into a teflon-lined stainless steel autoclave, and the mixture was kept at 220°C for 8 h. After this time the reactor was allowed to cool down slowly to room temperature together with the oven. The product was separated by centrifugation and washed with DMF until the supernatant was colorless. Than the raw (Cr)MIL-101 was washed three more times with DMF using centrifuge and treated twice with DMF (20 ml) at 85°C followed by refluxing twice in EtOH (20 ml) for 24 h each time to remove the excess of H_2BDC. Finally, the MOF was dried under vacuum at 150°C for 24h.

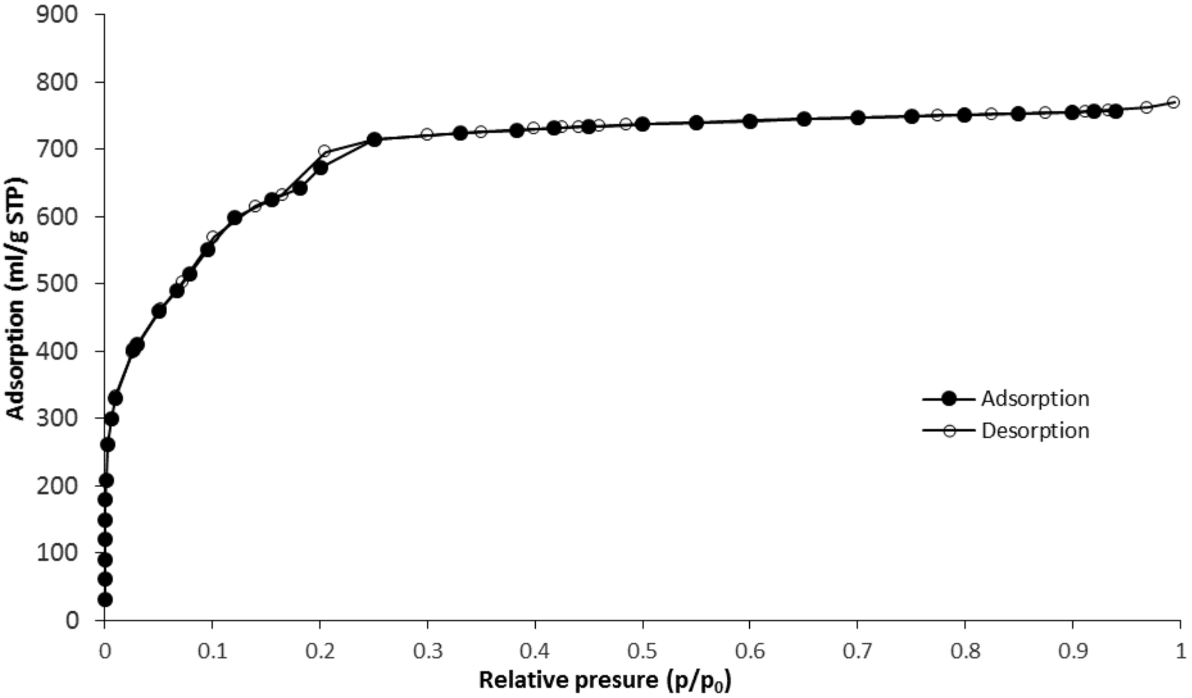

Figure S5. The N_2 adsorption isotherm of activated (Cr)MIL-101. S_{BET} = 2478 m^2/g.

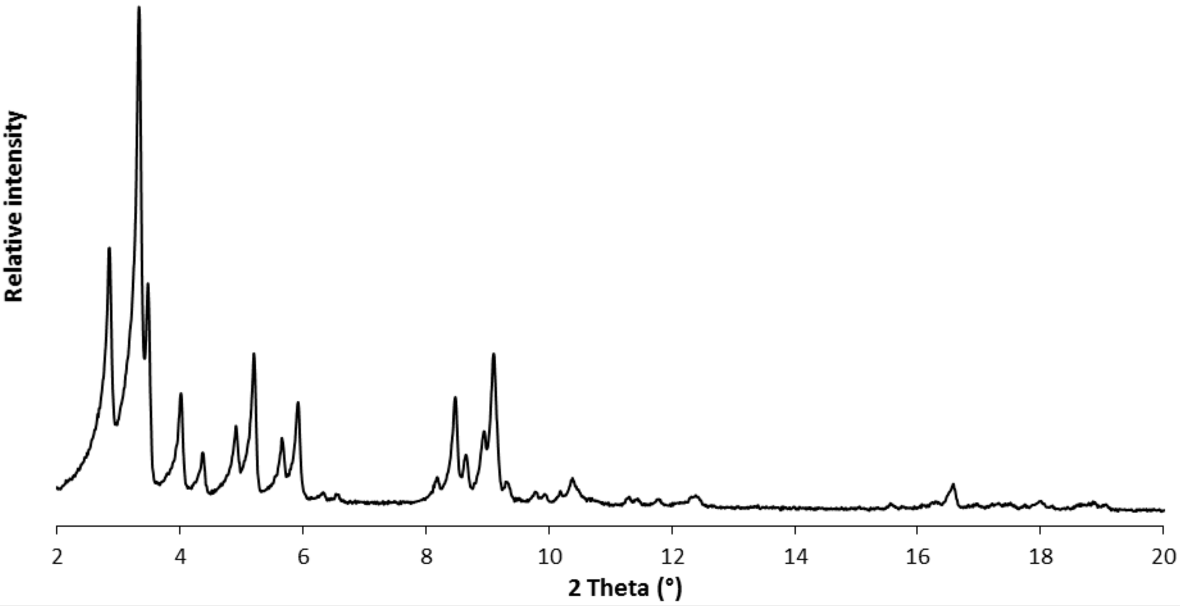

Figure S6. Powder X-ray diffraction pattern (PXRD) of activated (Cr)MIL-101.

2.4 (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2

(Al)MIL-101-NH_2 by a modified Gascon method (150 mg, *ca.* 0.62 mmol of NH_2 groups), 4-nitrobenzoyl chloride (115 mg, 0.62 mmol) and DCM (3 ml) were placed in 4 ml vial. The resulting suspension was sonicated for 5 seconds and then left at room temperature for 30 min. After this time the mixture was filtered and the solid reside was washed with DCM, MeOH and again with DCM (20 ml each). The MOF was dried under vacuum. A small sample was digested in 1 wt % NaOD/D_2O and analysed by ^1H NMR.

^1H NMR (400 MHz, Deuterium Oxide) δ 8.64 (d, *J* = 1.7 Hz, 1H), 8.27 – 8.22 (m, 2H), 8.07 – 8.01 (m, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 8.1, 1.7 Hz, 1H).

Ca. 50% of ligands were functionalized. The sample contains *ca.* 0.013 equivalents of hydrolyzed *p*-nitrobenzoyl chloride per each ligand.

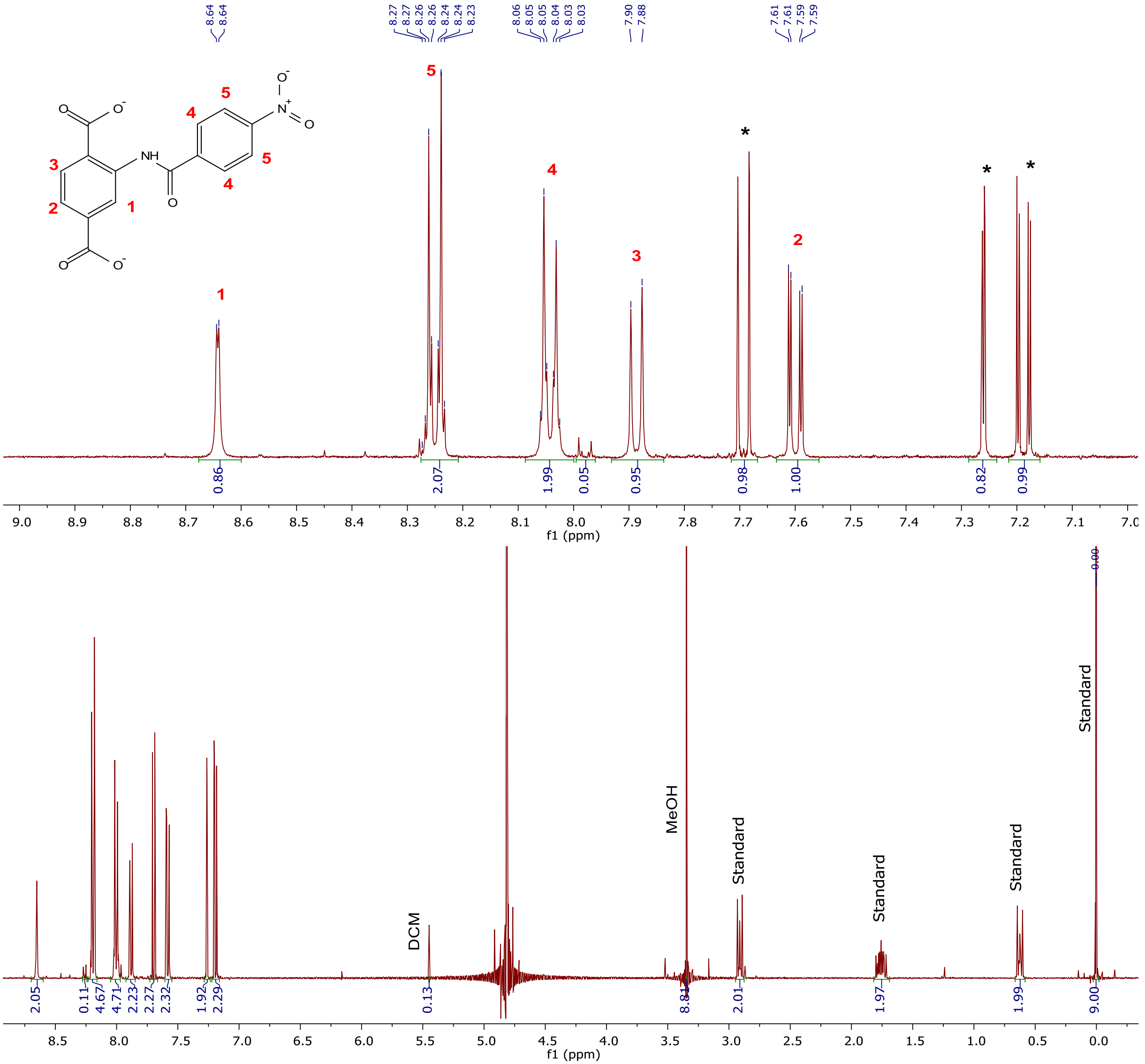

Figure 7. ^1H NMR spectrum of (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2 digested in 1 wt % NaOD/D_2O. The signals of unreacted BDC-NH_2 are marked with asterisks.

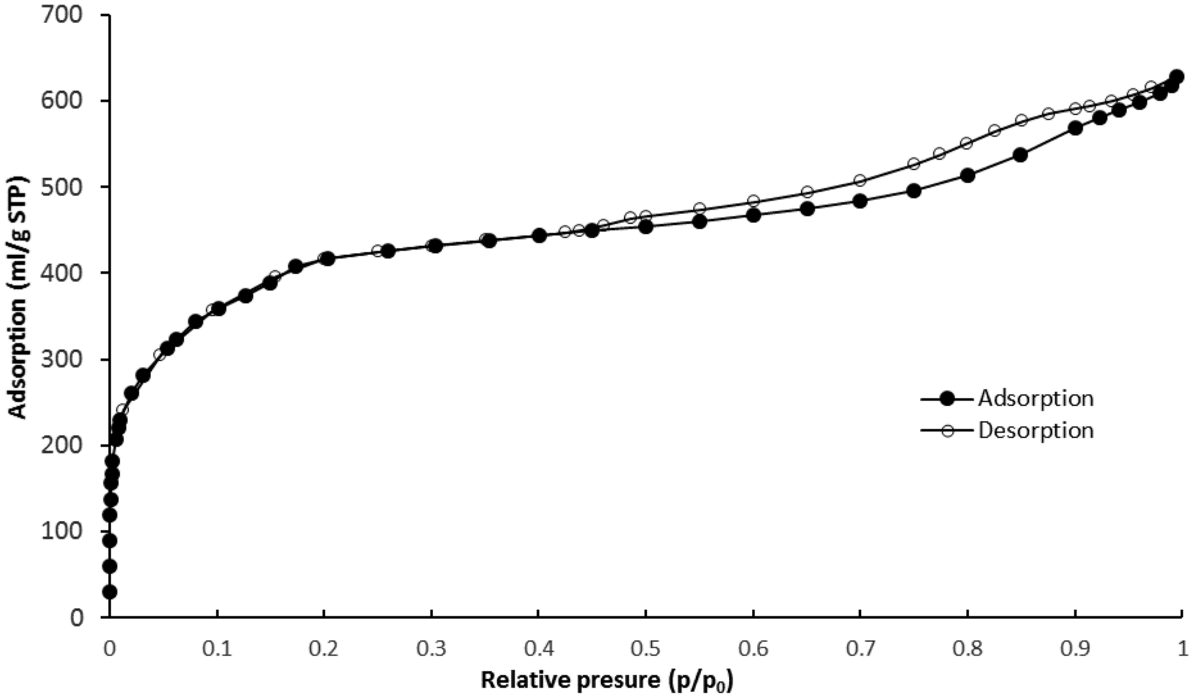

Figure S8. The N_2 adsorption isotherm of activated (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2. S_{BET} = 1522 m^2/g.

