Supplementary Data

Sulfonyl chlorides as an efficient tool for the postsynthetic modification of Cr-MIL-101-SO_3H and CAU-1-NH_2

Arne Klinkebiel, Nele Reimer, Martin Lammert, Norbert Stock and Ulrich Lüning

Otto-Diels Institut für Organische Chemie, Otto-Hahn-Platz 4, 24118 Kiel, Germany.
E-Mail: luening@oc.uni-kiel.de

Institut für Anorganische Chemie, Max-Eyth-Strasse 2, 24118 Kiel, Germany.
E-Mail: stock@ac.uni-kiel.de

Contents

1 General

1.1 Chemicals

Dimethylformamide, methylamine, ethylamine, sodium hypochlorite acid and 2-mercaptopyridine were bought from Sigma-Aldrich Chemicals Co. Propylamine, oxalylchloride, 2-aminotherephthalic acid and methyl sulfonylchloride were purchased from ABCR GmbH & Co. KG, dimethylamine from Alfa Aesar GmbH & Co. KG. Monosodium 2-sulfoterephthalic acid was recieved from TCI, methanol from Baker and aluminium chloride hexahydrate from Grüssing. Benzylamine, aniline, pyridine, aminopyridine, chromium trioxide and tetrahydrofuran were commercially available from Merck. Tetrahydrofuran was dried using lithiumalumnium hydride, pyridine was purified using basic aluminium oxide. All other chemicals were used without any further purification.

1.2 Characterization

NMR spectra were recorded on Bruker DRX 500 or AV 600 instruments. Assignments are supported by COSY, HSQC, and HMBC. Even when obtained by DEPT, the type of ^{13}C signal is always listed as singlet, doublet, etc. All chemical shifts are referenced to the residual proton or carbon signal of the solvent. Unless otherwise noted, deuterated sodium hydroxide was used as the solvent, so the carboxylic acids are deprotonated. Under this condition, all hydrogen atoms of the sulfonamides are exchanged by deuterium. Part of the amides may be deprotonated. However, in the drawings structures are drawn with N-H-groups.

Approximation of conversion degrees was determined by comparing the relative integrals in ^{1}H-NMR spectra of the digested material after synthesis and removal of chromium. In the spectra shown below, the unfunctionalized linker has been removed by aqueous extraction as described below.

IR spectra were recorded with a Perkin-Elmer 100 equipped with a MKII Golden Gate TM Single Reflection ATR unit.

Nitrogen sorption isotherms were recorded at 77 K with a BELSORP-max or if mentioned with a BELSORP-mini apparatus (BEL JAPAN INC.). Micropore volumes were calculated from the adsorption branch at $p/p_0 = 0.5$.

The initial characterization by means of PXRD methods was carried out on a STOE-Stadi-P Combi diffractometer (Cu $K_{\alpha 1}$ radiation) equipped with a xy stage and an image plate detector.

2 Post-Synthetic modification of Cr-MIL-101-SO_3H

2.1 Synthesis of Cr-MIL-101-SO_3H (1)

Cr-MIL-101-SO_3H was prepared according to a literatures procedure[1]. A 100 mL teflon reactor was loaded with 1.25 g (12.5 mmol) of chromium trioxide and 3.35 g (12.5 mmol) of monosodium 2-sulfoterephthalic acid. After the addition of 50 mL of demineralized water and 910 mg (25.0 mmol) concentrated hydrochloric acid, the reactor was sealed and heated to 180 °C within 1 h. The temperature was held for 144 h and the reactor was cooled to room temperature within 6 h. The green solid was collected by centrifugation and dispersed in 100 mL of demineralized water (this process was repeated two times with water and three times with ethanol). The resulting green solid was dried in air at 70°C.

2.2 Synthesis of Cr-MIL-101-SO_2Cl (2)

General procedure

A schlenck tube was loaded with 100 mg of Cr-MIL-101-SO_3H, sealed and evacuated for 2 h at room temperature. After flushing the tube with nitrogen, 2 mL of a 1.5 M solution of oxalylchloride in dry tetrahydrofuran was added followed by *N*,*N*-dimethylformamide (5-15 µL). After stirring the sample under nitrogen for 24 h at room temperature the precipitate was washed two times using tetrahydrofuran and separated by centrifugation. The sample was dried in vacuo.

2.3 Synthesis of Cr-MIL-101-SO_2NHR (3a-f)

General procedure

A Schlenck tube was loaded with 100 mg of Cr-MIL-101-SO_2Cl, sealed and evacuated for 2 h. After flushing the tube with nitrogen, a 2 M solution of amine in dry tetrahydrofuran was added. After stirring the sample under nitrogen for 24 h at room temperature the precipitate was separated by centrifugation and washed using tetrahydrofuran (2 x 2 mL, 2 x 15 min), methanol (4 x 2 mL, 3 x 15 min, 1 x 12 h), and water (4 x 2 mL, 3 x 15 min, 1 x 12 h). The sample was dried for 24 h at 60 °C in vacuo.

For ^{1}H-NMR analyses, the respective MOF was dissolved in 2 mL of 2 M sodium hydroxide solution. After a pH = 10 – 12 was reached by adding conc. hydrochloric acid, the precipitate was filtered off. The basic filtrate was washed three times using 5 mL of *tert*-butyl methyl ether, acidified and extracted using 5 mL of *tert*-butyl methyl ether. The organic phase was dried using magnesium sulfate, filtered and the solvent was removed in vacuo.

2.4 Characterisation of Cr-MIL-101-NHR

2.4.1 Cr-MIL-101-SO_2NHMe (3a)

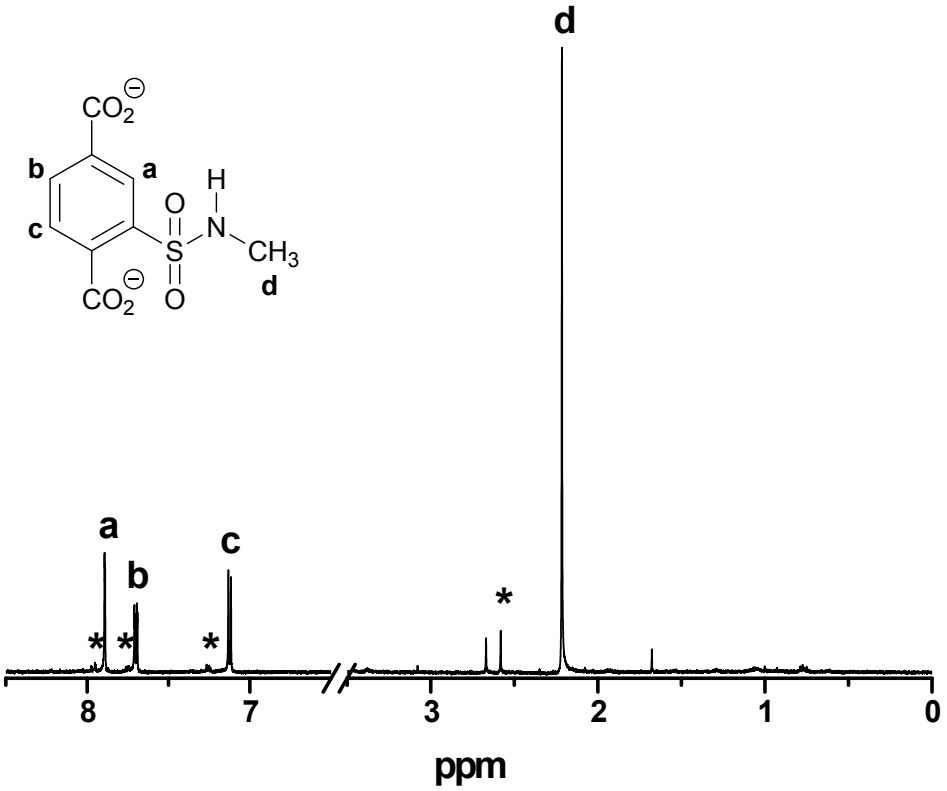


Fig. S1. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NHMe **3a** (500 MHz, 5 % NaOD in D_2O): (**a-c**) aromatic protons, (**d**) methyl group, (*) sideproduct *N*,*N*-dimethyl sulfonamide **3d** (< 2 %).

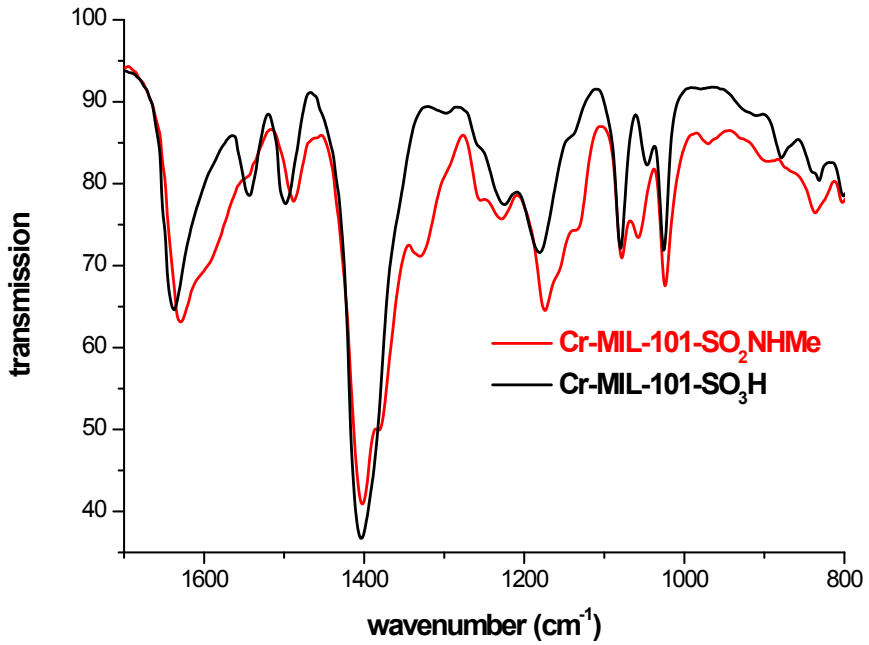


Fig. S2. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHMe **3a** (**red**). Characteristical frequencies: 1380 cm^{-1} (SO_2NH), 1329 cm^{-1} (CH_3), 1057 cm^{-1} (S=O). No significant band between 3000 – 2800 cm^{-1} for CH_3 stretch were observed.