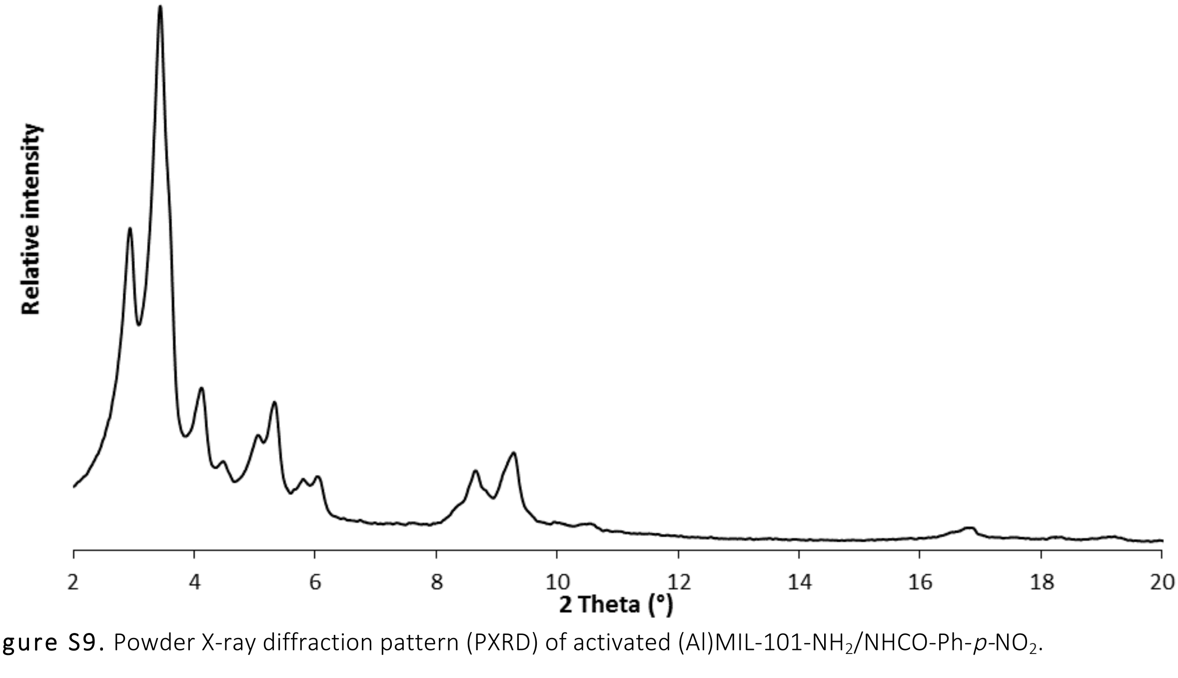

Figure S9. Powder X-ray diffraction pattern (PXRD) of activated (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2.

2.5 (Al)MIL-101-NH$_2$/NHCO-Ph-4-(*t*-Bu)

(Al)MIL-101-NH$_2$ by a modified Gascon method (120 mg, *ca.* 0.5 mmol of NH$_2$ groups), 4-*tert*-butylbenzoyl chloride (0.20 ml, 1.0 mmol) and DCM (3 ml) were placed in a 4 ml vial. The resulting suspension was sonicated for 10 seconds and then left at room temperature for 30 min. After this time the reaction mixture was filtered and the solid residue was washed with DCM, MeOH and again DCM (20 ml each). The MOF was dried under vacuum. A small sample was digested in 1 wt % NaOD/D$_2$O and analysed by ^{1}H NMR.

^{1}H NMR (400 MHz, Deuterium Oxide) δ 8.86 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.99 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.70 – 7.66 (m, 2H), 7.67 (d, *J* = 1.7 Hz, 1H), 1.34 (s, 9H).

Ca. 45% of ligands were functionalized. The sample contains *ca.* 0.03 equivalents of hydrolyzed 4-*tert*-butylbenzoyl chloride per ligand.

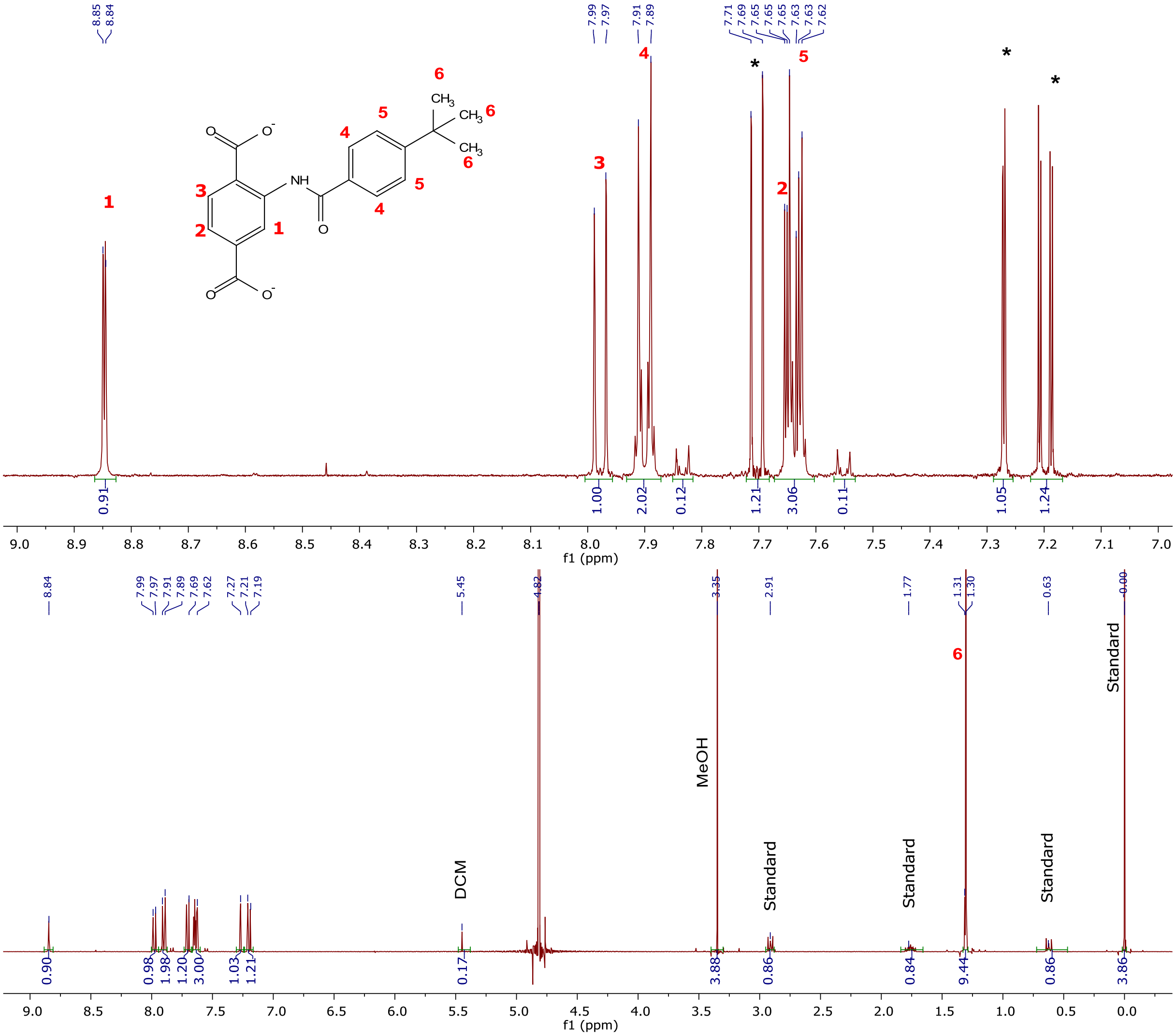

Figure S10. ^{1}H NMR spectrum of (Al)MIL-101-NH$_2$/NHCO-Ph-4-(*t*-Bu) digested in 1 wt % NaOD/D$_2$O. The signals of unreacted BDC-NH$_2$ are marked with asterisks.

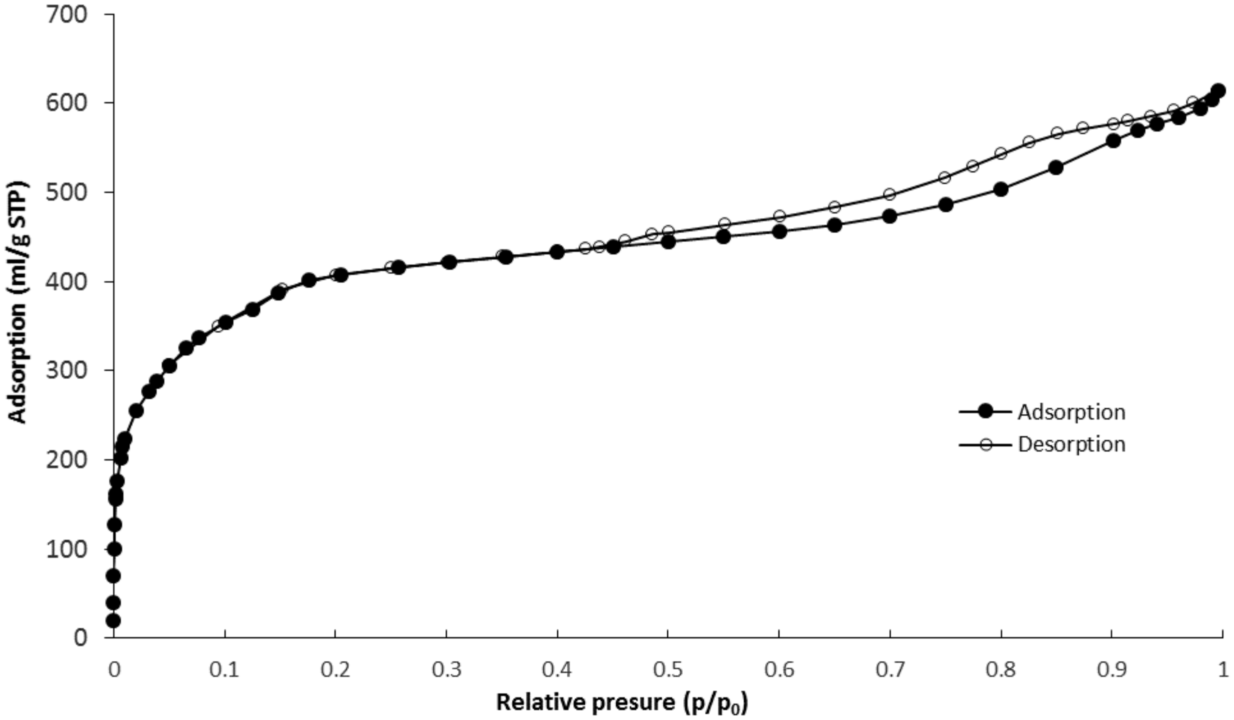

Figure S11. The N_2 adsorption isotherm of activated (Al)MIL-101-NH_2/NHCO-Ph-4-(*t*-Bu). S_{BET} = 1494 m^2/g.

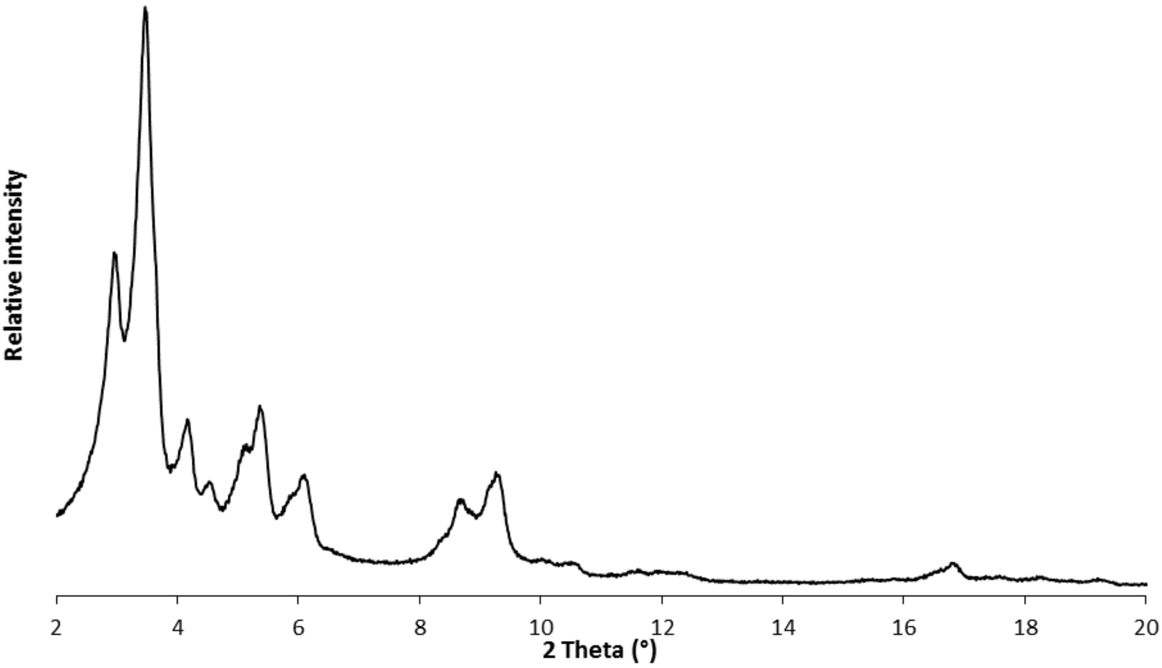

Figure S12. Powder X-ray diffraction pattern (PXRD) of activated (Al)MIL-101-NH_2/NHCO-Ph-4-(*t*-Bu).

2.6 (Al)MIL-101-NH$_2$/NHCO-CH$_2$-*t*-Bu

(Al)MIL-101-NH$_2$ (120 mg, *ca.* 0.5 mmol of NH$_2$ groups), *tert*-butylacetyl chloride (68 mg, 0.50 mmol) and DCM (2 ml) were placed in a 4 ml vial. The resulting suspension was sonicated for 10 seconds and then left at room temperature for 60 min. After this time the reaction mixture was filtered and washed with DCM, MeOH and again DCM (20 ml each). The MOF was dried under vacuum. A small sample was digested in 1 wt % NaOD/D$_2$O and analysed by ^{1}H NMR.

^{1}H NMR (400 MHz, Deuterium Oxide) δ 8.54 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.84 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.7 Hz, 1H), 2.33 (s, 2H), 1.07 (s, 9H).

Ca. 55% of ligands were functionalized. The sample contains *ca.* 0.02 equivalents of hydrolyzed *tert*-butylacetyl chloride per ligand.

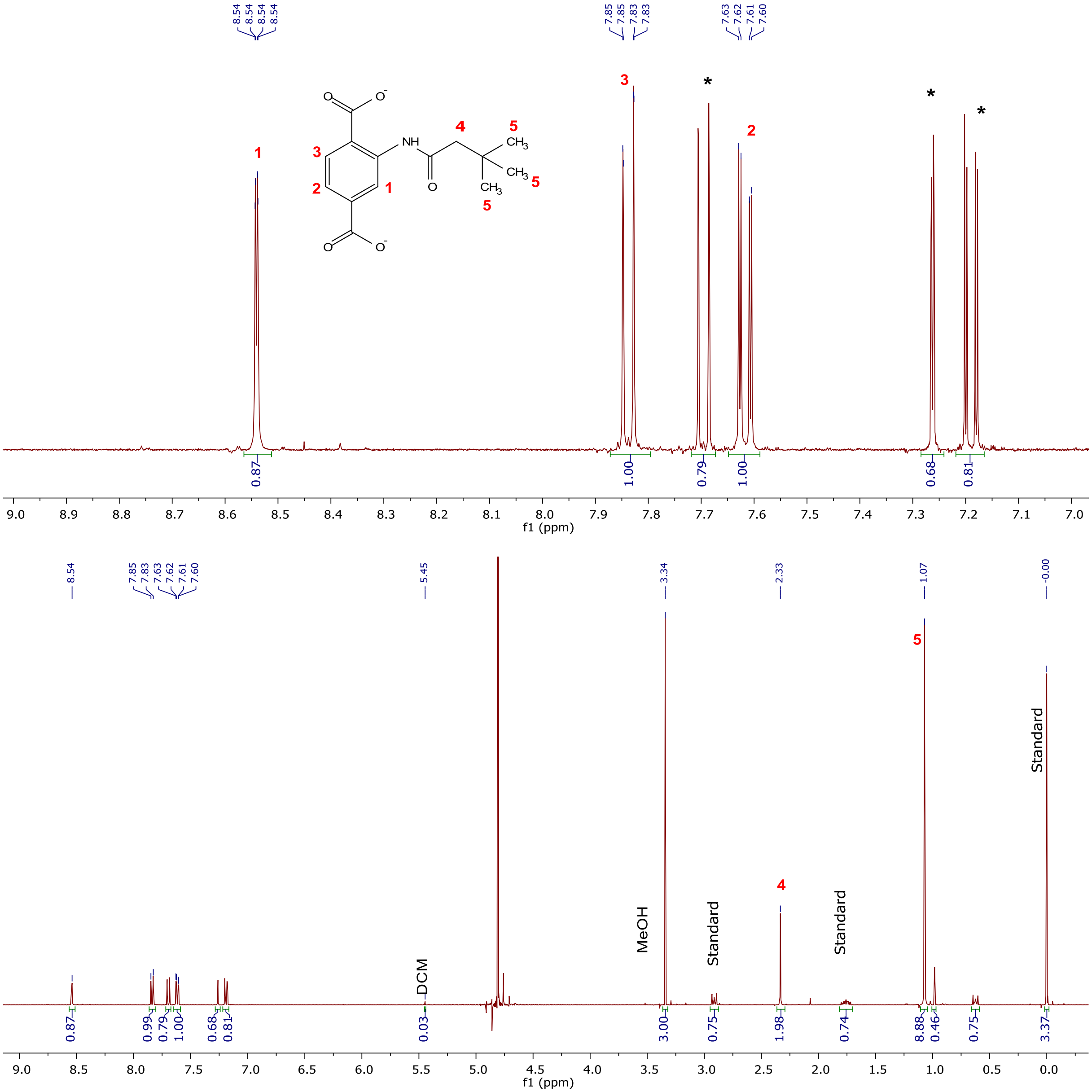

Figure S13. ^{1}H NMR spectrum of (Al)MIL-101-NH$_2$/NHCO-CH$_2$-*t*-Bu digested in 1 wt % NaOD/D$_2$O. The signals of unreacted BDC-NH$_2$ are marked with asterisks.

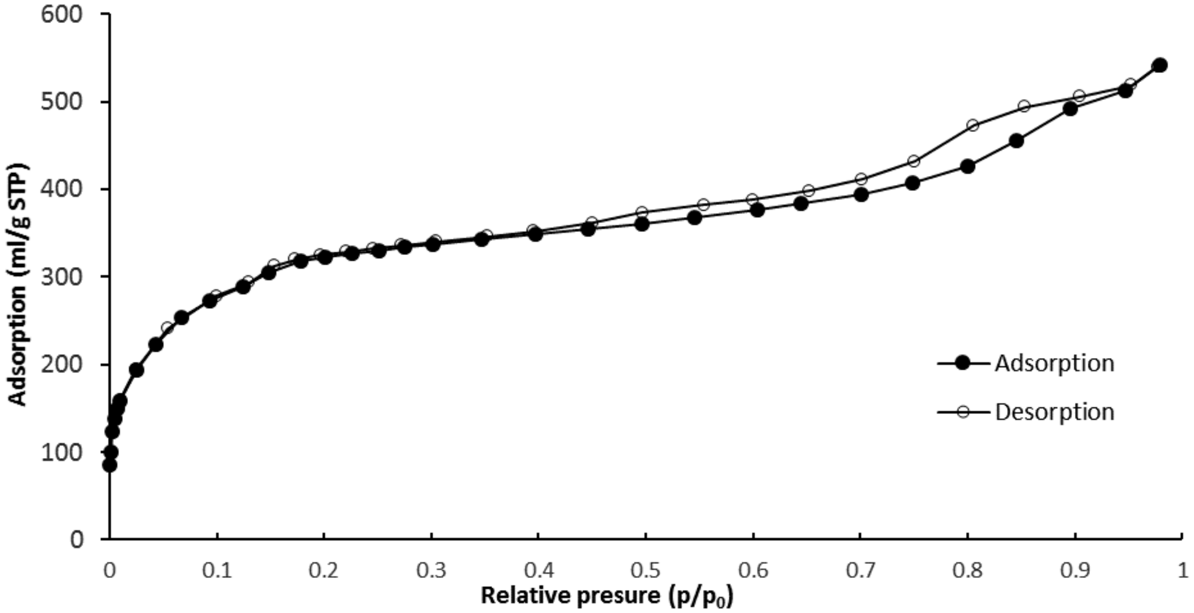

Figure S14. The N_2 adsorption isotherm of activated (Al)MIL-101-NH_2/NHCO-CH_2-*t*-Bu. S_{BET} = 1195 m^2/g.

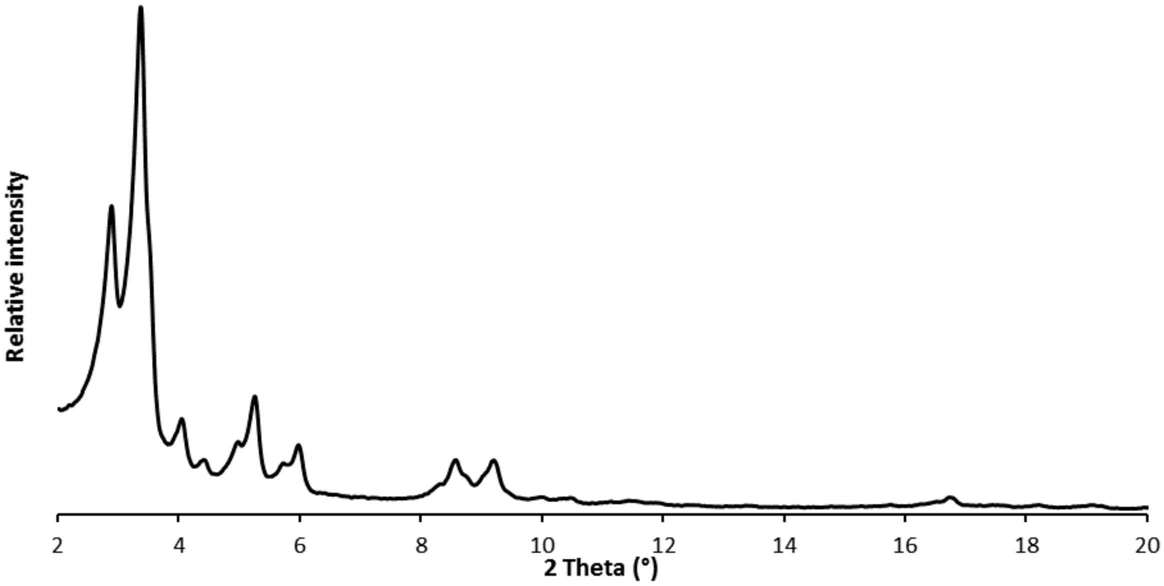

Figure S15. Powder X-ray diffraction pattern (PXRD) of activated (Al)MIL-101-NH_2/NHCO-CH_2-*t*-Bu.

3. The optimization of the reaction conditions of the deamination reaction

General procedure:
A 4 ml screw-capped vial (or 20 ml vial in case of larger scale) was charged with (Al)MIL-101-NH$_2$ obtained by the Gascon method (10 mg, ca. 0.041 mmol NH$_2$, unless stated otherwise in Table S1), *t*-butyl nitrite and an appropriate solvent (1 ml per 10 mg of the MOF). More details and order of addition are given in table S1. The reaction mixture was left without stirring for a given time and then placed in an oven (in some cases the excess of t-BuONO was washed with MeOH (3x3 ml) prior to heating in the oven) and heated for a given time at specified temperature. Finally, the deaminated MOF was collected by centrifugation, washed and analysed by 1H NMR after digestion in 1 wt % NaOD/D$_2$O. The results are presented in table S1.

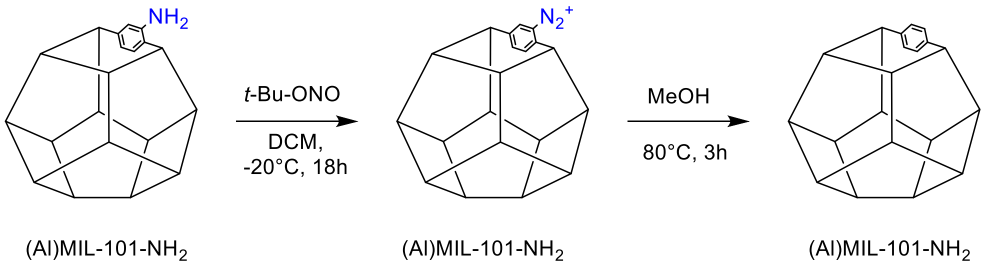

Figure S16. The deamination of MOFs.

Table S1. The reaction conditions and the results of the deamination of (Al)MIL-101-NH$_2$.