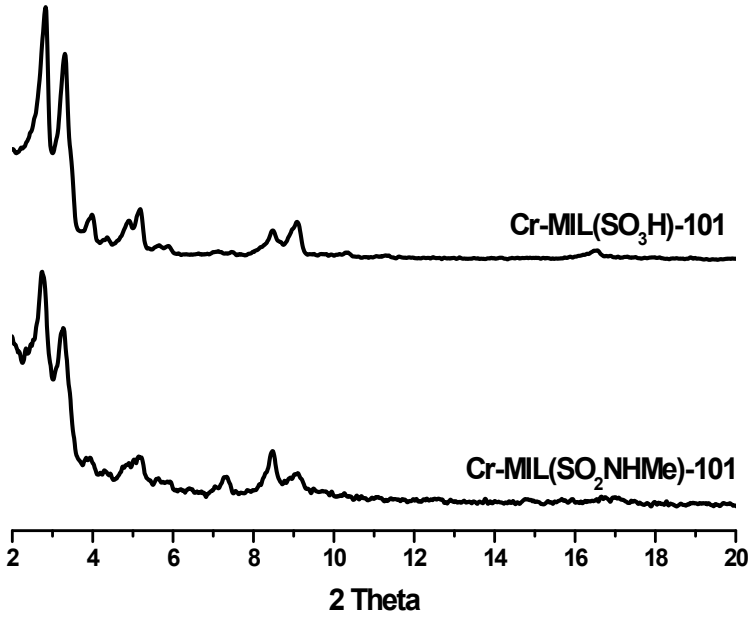


Fig. S3. PXRD pattern of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHMe **3a** (bottom).

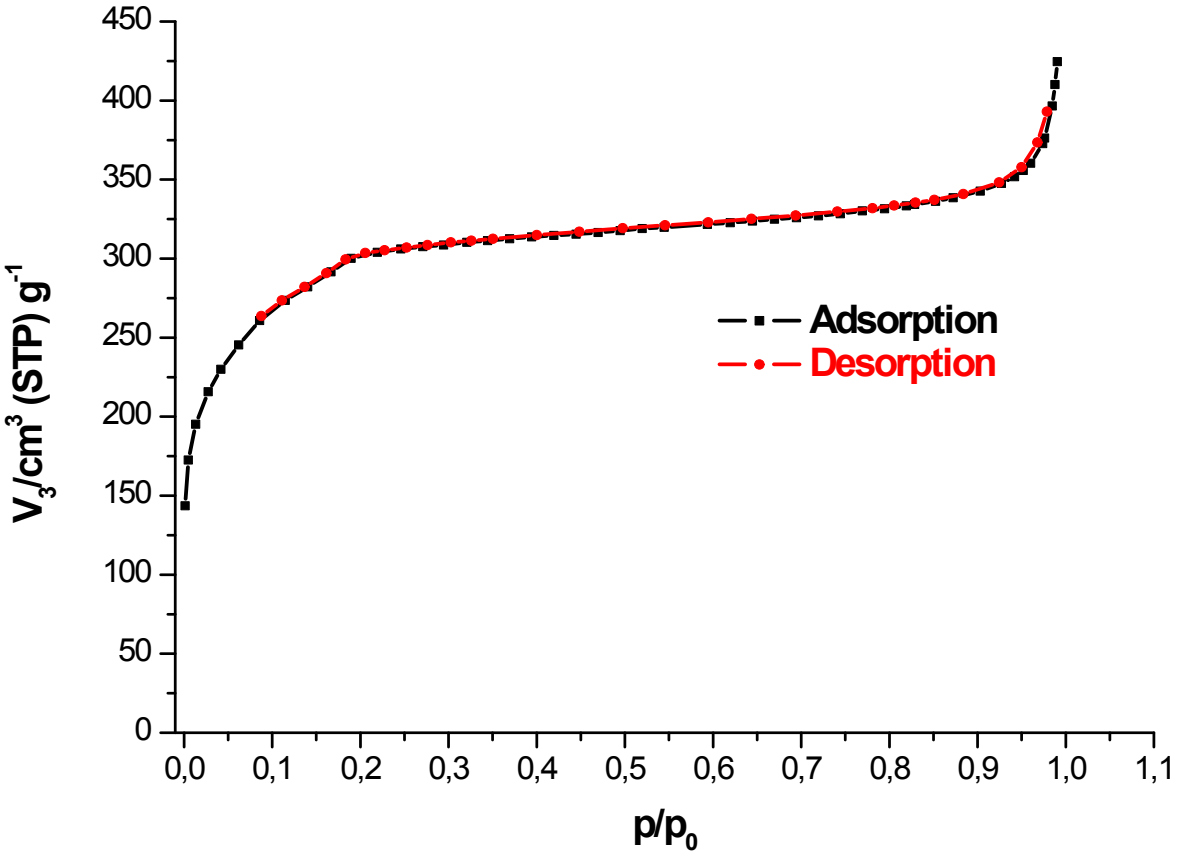


Fig. S4. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NHMe **3a**: $a_{s,BET}$ = 1070 m^2/g, total pore volume = 0.443 cm^3/g (starting material **1**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.624 cm^3/g).

2.4.2 Cr-MIL-101-SO_2NHEt (3b)

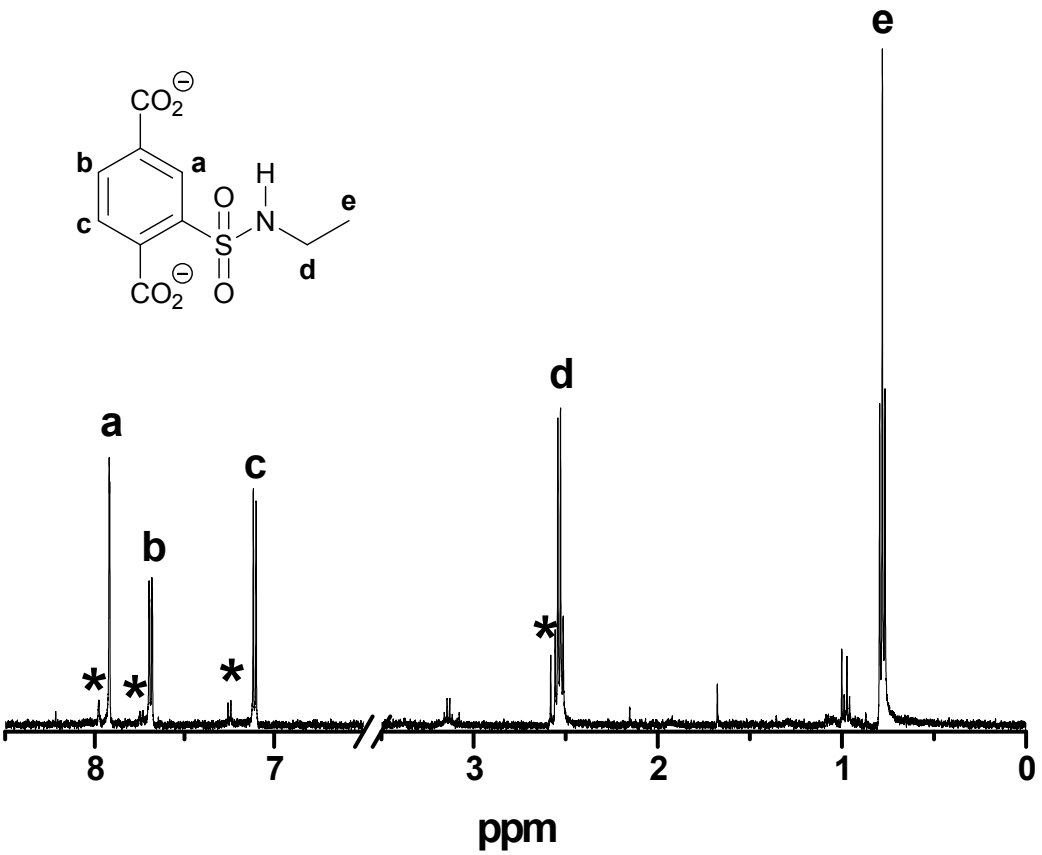


Fig. S5. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NHEt **3b** (500 MHz, 5 % NaOD in D_2O): (**a-c**) aromatic protons, (**d-e**) ethyl group, (*) sideproduct *N*,*N*-dimethyl sulfonamide **3d** (~ 2 %).

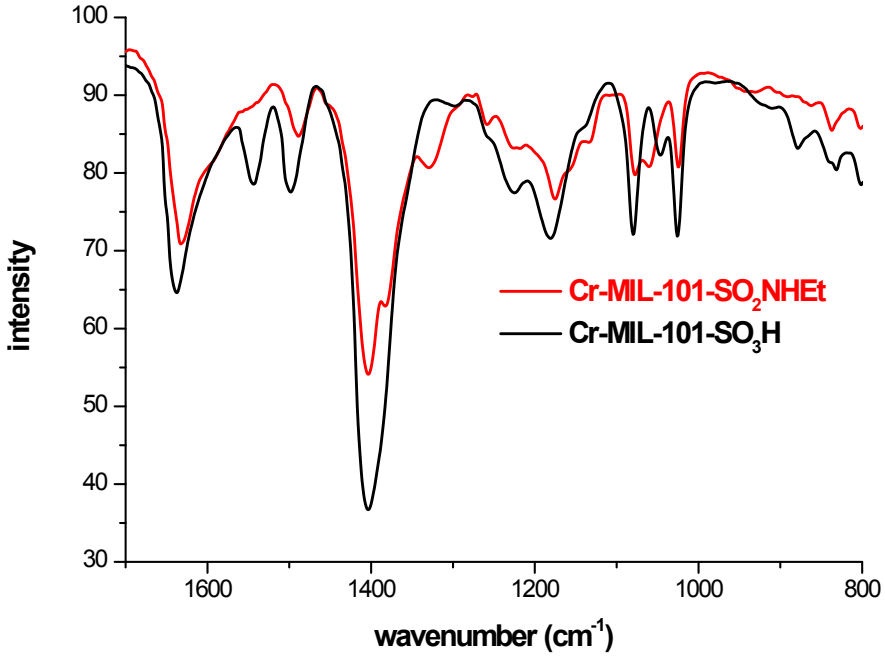


Fig. S6. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHEt **3d** (**red**). Characteristical frequencies: 1383 cm^{-1} (SO_2NH), 1330 cm^{-1} (CH_3), 1060 cm^{-1} (S=O). No significant bands between 3000 – 2800 cm^{-1} for CH_3/CH_2 stretch were observed.

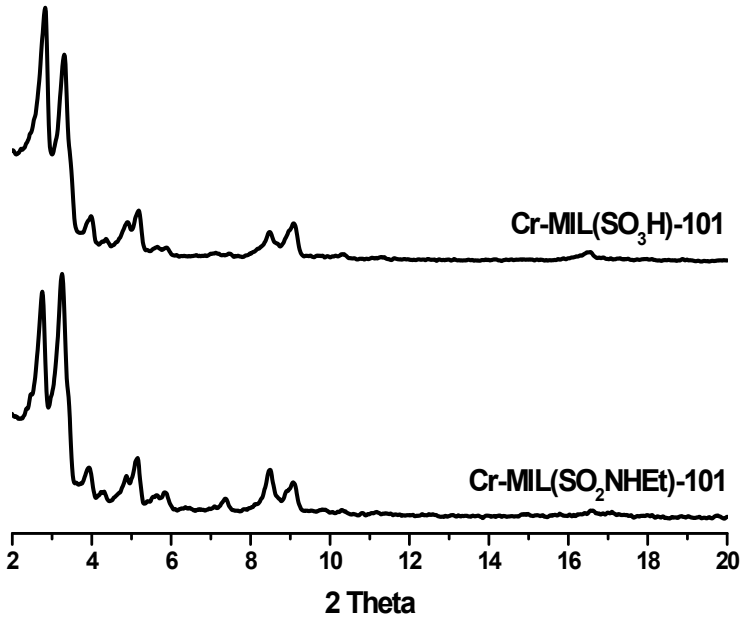


Fig. S7. PXRD pattern of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHEt **3b** (bottom).

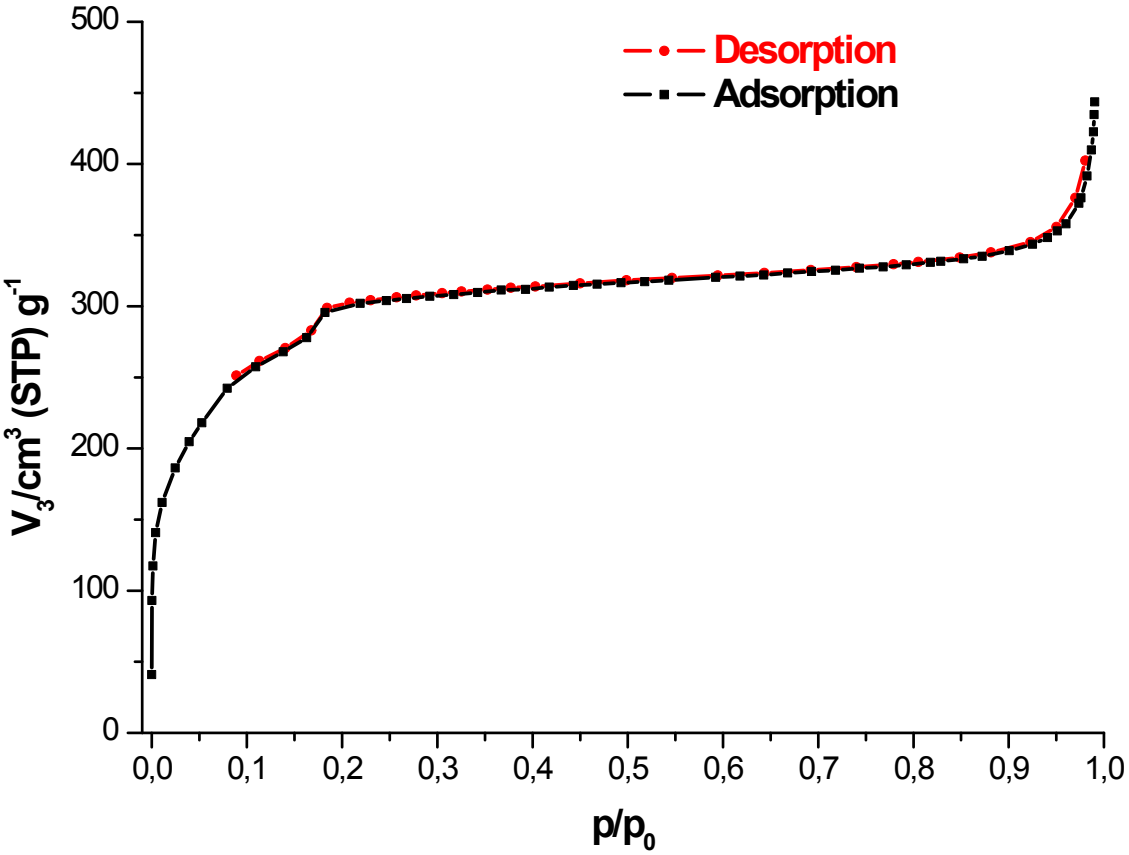


Fig. S8. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NHEt **3b**: $a_{s,BET}$ = 1050 m^2/g, total pore volume = 0.490 cm^3/g (starting material **1**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.624 cm^3/g).

2.4.3 Cr-MIL-101-SO_2NHPr (3c)

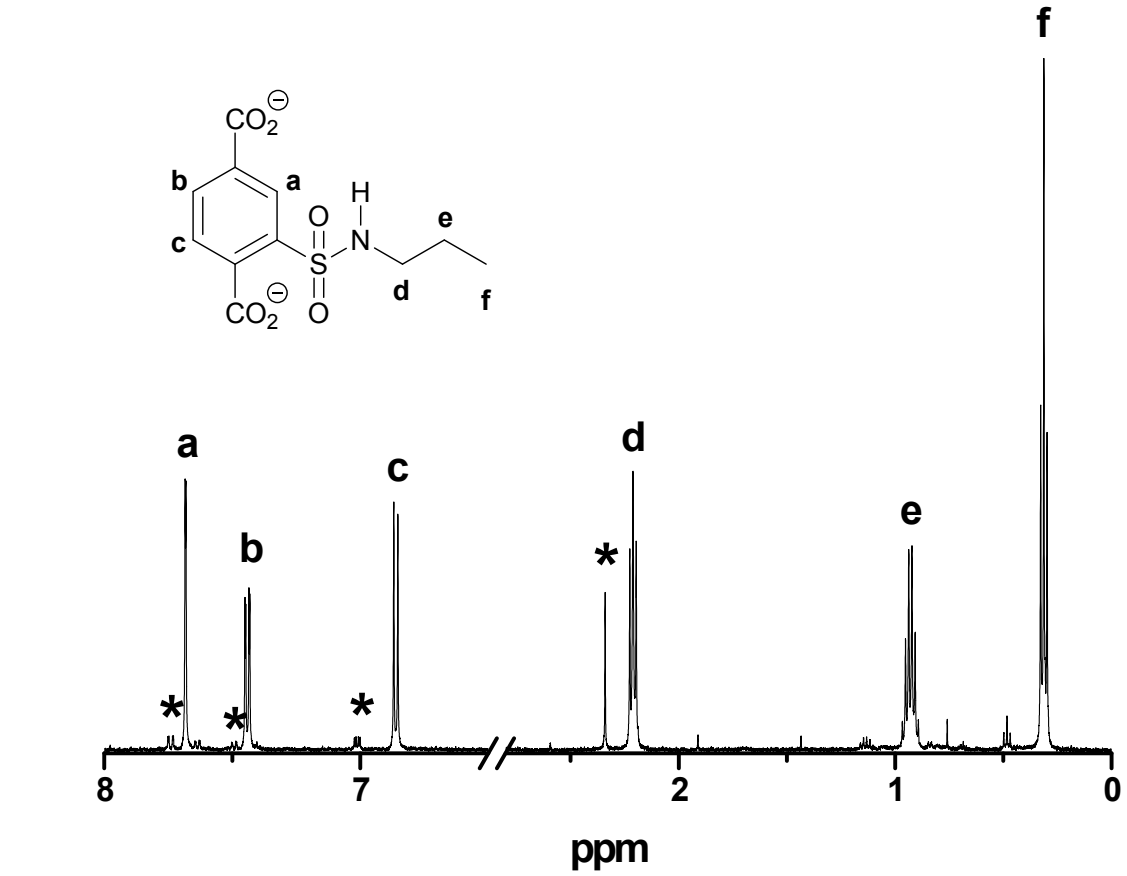


Fig. S9. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NHPr **3c** (500 MHz, 5 % NaOD in D_2O): (**a-c**) aromatic protons, (**d-f**) propyl group, (*) side product *N*,*N*-dimethyl sulfonamide **3d** (< 2 %)

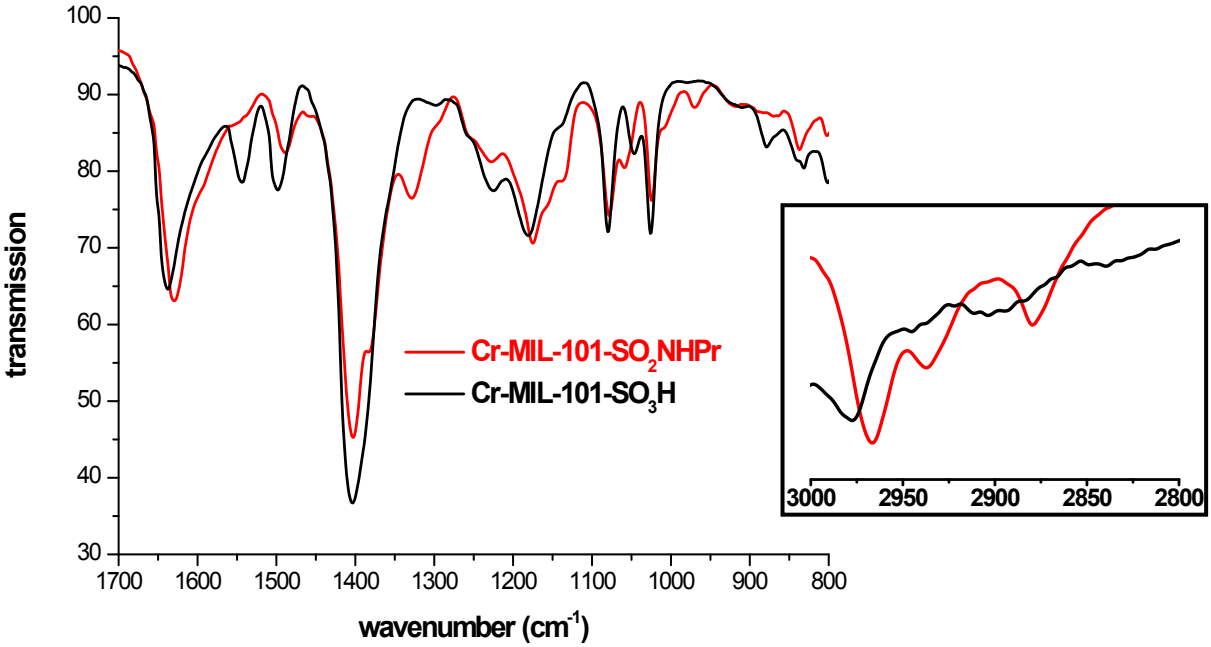


Fig. S10. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHPr **3c** (**red**). Characteristical frequencies: 2976, 2937, 2880 cm^{-1} (CH_3/CH_2 stretch), 1383 cm^{-1} (SO_2NH), 1328 cm^{-1} (CH_3), 1059 cm^{-1} (S=O).