Entry	Conditions of the diazotization	Conditions of the hydrodediazotization	Measures of conversion and purity - the sum of integrals of a given product divided by the total integral of the aromatic region (from 6.9 to 9.0 ppm)				The sum of integrals of a given product divided by the sum of integrals of all three (BND-NH$_2$ + BDC + BDC-N_2^+)		
			BDC-NH$_2$	BDC	BDC-N_2^+	'Tars'	BDC-NH$_2$	BDC	BDC -N_2^+
A	1. MOF, MeOH 2. 5 eq *t*-Bu-ONO, rt, 24h	80^{0}C, 1h	0.72	0.12	0	0.16	86	14	0
B	1. MOF, MeOH 2. 10eq *t*-Bu-ONO, rt, 24h	80^{0}C, 1h	0.22	0.57	0.01	0.20	28	71	1
C	1. MOF, 10eq *t*-Bu-ONO, rt, 5min 2. MeOH$_{anhydr.}$, rt, 24h	60^{0}C, 4h	0.00	0.60	0.03	0.37	0	95	5
D	1.MOF, 10eq *t*-Bu-ONO, rt, 15min 2. MeOH$_{anhydr}$, rt, 24h	60^{0}C, 4h	0.00	0.64	0.04	0.32	0	94	6
E	1. MOF, 10eq *t*-Bu-ONO, rt, 60 min 2. MeOH$_{anhydr}$, rt, 24h	60^{0}C, 4h	0.00	0.71	0.06	0.23	0	92	8
F	1. MOF, 10eq *t*-Bu-ONO, rt, 15min 2. MeOH$_{bezw}$, rt, 5min	60^{0}C, 4h	0.00	0.61	0.04	0.35	0	94	6
G	1. 10eq *t*-Bu-ONO, rt, 15 min 2. MeOH$_{bezw}$, rt, 5min	80^{0}C, 3h	0.00	0.60	0.00	0.40	0	100	0
H	1. 10eq *t*-Bu-ONO, rt, 15 min 2. MeOH rt, 15min	60°C, 18h	0.00	0.68	0.0.	0.32	0	100	0
I	1. 10eq *t*-Bu-ONO, rt, 60 min	1. wash 2. MeOH, 60°C, 18h	0.00	0.58	0.00	0.42	0	100	0
J	1. 80eq *t*-Bu-ONO, rt, 60 min	1. wash 2. MeOH, 60°C, 18h	0.00	0.69	0.00	0.31	0	100	0

K	1. 20eq *t*-Bu-ONO, -20°C, 60 min	1. wash 2. MeOH, 80°C, 3h	0.20	0.50	0.00	0.30	29	71	0
L	1. 10eq *t*-Bu-ONO, -20°C, 18h	MeOH, 60°C, 18h	0.02	0.74	0.00	0.24	3	97	0
M	1. 10eq *t*-Bu-ONO, -20°C, 18h	1.wash 2. MeOH, 60°C, 18h	0.43	0.43	0.00	0.14	50	50	0
N	1. 20eq *t*-Bu-ONO, -20°C, 18h	MeOH, 60°C, 18h	0.00	0.79	0.00	0.21	0	100	0
O	1. 20eq *t*-Bu-ONO, -20°C, 18h	1. wash 2. MeOH, 60°C, 18h	0.41	0.42	0.00	0.17	49	51	0
P	1. 40eq *t*-Bu-ONO, -20°C, 1h -> DCM, -20°C, 18h ->	1. wash 2. MeOH, 80°C, 3h	0.19	0.70	0.00	0.11	21	79	0
Q	1. 80eq *t*-Bu-ONO, -20°C, 18h	1. wash 2. MeOH, 60°C, 18h	0.06	0.84	0.00	0.10	7	93	0
R	1. 80eq *t*-Bu-ONO, -20°C, 60min 2. MeOH, -20°C, 18h	1. wash 2. MeOH, 60°C, 18h	0.00	0.86	0.00	0.14	0	100	0
S	1. MeOH, 2. 80eq *t*-Bu-ONO, -20°C, 18h	1. wash 2. MeOH, 60°C, 18h	0.26	0.63	0.00	0.11	29	71	0
T	100mg 1. 80eq *t*-Bu-ONO, -20°C, 60min 2. MeOH, -20°C, 18h	1. wash 2. MeOH, 80°C, 3h	0.09	0.79	0.00	0.12	10	90	0
U	100mg 1. 80eq *t*-Bu-ONO, -20°C, 60min 2. MeOH, -20°C, 18h	1. wash 2. MeOH, 60°C, 18h	0.10	0.79	0.00	0.11	11	89	0
V	1. 80eq *t*-Bu-ONO, -20°C, 60min 2. DCM, -20°C, 18h	1. wash 2. MeOH, 80°C, 3h	0.00	0.88	0.00	0.12	0	100	0
W	50mg 1. 80eq *t*-Bu-ONO, -20°C, 60min 2. DCM, -20°C, 18h	1. wash 2. MeOH, 80°C, 3h	0.00	0.84	0.00	0.16	0	100	0
X	100mg 1. 80eq *t*-Bu-ONO, -20°C, 1h 2. DCM, -20°C, 18h	1. wash 2. MeOH, 60°C, 18h	0.02	0.83	0.00	0.15	2	98	0

4. The deamination of (Al)MIL-101-NH_2

4.1 (Al)MIL-101 by the deamination of (Al)MIL-101-NH_2 'Gascon'

In a typical procedure, a 4 ml screw-capped amber vial was loaded with *t*-BuONO (433 µl, 3.28 mmol), cooled down to -20°C and then (Al)MIL-101-NH_2 (10.0 mg, 41 µmol of NH_2 groups) was added. After 1 hour DCM (1 ml) was added and the mixture was sonicated for 5 s to obtain fine suspension. The reaction mixture was left at minus 20°C without stirring overnight. After this time the MOF was centrifuged off and washed with methanol (3 x 3 ml). Methanol (1ml) was added and the vial was tightly capped and put into a preheated oven at 80^oC for 3 hr. After this time the mixture was centrifuged and the resultant solid was washed with methanol (3 x 1 ml) and dichloromethane (3 x 1 ml), changing the solvent every hour, and finally dried under vacuum (approx. 10 µbar).

4.2 (Al)MIL-101 (scaled up)

A 20 ml screw-capped amber vial was loaded with *t*-BuONO (4.0 ml, 30 mmol), cooled down to -20°C and then (Al)MIL-101-NH_2 (100 mg, 0.40 mmol of NH_2 groups) was added. After 1 hour at -20°C dichloromethane (8 ml) was added and the mixture was sonicated for 5 s to obtain fine suspension. The reaction mixture was left at minus 20°C without stirring overnight. After this time the MOF was filtered off on a G4 glass frit under vacuum and washed with methanol (approx. 20 ml). The solid was loaded into a 4 ml amber vial, followed by the addition of methanol (2 ml). The vial was tightly sealed and placed into a pre-heated oven at 80°C for 3 hr. . After this time the mixture was filtered through a G4 glass frit and the resultant solid was washed with methanol (approx. 20 ml) and dichloromethane (20 ml) and finally dried under vacuum (approx. 10 µbar).

Note: heating in methanol in a high-pressure tube at 80^oC can be replaced by overnight heating at 60°C. If the conversion of amino groups is lower than 100% (different batches of (Al)MIL-101-NH_2 may differ in reactivity), the deamination can be repeated to get full conversion.

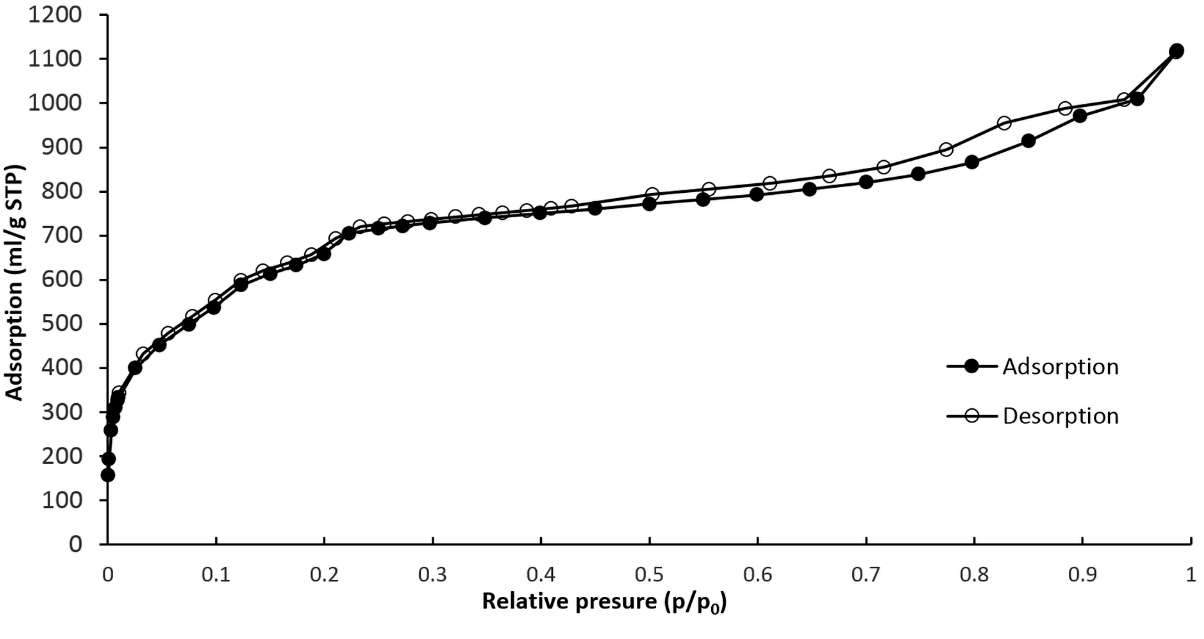

Figure S17. The N_2 adsorption isotherm of (Al)MIL-101 obtained by deamination of (Al)MIL-101-NH_2 (which in turn was obtained by the Gascon method). S_{BET} = 2455 m^2/g.

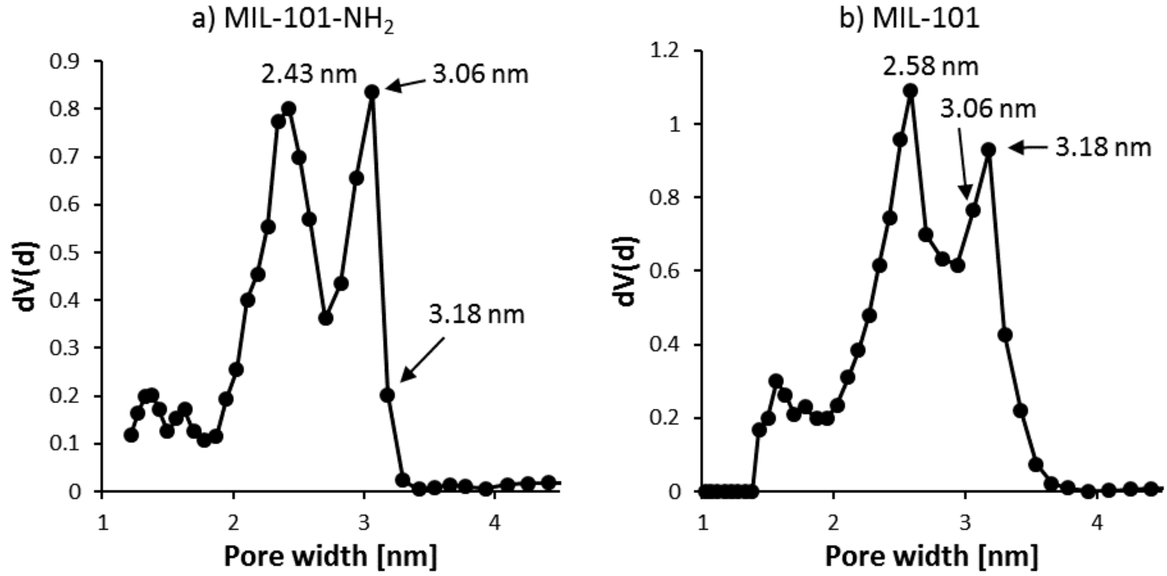

Figure S18. The copmparison of the pore size distribution of a) (Al)MIL-101-NH$_2$ obtained by the Gascon method and b) (Al)MIL-101 obtained by deamination. Pore size distribution was calculated by DFT method with model: N$_2$ at 77K on silica (cylindr./sphere. pore, NLDFT ads. model).

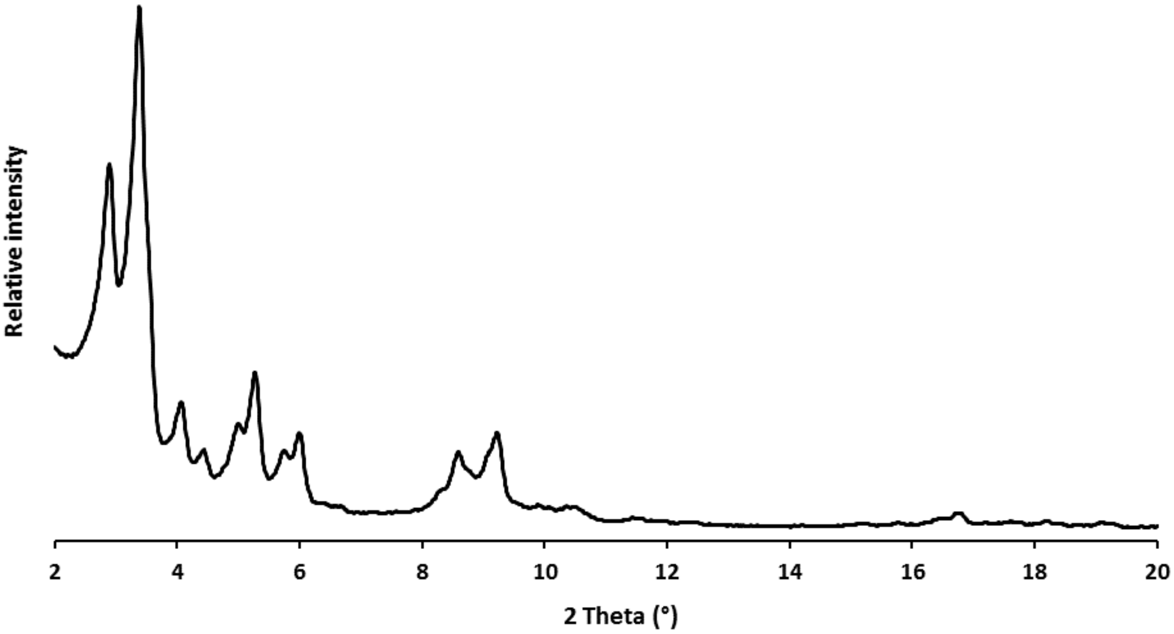

Figure S19. Powder X-ray diffraction pattern (PXRD) of (Al)MIL-101 obtained by deamination of (Al)MIL-101-NH$_2$ (which in turn was obtained by the Gascon method).