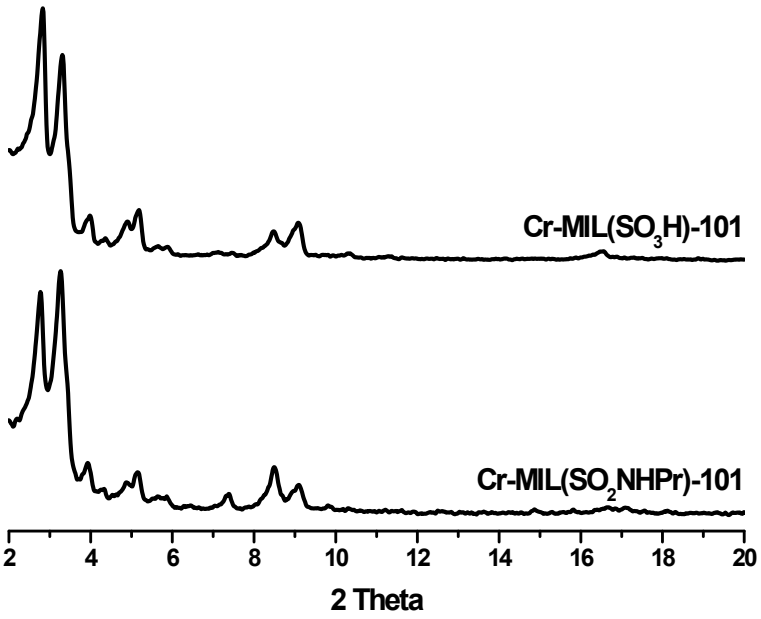


Fig. S11. PXRD pattern of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHPr **3c** (bottom).

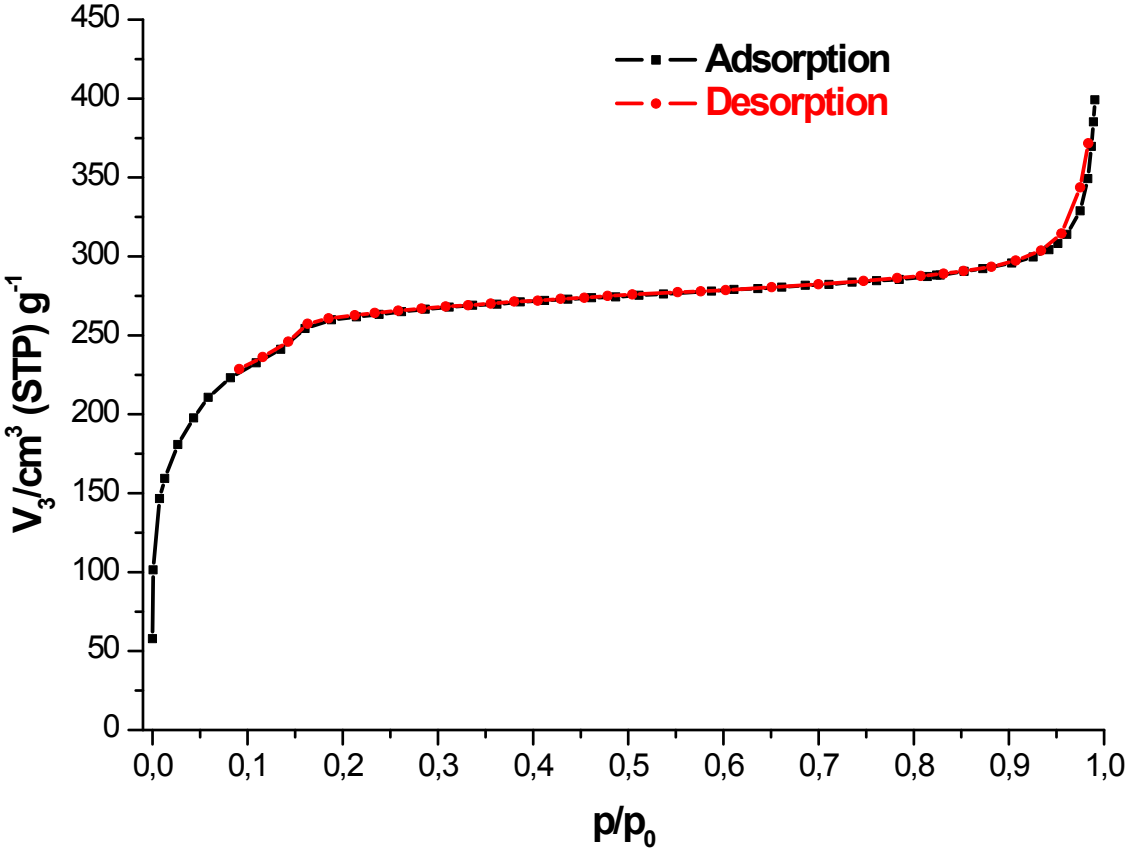


Fig. S12. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NHPr **3c**: $a_{s,BET}$ = 940 m^2/g, total pore volume = 0.425 cm^3/g (starting material **1**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.624 cm^3/g).

2.4.4 Cr-MIL-101-SO_2NMe_2 (3d)

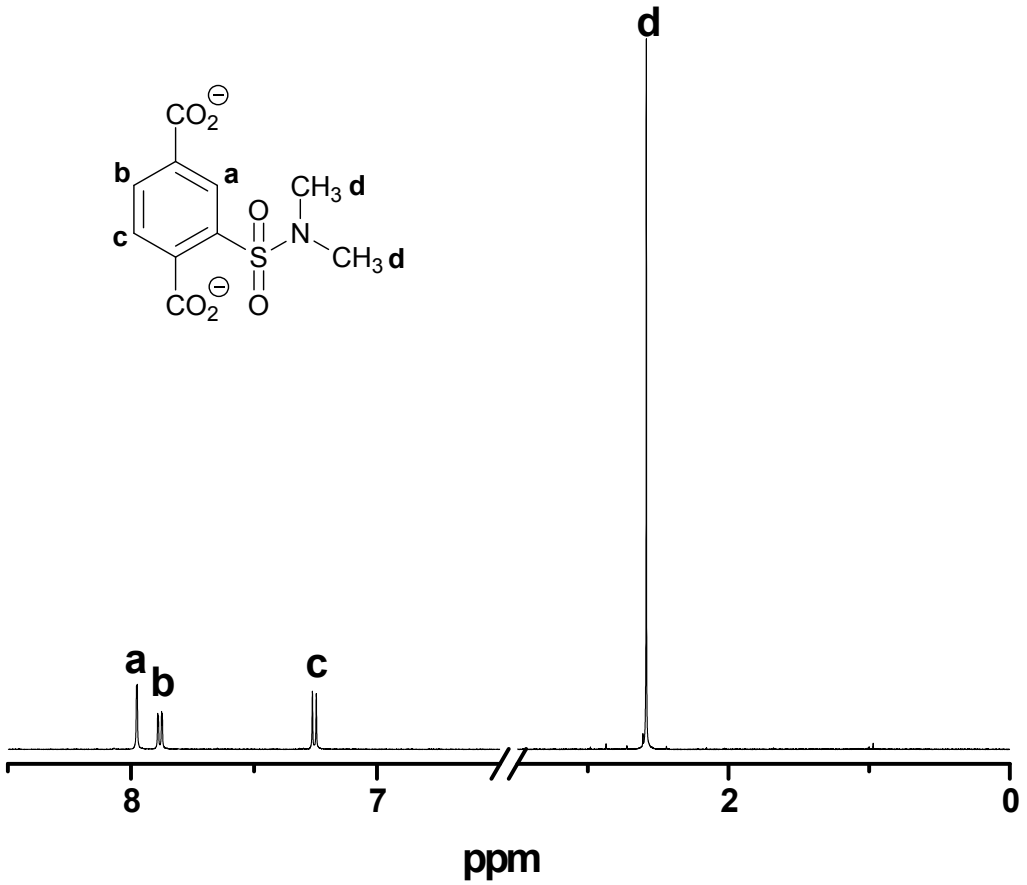


Fig. S13. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NMe_2 **3d** (500 MHz, 5 % NaOD in D_2O): (**a-c**) aromatic protons, (**d**) methyl groups.

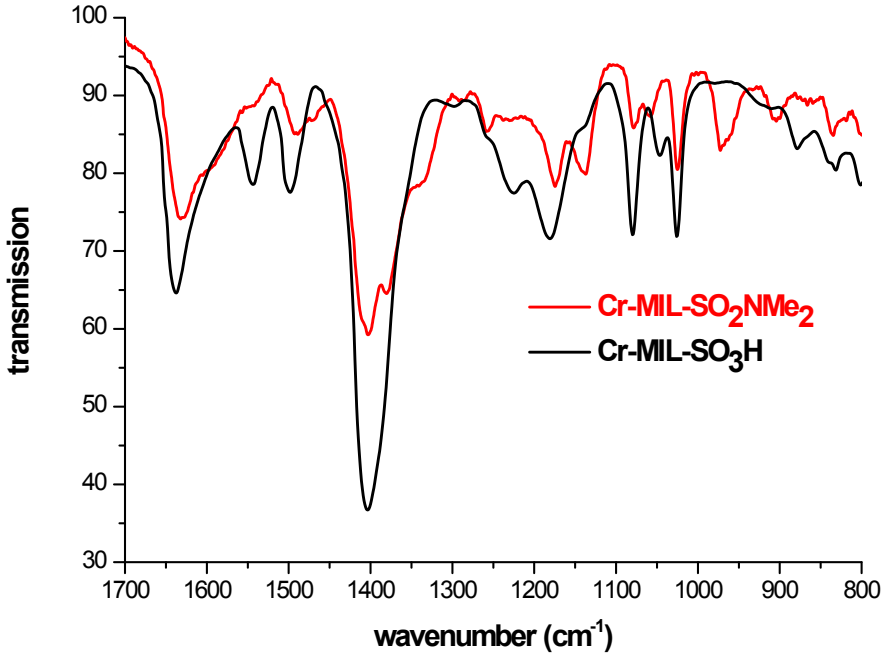


Fig. S14. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHMe_2 **3d** (**red**). Characteristical frequencies: 1381 cm^{-1} (SO_2NH), 1338 cm^{-1} (CH_3), 1059 cm^{-1} (S=O). No significant bands between 3000 – 2800 cm^{-1} for CH_3 stretch were observed.

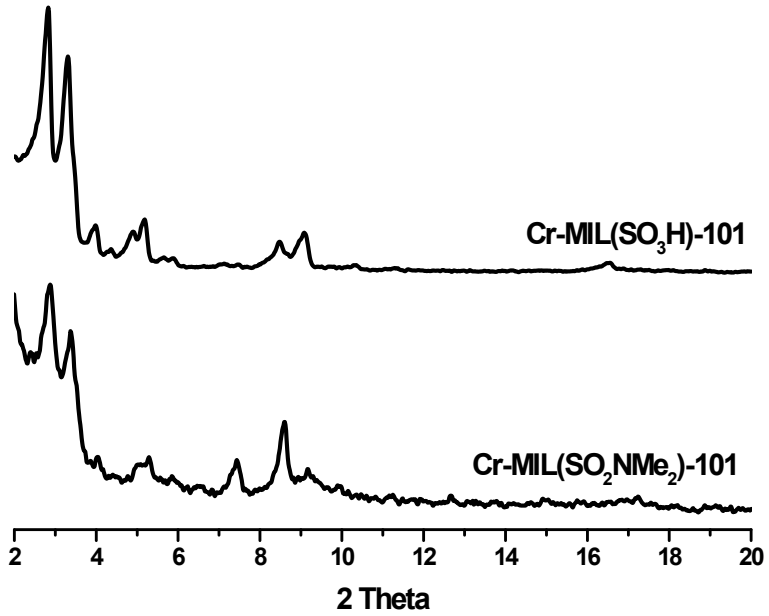


Fig. S15. PXRD pattern of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHMe_2 **3d** (bottom).

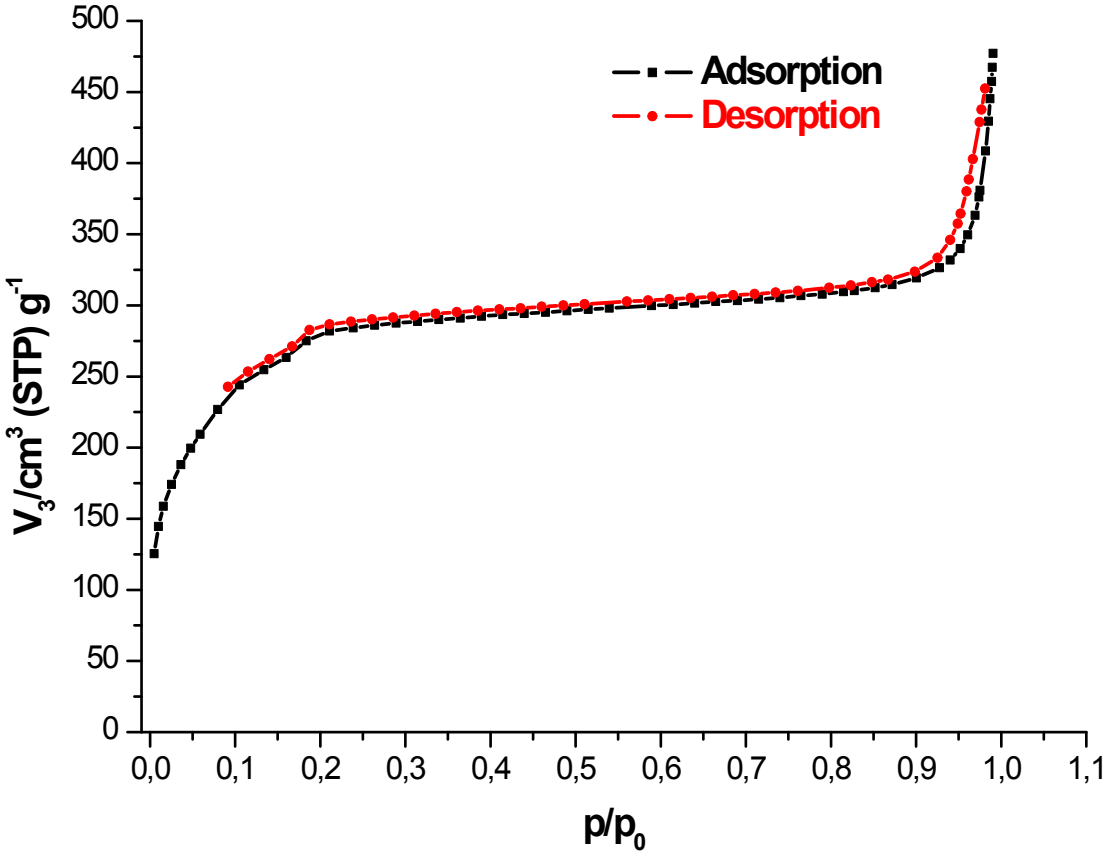


Fig. S16. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NMe_2 **3d**: $a_{s,BET}$ = 1000 m^2/g, total pore volume = 0.459 cm^3/g (starting material **1**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.624 cm^3/g).

2.4.5 Cr-MIL-101-SO_2NHPh (3e)

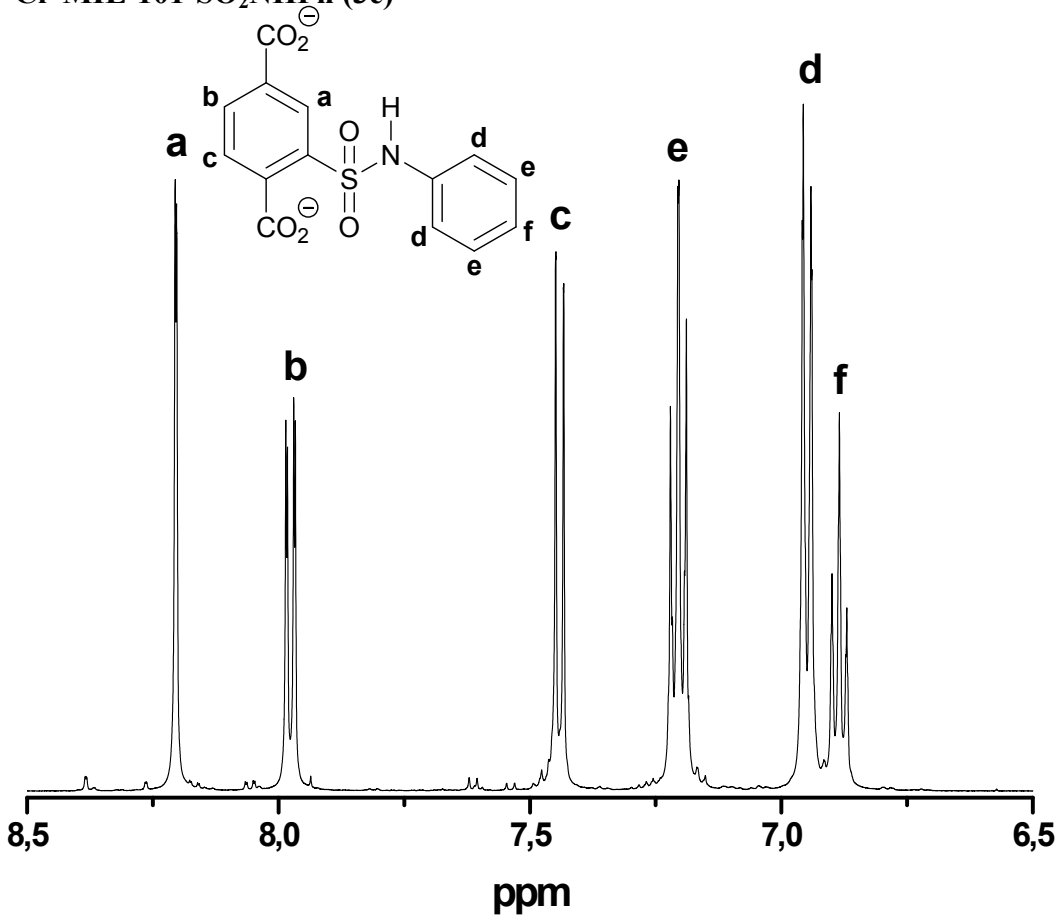


Fig. S17. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NHPh **3e** (500 MHz, 5 % NaOD in D_2O): (**a-c**) terephthalic protons, (**d-f**) phenyl protons.