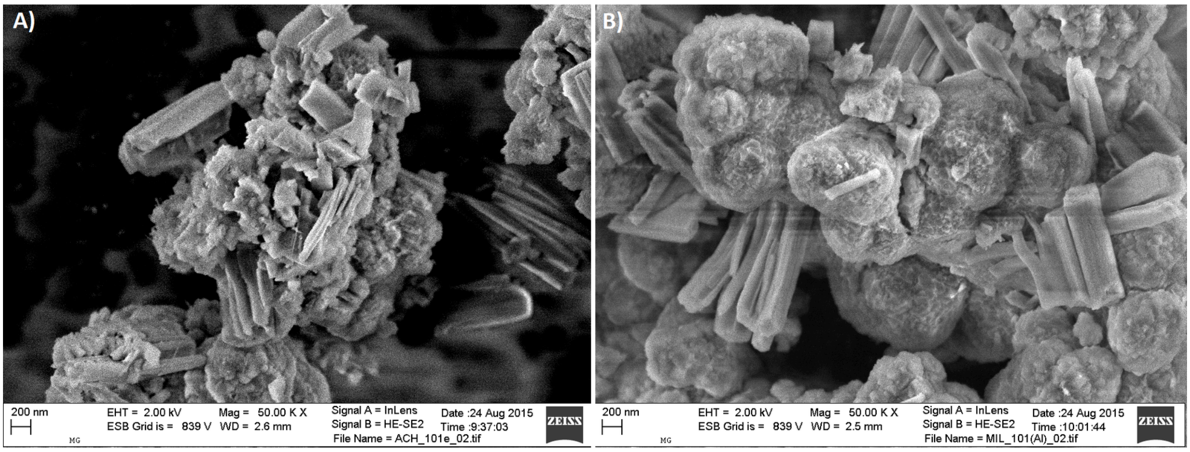

Figure S20. Comparison of morphology of (Al)MIL-101-NH_2 before (A) and after (B) deamination reaction.

4.3 (Al)MIL-101 by the deamination of (Al)MIL-101-NH_2 'Hartmann'

The deamination was performed on 100 mg scale according to the procedure described in section 4.2 above.

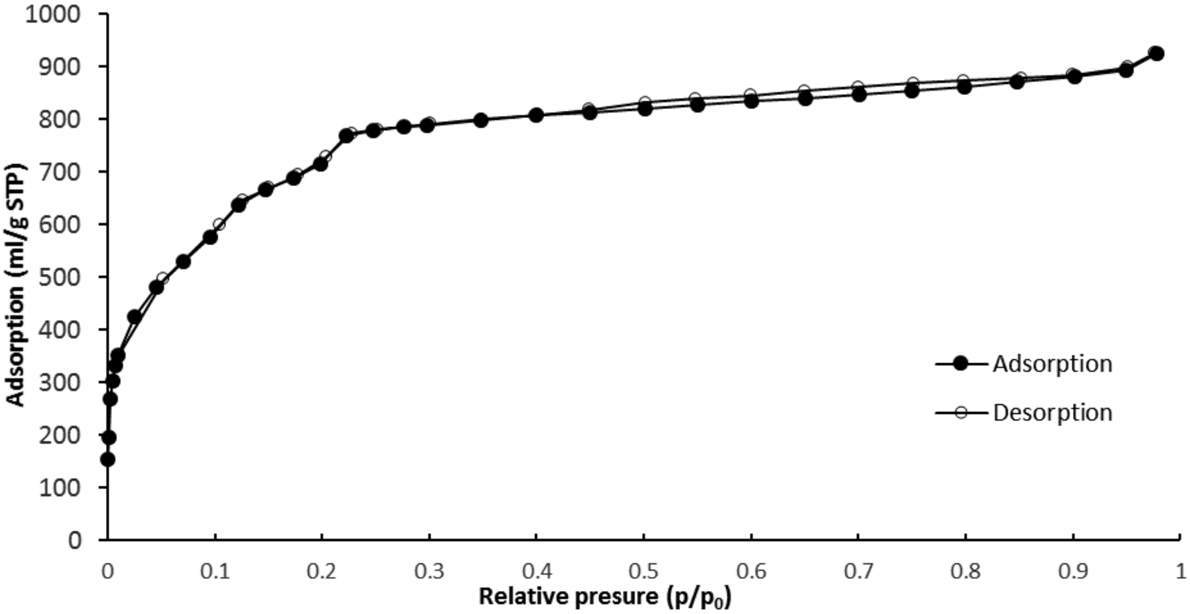

Figure S21. The N_2 adsorption isotherm of (Al)MIL-101 obtained by the deamination of (Al)MIL-101-NH_2 (which in turn was obtained by the Hartmann method). S_{BET} = 2738 m^2/g

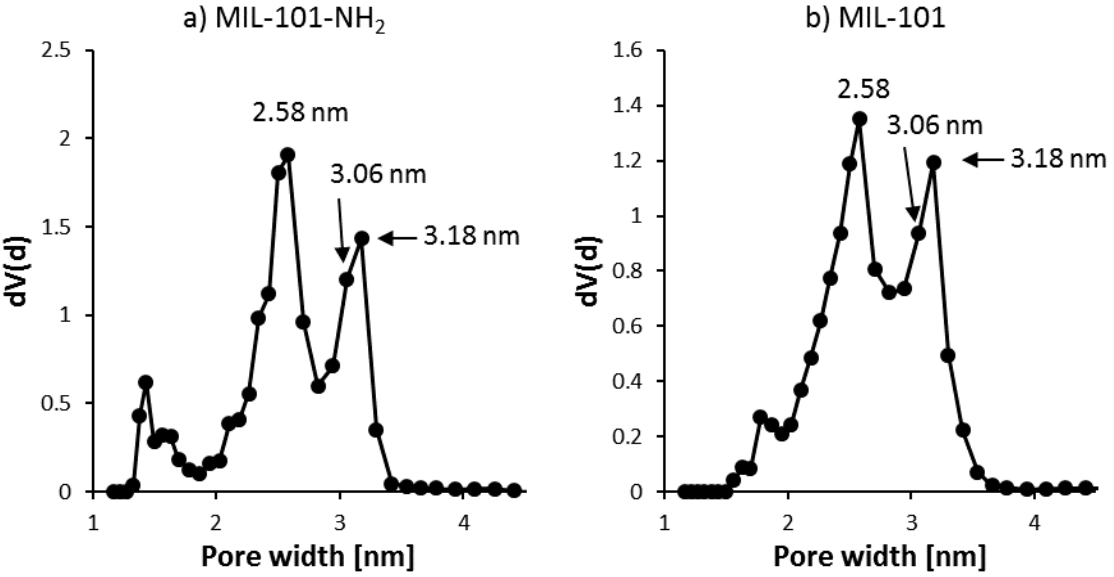

Figure S22. The copmparison of the pore size distribution of a) (Al)MIL-101-NH$_2$ obtained by the Hartmann method and b) (Al)MIL-101 obtained by deamination. DFT method – calc. model: N_2 at 77K on silica (cylindr./sphere. pore, NLDFT ads. model).

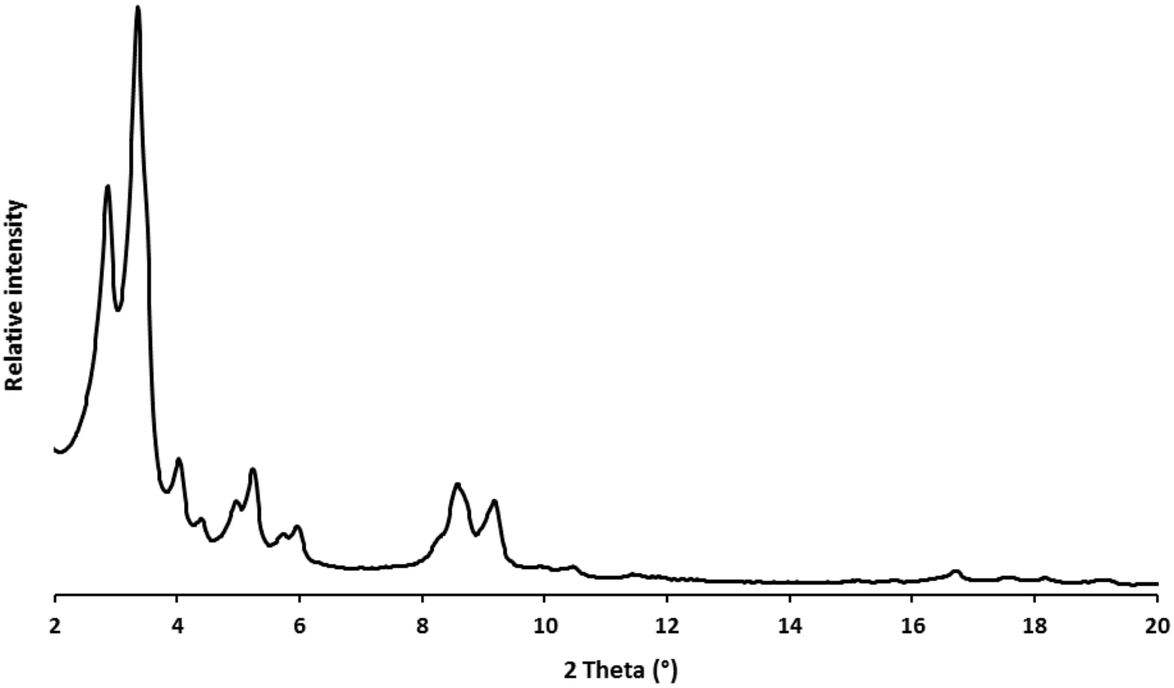

Figure S23. Powder X-ray diffraction pattern (PXRD) of (Al)MIL-101 obtained by deamination of (Al)MIL-101-NH$_2$ (which in turn was obtained by the Hartmann method).

4.4 The deamination of partially functionalized MIL-101-NH_2(Al)

Partially functionalized (Al)MIL-101-NH_2/NHCOR materials were deaminated under the same optimized conditions as the pristine (Al)MIL-101-NH_2:

A 4 ml screw-capped amber vial was loaded with *t*-BuONO (0.4 ml per 10 mg of MOF), cooled down to -20°C and then (Al)MIL-101-NH_2/NHCOR (10.0 mg) was added. After 1 hour DCM (1 ml) was added and the mixture was sonicated for 5 s to obtain fine suspension. The reaction mixture was left at -20°C without stirring overnight. After this time the MOF was centrifuged off and washed with methanol (3 x 3 ml). Methanol (1ml) was added and the vial was tightly capped and put into a preheated oven at 80^{o}C for 3 hr. After this time the mixture was centrifuged and the resultant solid was washed with methanol (3 x 3 ml) and dichloromethane (3 x 3 ml), changing the solvent every hour, and finally dried under high vacuum.

Table S2. The content of NH_2 and RCONH groups in the partially functionalized MOFs before and after the deamination. The content was derived from integration of ^{1}H NMR spectra using sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid as an internal standard.

	NH_2 (%)			mmol R/g MOF		
R	before deamination	after 1st deamination	after 2nd deamination	before deamination	after 1st deamination	after 2nd deamination
t-BuCH_2-	45%	2%	0%	1.75	1.73	1.75
t-BuPh-	55%	1%	0%	1.28	1.28	1.29
4-NO_2Ph-	50%	2%	0.5%	1.45	1.43	1.49

4.4.1 (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2 after deamination:

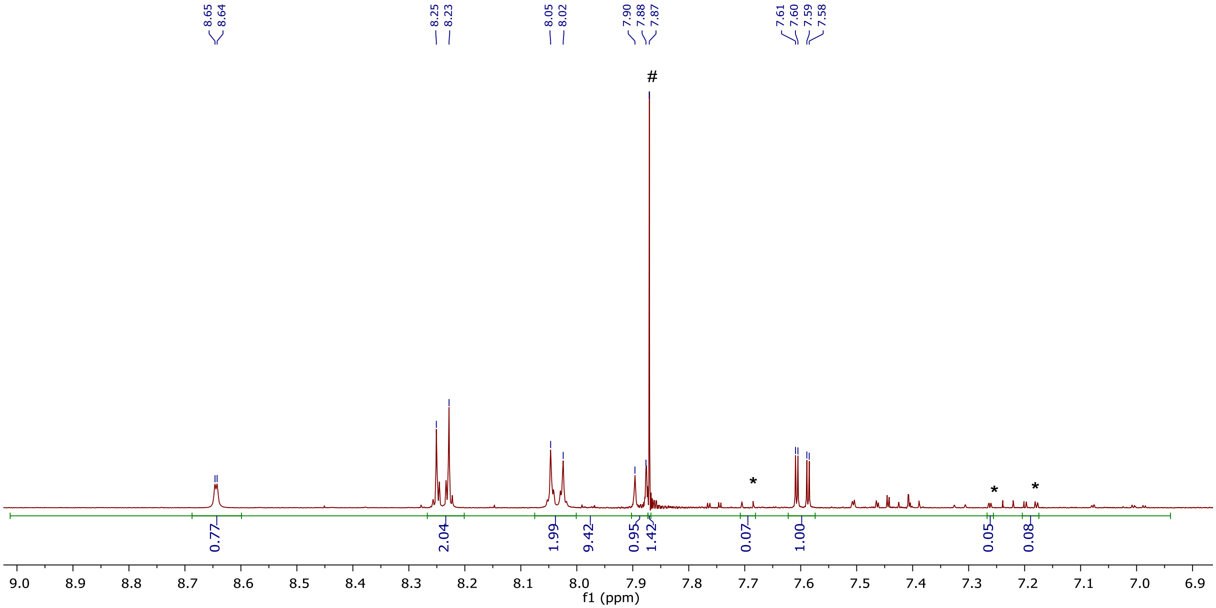

Figure S24. ^{1}H NMR spectrum of deaminated (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2 digested in 1 wt % NaOD/D_2O. The signals of the unreacted BDC-NH_2 is marked with asterisk and the signal of the BDC with hash mark.