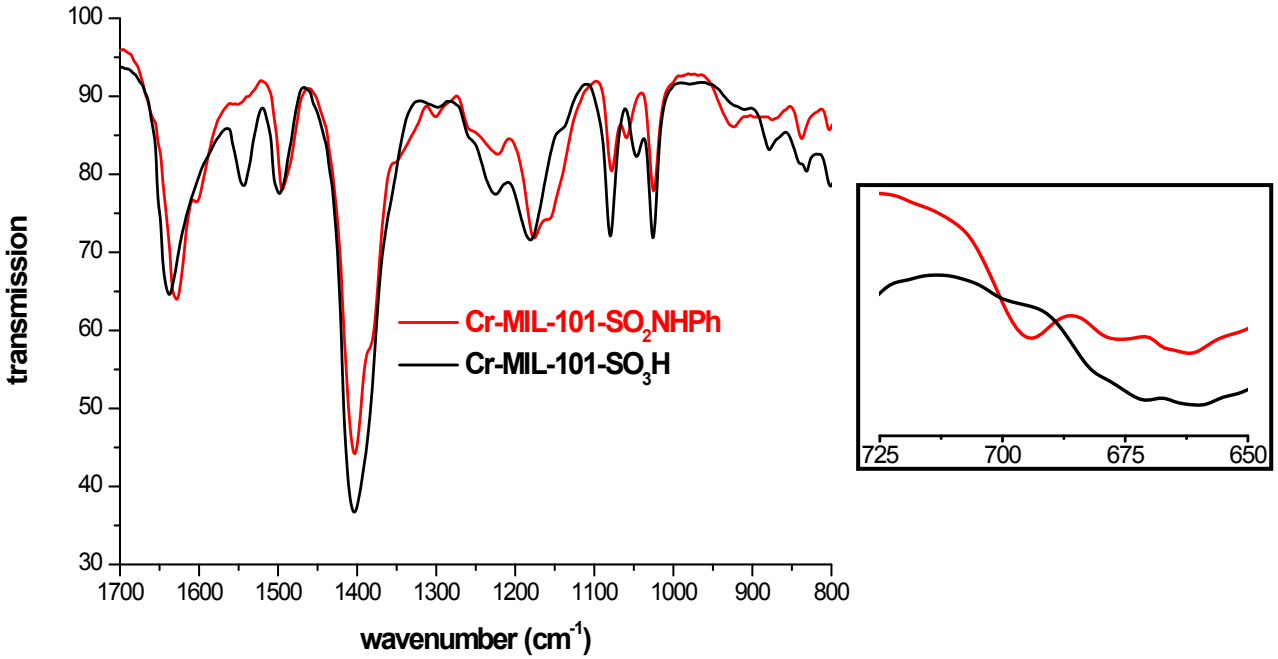


Fig. S18. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHPh **3e** (**red**). Characteristical frequencies: 1383 cm^{-1} (SO_2NH), 1060 cm^{-1} (S=O), 695 cm^{-1} (mono substituted benzene).

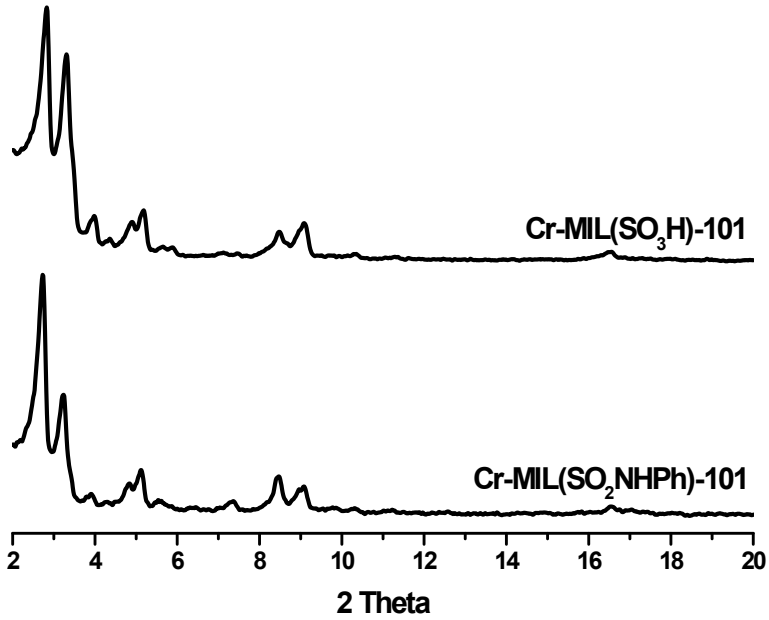


Fig. S19. PXRD pattern of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHPh **3e** (bottom).

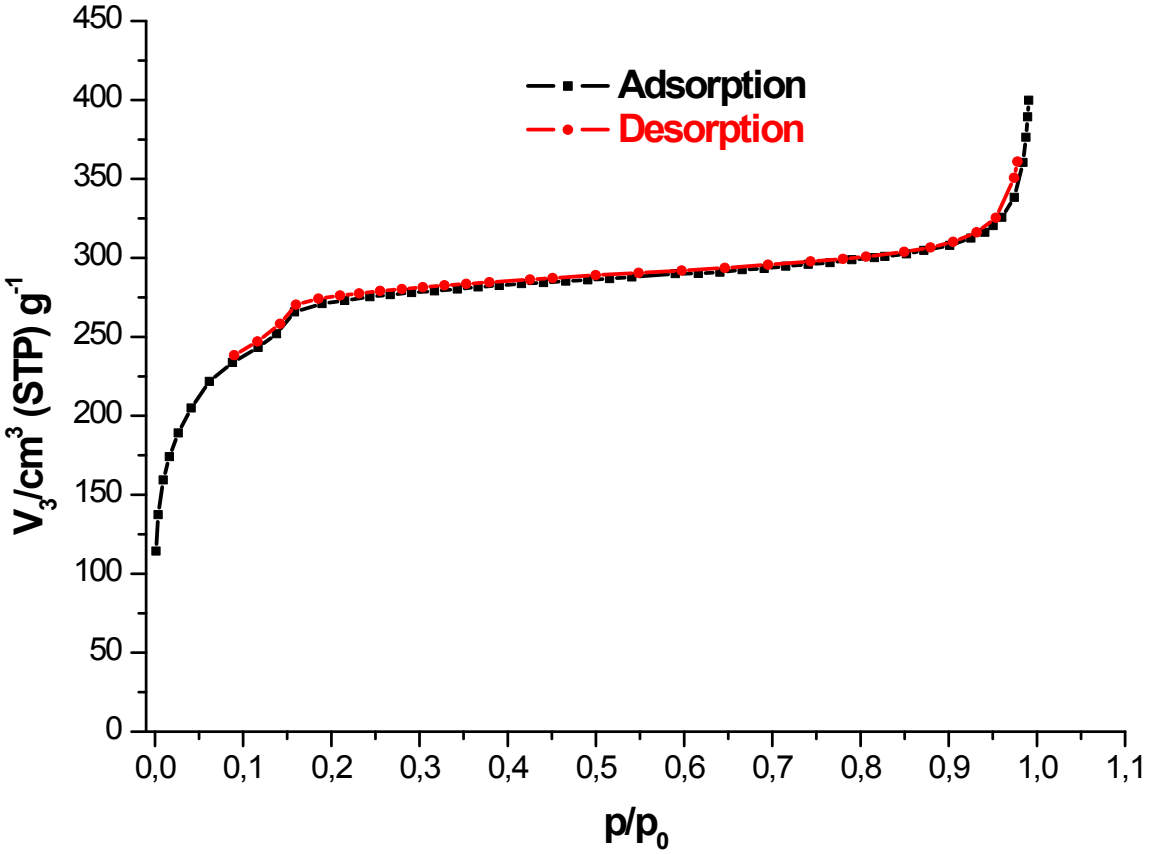


Fig. S20. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NHPh **3e**: $a_{s,BET}$ = 980 m^2/g, total pore volume = 0.443 cm^3/g (starting material **1**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.624 cm^3/g).

2.4.6 Cr-MIL-101-SO_2NHCH_2Ph (3f)

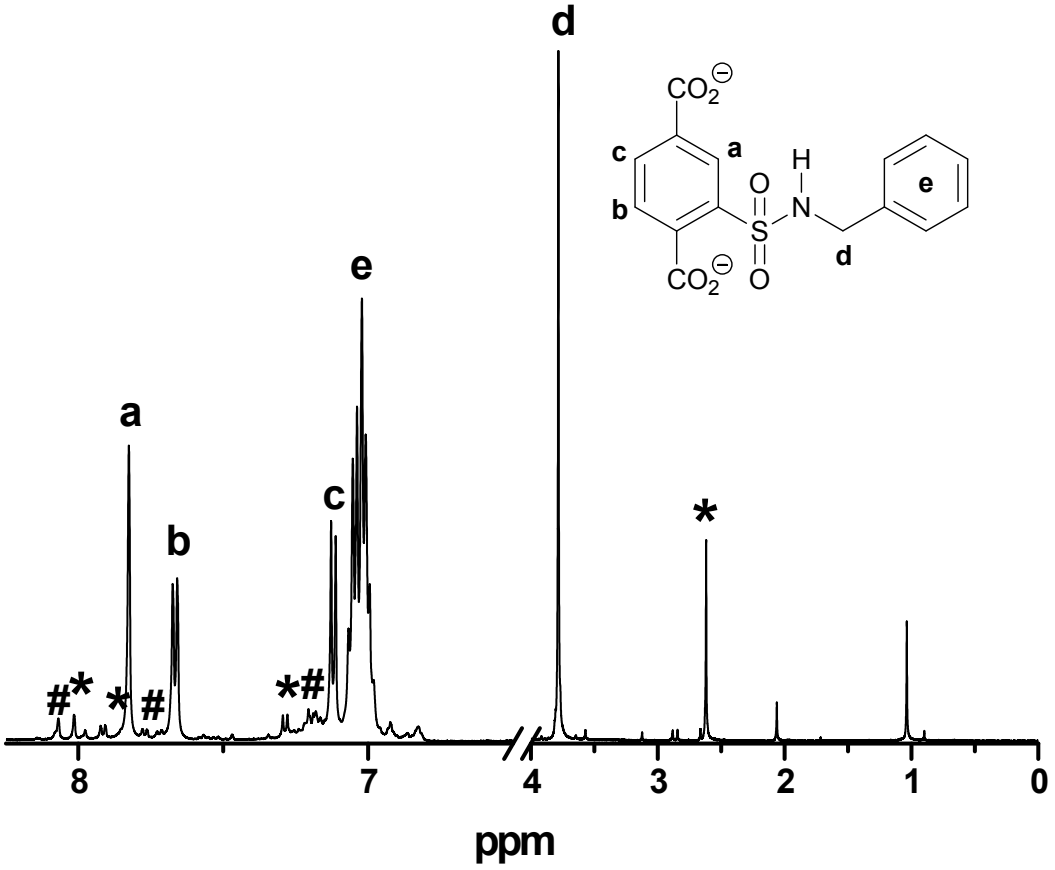


Fig. S21. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NHBn **3f** (500 MHz, 5 % NaOD in D_2O): (**a-c**) terephthalic protons, (**d**) methylene protons, (**e**) phenyl protons (*) side product *N*,*N*-dimethyl sulfonamide **3d** (< 5%), (#) residue of starting material **1**.