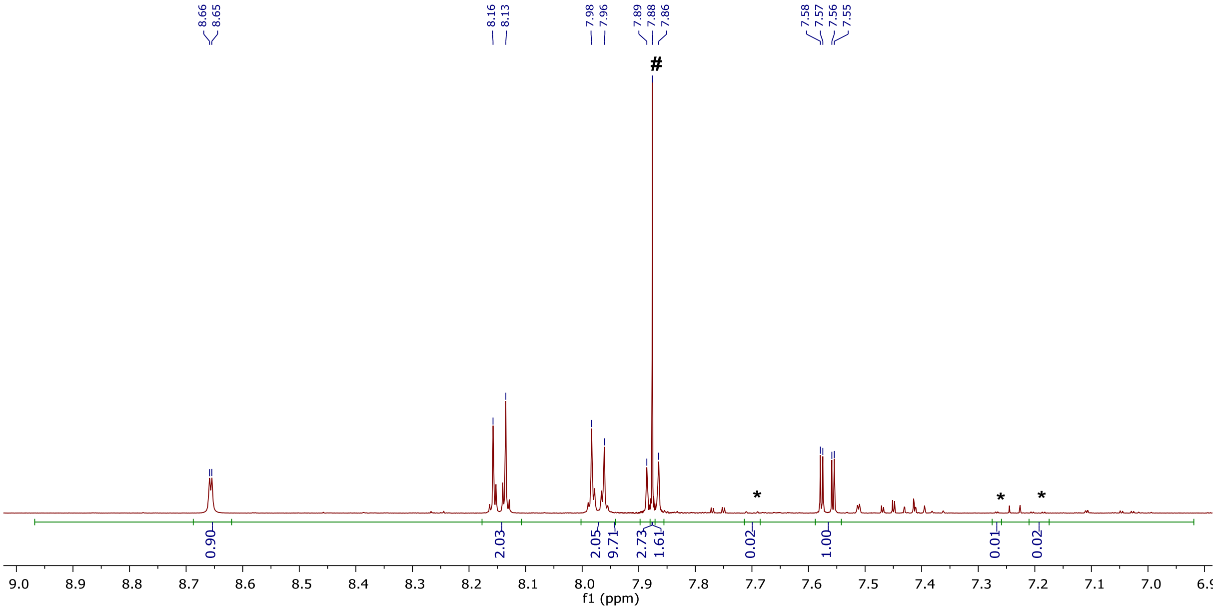

Figure S25. ^{1}H NMR spectrum of deaminated (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2 after second deamination and digested in 1 wt % NaOD/D_2O. The signals of the unreacted BDC-NH_2 is marked with asterisk and the signal of the BDC with hash mark.

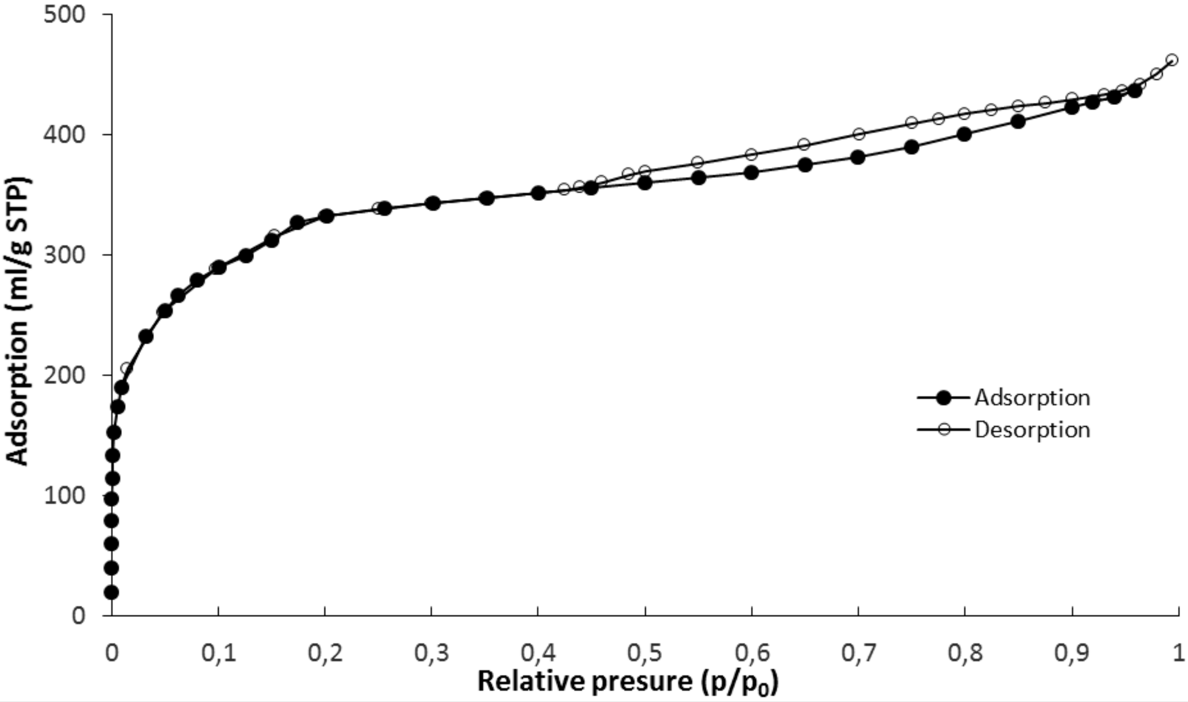

Figure S26. The N_2 adsorption isotherm of the deaminated (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2. S_{BET} = 1200 m^2/g.

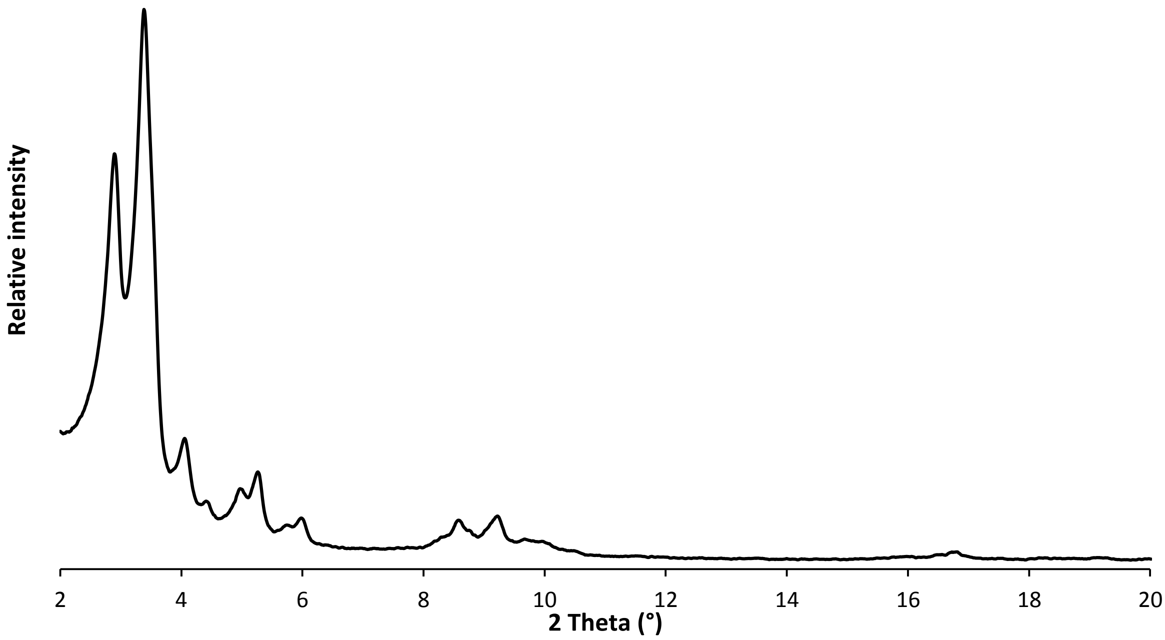

Figure S27. Powder X-ray diffraction pattern (PXRD) of deaminated (Al)MIL-101-NH_2/NHCO-Ph-*p*-NO_2.

4.4.2 (Al)MIL-101-NH_2/NHCO-Ph-4-(*t*-Bu) after deamination:

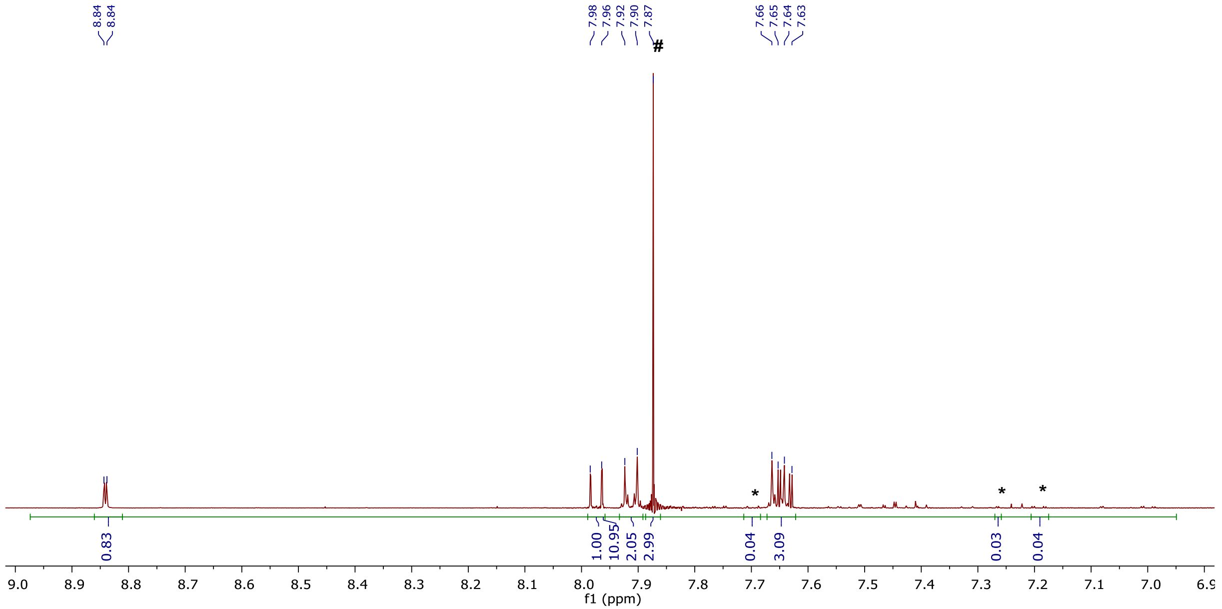

Figure S28. ^1H NMR spectrum of deaminated (Al)MIL-101-NH_2/NHCO-Ph-4-(*t*-Bu) digested in 1 wt % NaOD/D_2O. The signals of the unreacted BDC-NH_2 is marked with asterisk and the signal of the BDC with hash mark.

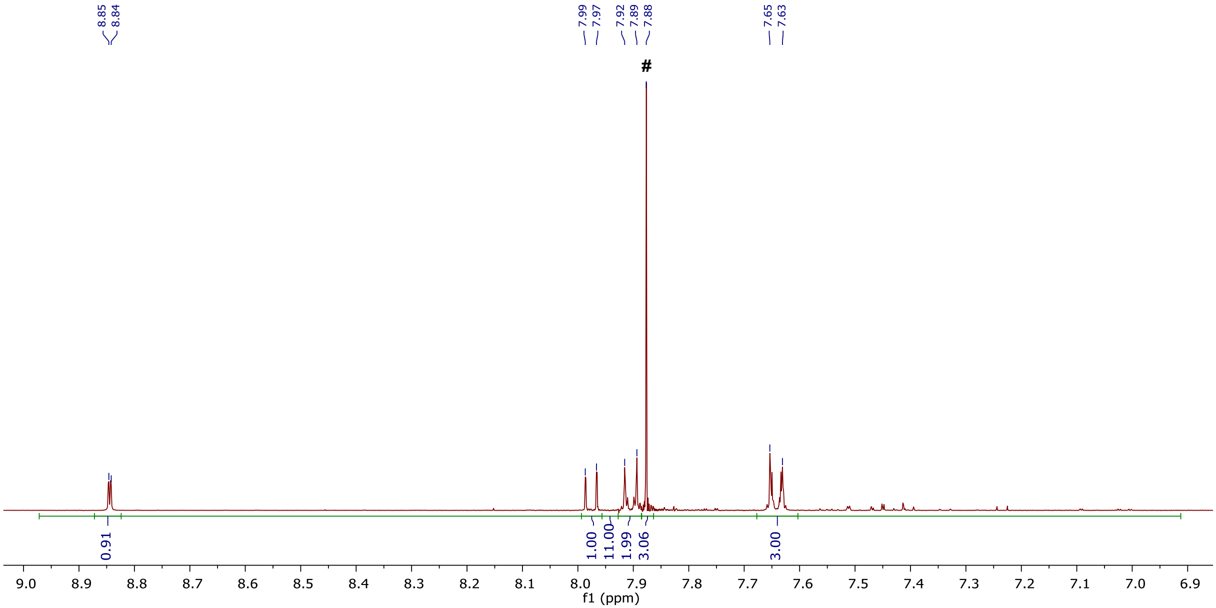

Figure S29. ^{1}H NMR spectrum of (Al)MIL-101-NH$_2$/NHCO-Ph-4-(*t*-Bu) after second deamination digested in 1 wt % NaOD/D$_2$O. The signal of the BDC is marked with hash symbol.