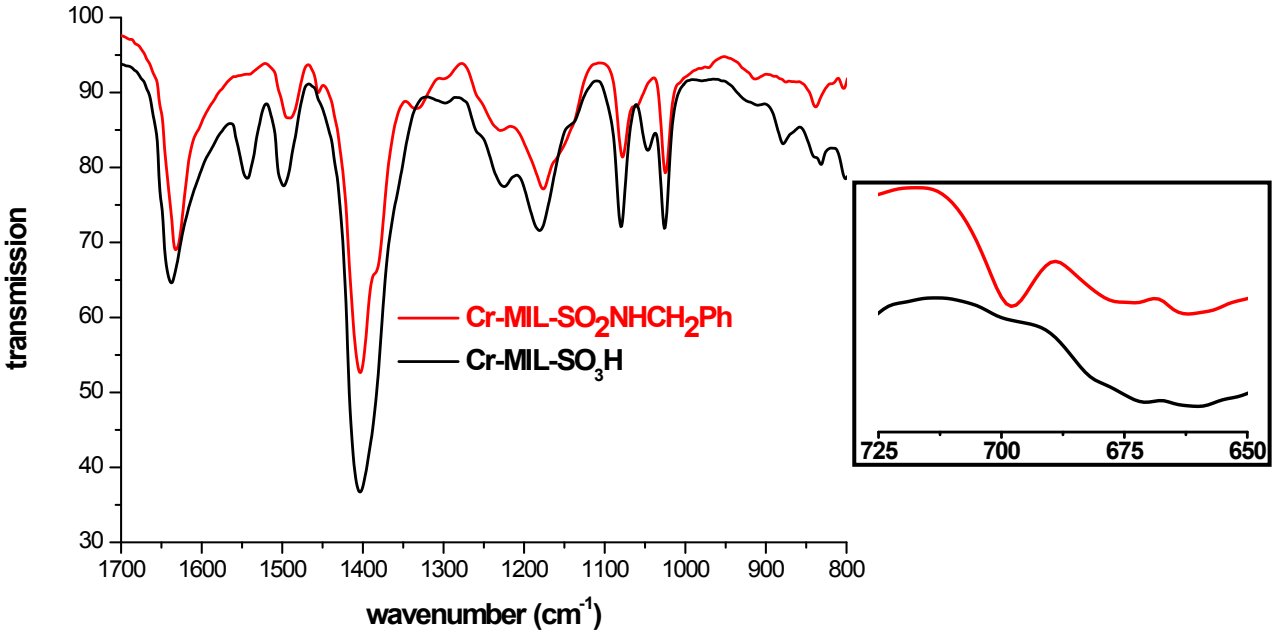


Fig. S22. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHBn **3f** (**red**). Characteristical frequencies: 1383 cm^{-1} (SO_2NH), 1331 cm^{-1} (CH_3), 1060 cm^{-1} (S=O), 698 cm^{-1} (mono substituted benzene). No significant vibration between 3000 – 2800 cm^{-1} for CH_2 stretch.

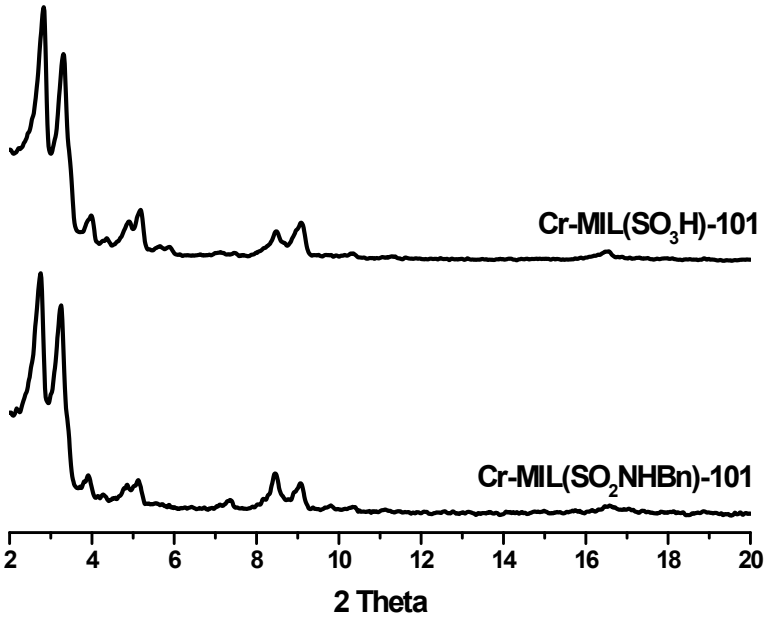


Fig. S23. PXRD PATTERN of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHBn **3f** (bottom).

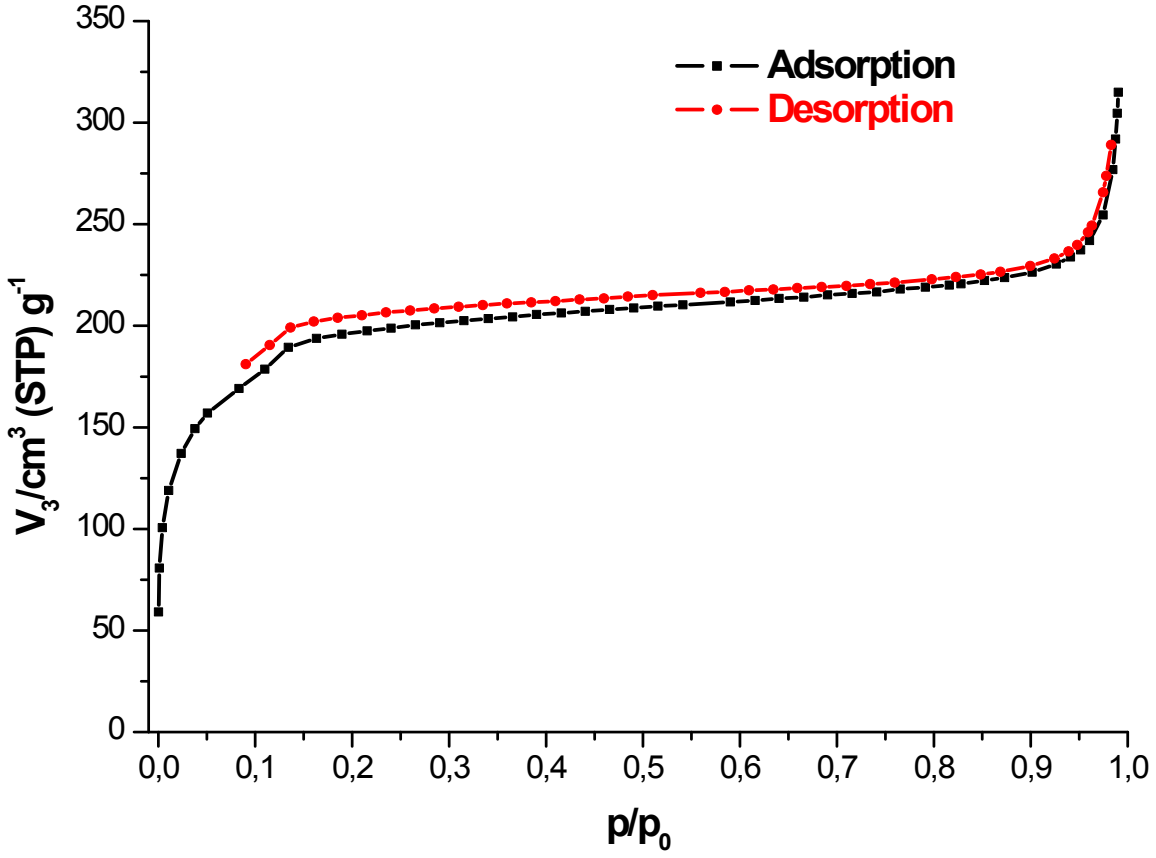


Fig. S24. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NHBn **3f**: $a_{s,BET}$ = 720 m^2/g, total pore volume = 0.323 cm^3/g (starting material **1**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.624 cm^3/g).

2.4.7 Cr-MIL-101-SO_2NHPy (3g)

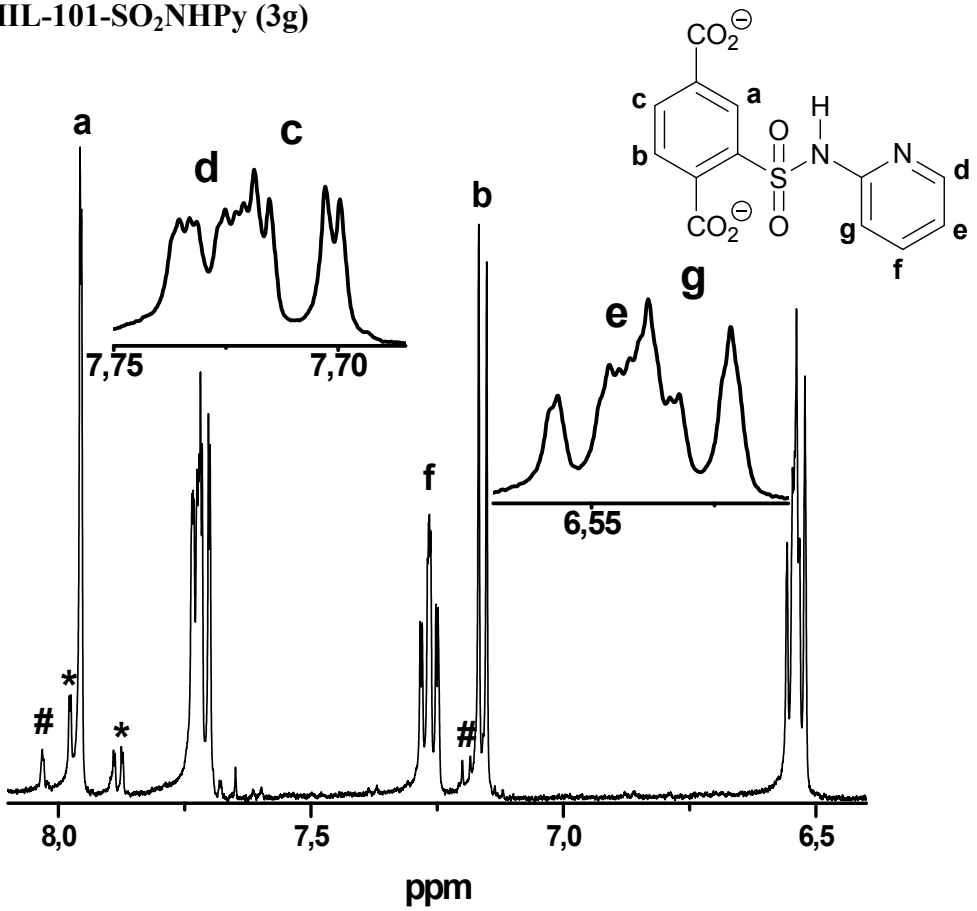


Fig. S25. ^{1}H-NMR spectrum of digested Cr-MIL-SO_2NHPy **3g** (500 MHz, 5 % NaOD in D_2O): (**a-c**) terephthalic protons, (**d-f**) pyridine protons (*) side product *N*,*N*-dimethyl sulfonamide **3d** (< 4 %), (#) residue of starting material **1**.