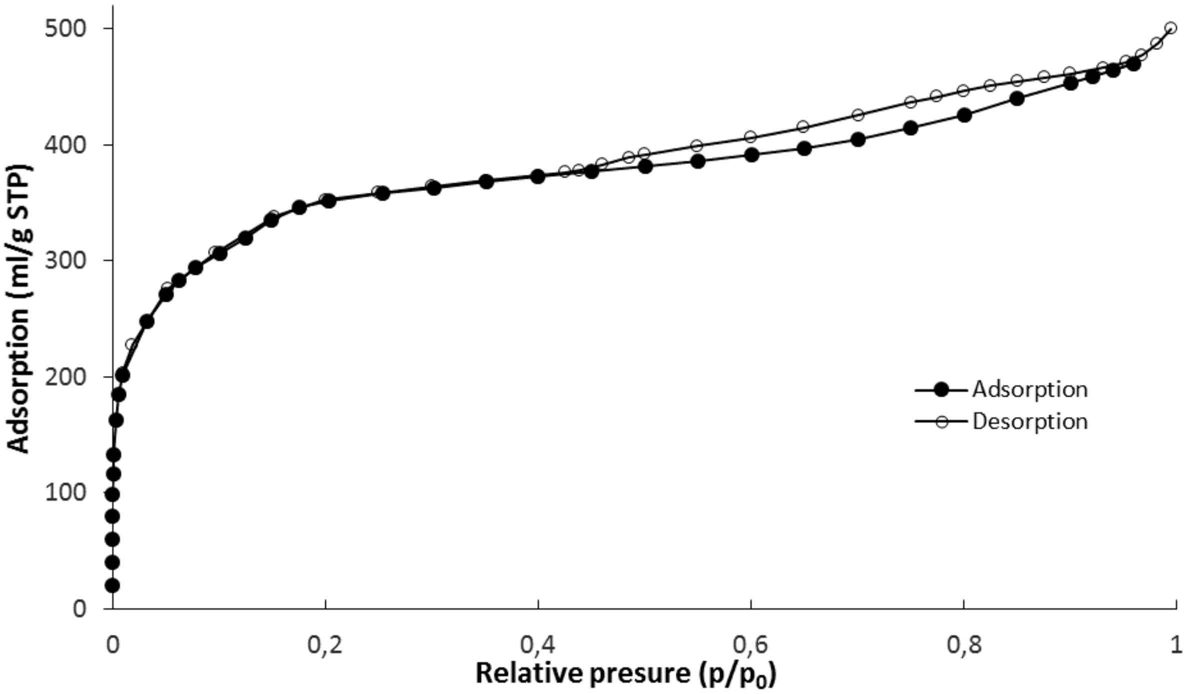

Figure S30. The N$_2$ adsorption isotherm of the deaminated (Al)MIL-101-NH$_2$/NHCO-Ph-4-(*t*-Bu). S_{BET} = 1279 m^2/g.

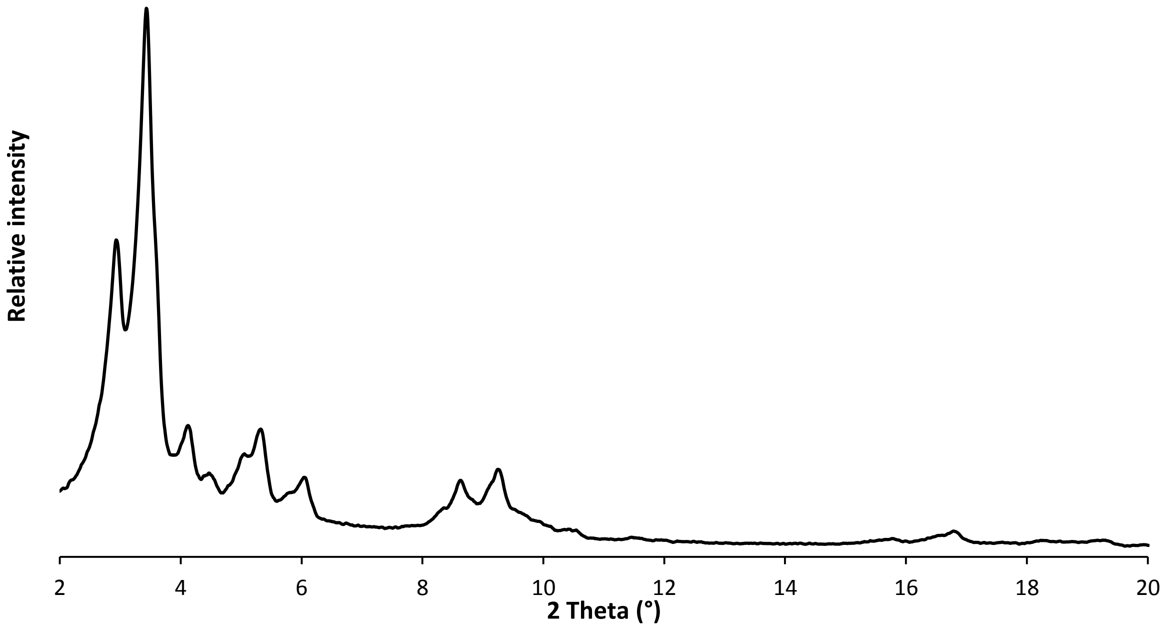

Figure S31. Powder X-ray diffraction pattern (PXRD) of deaminated (Al)MIL-101-NH_2/NHCO-Ph-4-(*t*-Bu).

4.4.3 (Al)MIL-101-NH$_2$/NHCO-CH$_2$-*t*-Bu after deamination:

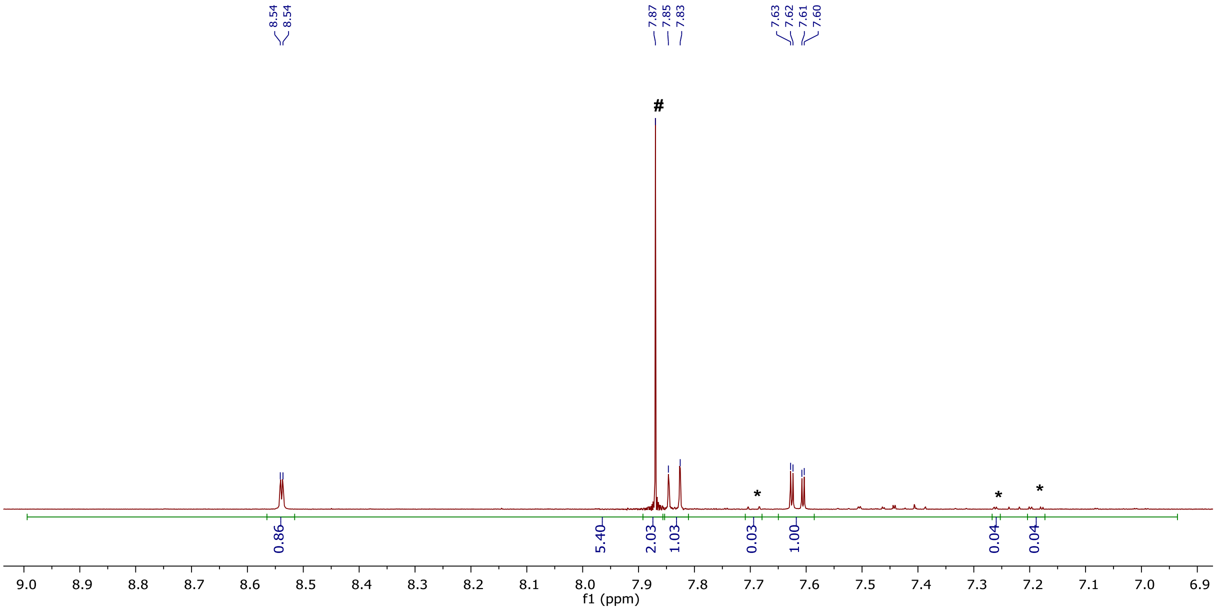

Figure S32. ^{1}H NMR spectrum of deaminated (Al)MIL-101-NH$_2$/NHCO-CH$_2$-*t*-Bu digested in 1 wt % NaOD/D$_2$O. The signals of the unreacted BDC-NH$_2$ is marked with asterisk and the signal of the BDC with hash mark.

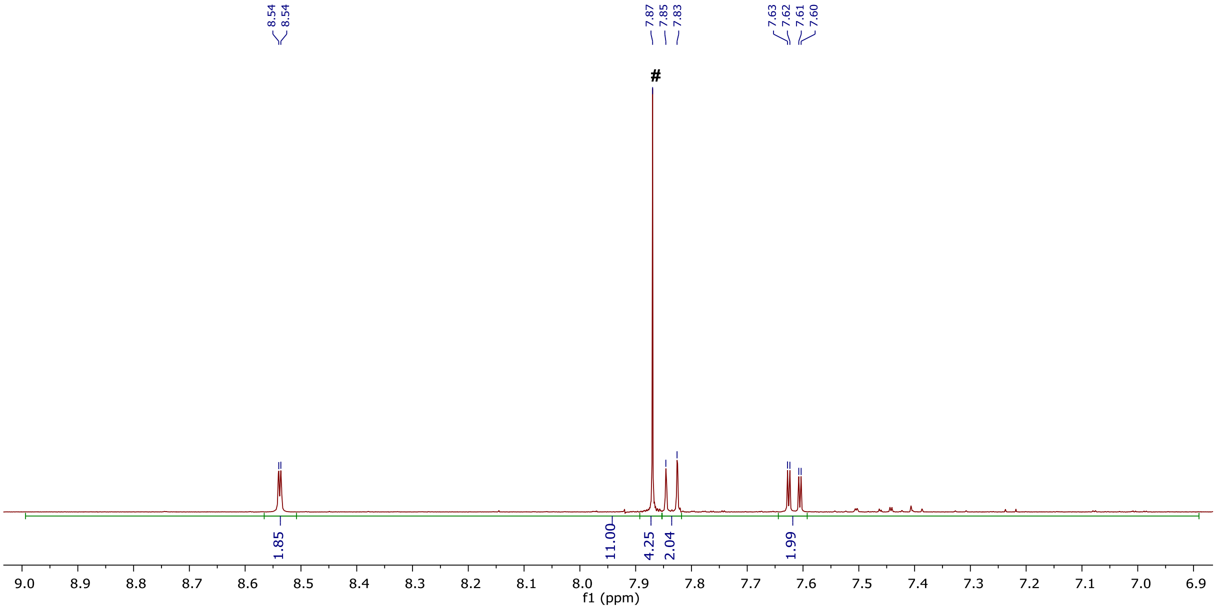

Figure S33. ^{1}H NMR spectrum of (Al)MIL-101-NH$_2$/NHCO-CH$_2$-*t*-Bu after second deamination and digested in 1 wt % NaOD/D$_2$O. The signal of the BDC is marked with hash symbol.

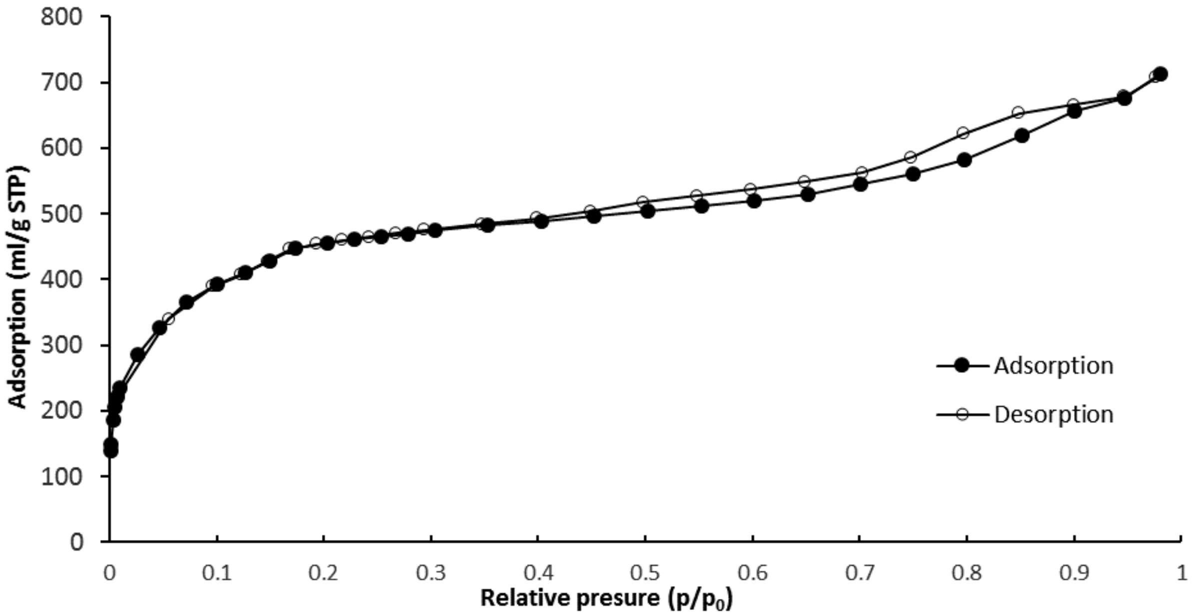

Figure S34. The N_2 adsorption isotherm of the deaminated (Al)MIL-101-NH_2/NHCO-CH_2-*t*-Bu. S_{BET} = 1664 m^2/g.

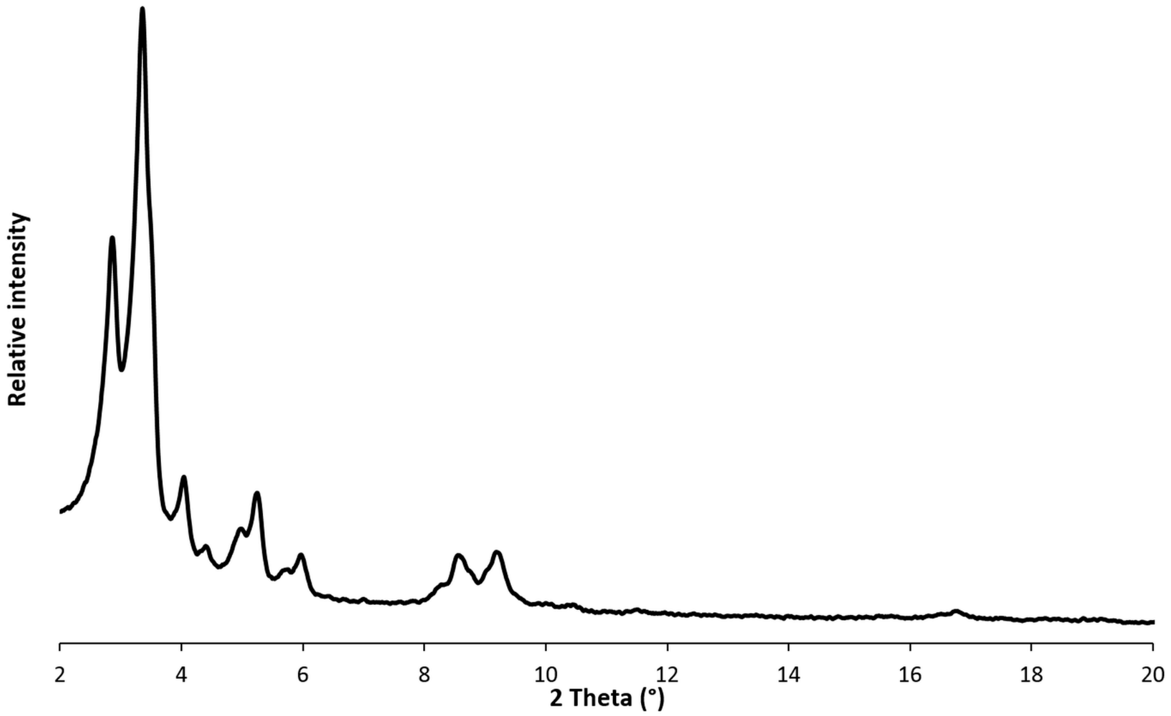

Figure S35. Powder X-ray diffraction pattern (PXRD) of deaminated (Al)MIL-101-NH_2/NHCO-CH_2-*t*-Bu.

5. IR Spectra

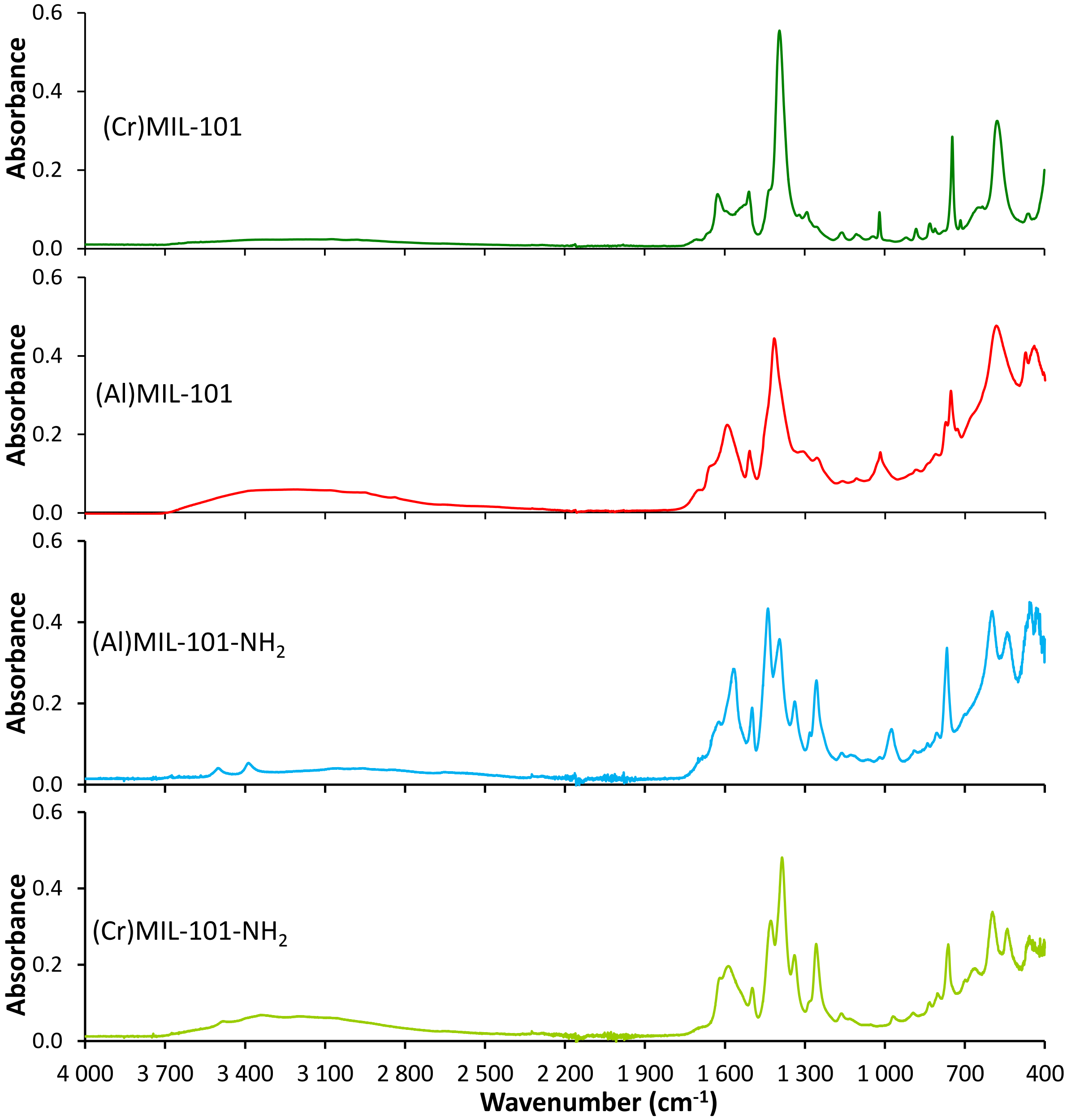

Figure S36. The comparison of ATR-IR spectra of four MOFs.

6. Sorption of catalysts on (Al)MIL-101-NH_2 and (Al)MIL-101

General procedure for heterogenization of the catalyst on MOFs. A 4 ml vial with a magnetic stirring bar and a septum cap was charged with (Al)MIL-101 (97 mg, *ca*. 0.43 mmol of BDC, *ca*. 12 µmol of mesopores), purged with argon and filled with DCM solution of the Ru complex (4 ml, 10.1 mg AquaMet™, 12.5 µmol). The resulting mixture was stirred at rt for 1 h. After this time the mixture was centrifuged, supernatant decanted with a syringe through septum, and the solid residue washed three times with dry DCM (3 x 3 ml). The solid was dried under vacuum for at least 2 hrs in 8 µbar). Supernatants were analyzed by UV-Vis spectroscopy to determine the amount of catalyst which was not adsorbed.[4]

Table S3. The amount of adsorbed Ru complex on MOFs

MOF	The amount of catalyst adsorbed in MOF (%)
(Al)MIL-101-NH_2	99.4
(Al)MIL-101	98.8
(Cr)MIL-101	99.0

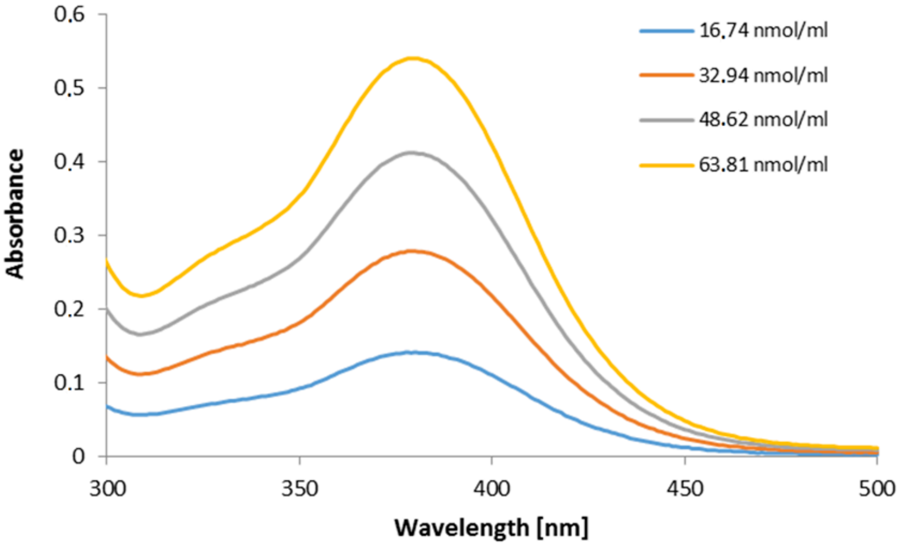

Figure S37. UV-vis spectra of AquaMet™ in DCM. The calculated molar absorption coefficient ε equals to 8467 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

7. Desorption (leaching) experiments

A sample of MOF containing *ca.* 1 molecule of AquaMet™ per cage (35 mg of the MOF, 3.5 µmol Ru) was suspended in toluene (*ca.* 3 ml) with short sonication and placed on a G4 fritted funnel with side inlet for argon. Toluene (47 ml) and other solvents (50 ml of each) were slowly passed through the sample under argon, collected in vials and analysed by UV-Vis spectroscopy for the presence of AquaMet™. The experiments were conducted under flow of argon.

8. Catalysis

General procedure for RCM experiments. A 4 ml vial with a magnetic stir bar and a septum cap was charged with catalyst@MOF (1.0 µmol of AquaMet™), toluene (2 ml) and an appropriate amount of substrate (DEDAM). The suspension was stirred in a vial with perforated septum (0.4 mm thick needle was stuck in the septum to release ethylene). After 24 h the reaction was quenched with 0.1 ml of 1M of Apeiron SnatchCat™ solution in DCM and subjected to GC analysis. Conversion values were measured by GC using calibration curve obtained from authentic samples.

Table S4. Comparison of catalytic activity of supported AquaMet™ on different MOFs with various loading of Ru in RCM reaction of DEDAM.

Entry	MOF	Ru-cat (mol %)	$C_{DEDAM,}$ (M)	T (h)	Conversion (%)
1	(Cr)MIL-101	2	0.05	24	4
2	(Al)MIL-101-NH_2	2	0.05	24	74
3	(Al)MIL-101-NH_2	1	0.1	24	74
4	(Al)MIL-101	1	0.1	24	65
5	(Al)MIL-101	2	0.05	24	74
6	(Al)MIL-101	0.1	0.5	24	13

To confirm the true heterogeneity of the catalyst, split tests were performed as described below.

A 4 ml vial with a magnetic stirring bar and a septum cap was loaded with catalyst@MOF (1.0 µmol of AquaMet^{TM}), dry toluene (2 ml) and diethyl diallylmalonate (DEDAM) (48 mg, 0.20 mmol). The suspension was stirred for specified time in a perforated vial. After that, half of the suspension was filtered through a syringe filter (PTFE, 0.2 µm). 0.1 ml of the filtrate was added to the vial containing 10 mg of Apeiron SnatchCat™ to quench the reaction, and the rest of the filtrate was used for a split test. After 24 h all the reactions were quenched with 0.1 ml of 1M SnatchCat™ solution in DCM and subjected to GC analysis.

Table S5. Test for heterogeneity of Ru catalyst@MOF

MOF	Split time	Conversion (%)		
		In Split	In filtrate after 24h	In suspension after 24h
(Al)MIL-101-NH_2	6 h	45	45	75
(Al)MIL-101	6 h	42	42	73

Literature

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