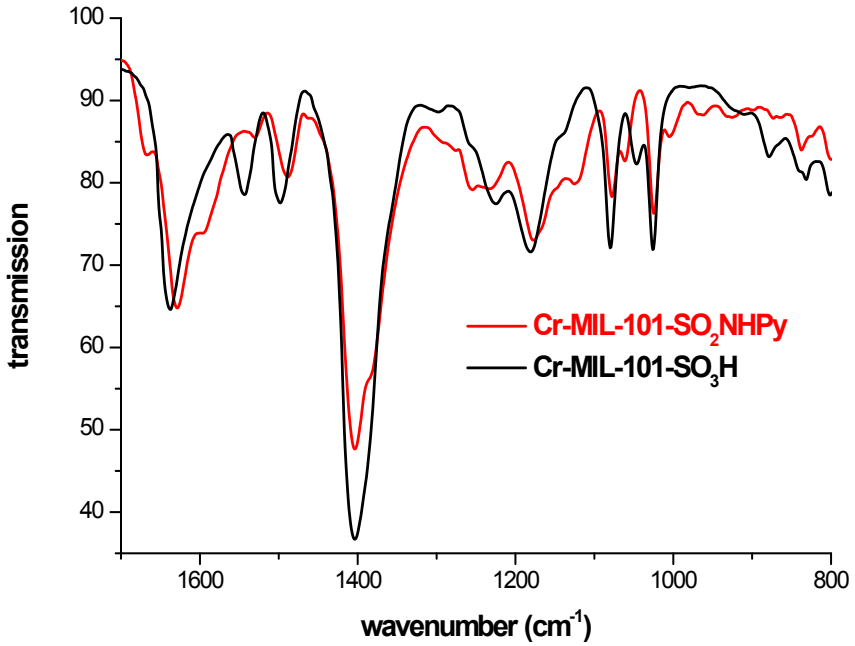


Fig. S26. FT-IR spectra of the starting material Cr-MIL-SO_3H **1** (**black**) and Cr-MIL-SO_2NHPy **3g** (**red**). Characteristical frequencies: 1385 cm^{-1} (SO_2NH), 1060 cm^{-1} (S=O).

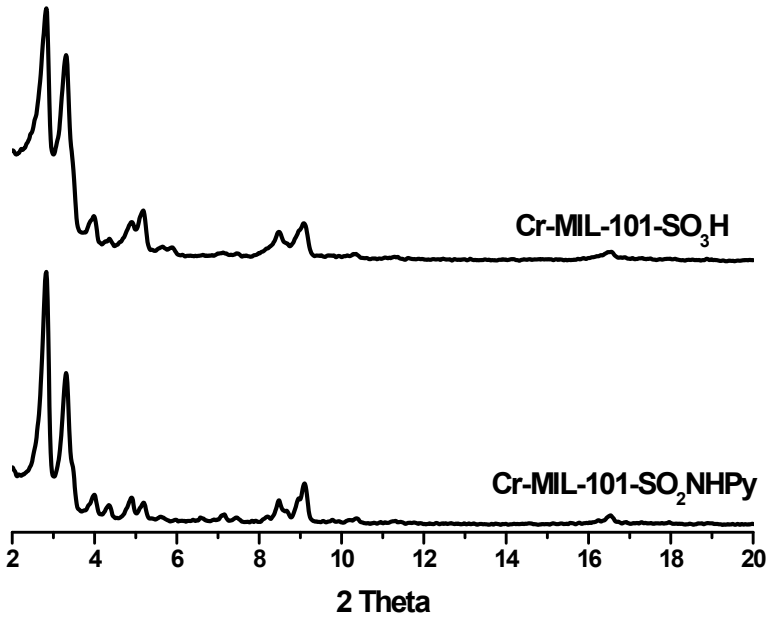


Fig. S27. PXRD PATTERN of the starting material Cr-MIL-SO_3H **1** (top) and Cr-MIL-SO_2NHPy **3g** (bottom).

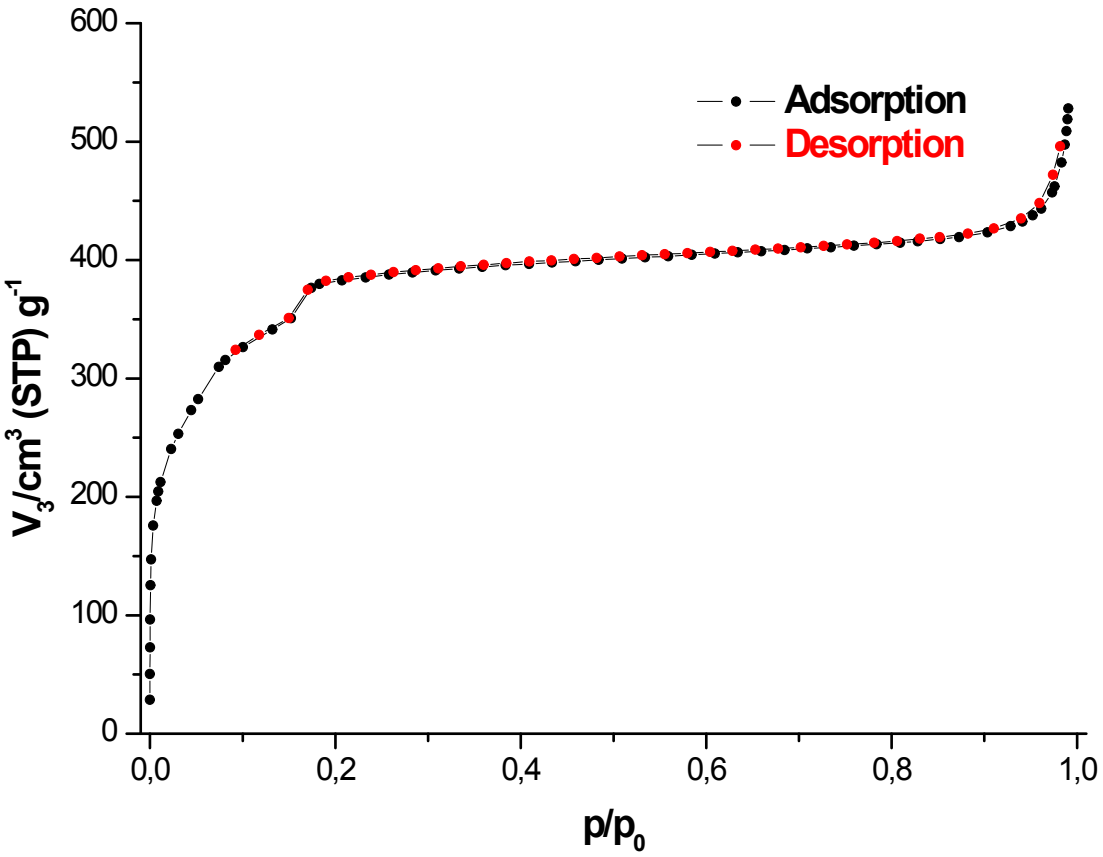


Fig. S28. N_2 adsorption isotherm (77 K) of Cr-MIL-SO_2NHPy **3g**: $a_{s,BET}$ = 1350 m^2/g, total pore volume = 0.620 cm^3/g (starting material **1**: $a_{s,BET}$ = 1860 m^2/g, total pore volume = 0.834 cm^3/g).

3 Postsynthetic modification of CAU-1-NH_2

3.1 Synthesis of CAU-1-NH_2 (5)

The synthesis of CAU-1-NH_2 was carried out in a microwave oven (Biotage Initiator) using 5 mL glass vials. A mixture of 232 mg (961 µmol) of aluminium trichloride hexahydrate, 58.0 mg (298 µmol) of 2-aminoterephthalic acid (BDC-NH_2) and 3.2 mL methanol was heated after 10 s of pre-stirring for 6 min to 145 °C. The reaction mixture was rapidly cooled to room temperature and a yellow microcrystalline dispersion was obtained. The dispersion was centrifuged and redispersed three times in water to remove chloride ions. The final product was dried in air resulting in CAU-1-NH_2 (**5**) with the molecular formula $[Al_4(OH)_2(OCH_3)_{1.69}(BDC\text{-}NH_2)_{2.89}(BDC\text{-}NHCH_3)_{0.11}]\cdot nH_2O$. The degrees of methoxy and aminomethyl groups were calculated from ^{1}H-NMR spectra of dissolved product **5**.

3.2 Synthesis and characterization of CAU-1-$NHSO_2Me$ (5)

3.2.1 Synthesis[2]

A 5 mL glass vial was loaded with 40 mg of CAU-1-NH_2, 2.0 mL of methyl sulfonyl chloride and 200 µL pyridine. The mixture was heated in a microwave oven after 1 min of pre-stirring tp 110 °C for 10 min. The precipitate was separated by centrifugation and washed using dichloromethane (2 mL, 2 x 15 min), methanol (2 mL, 3 x 15 min) and water (2 mL, 3 x 15 min). The sample was dried in vacuo at 60 °C for 12 h.

For ^{1}H-NMR analysis, the sample was digested in 5 % deuterated sodium hydroxide in deuterated water.

3.2.2 Characterization

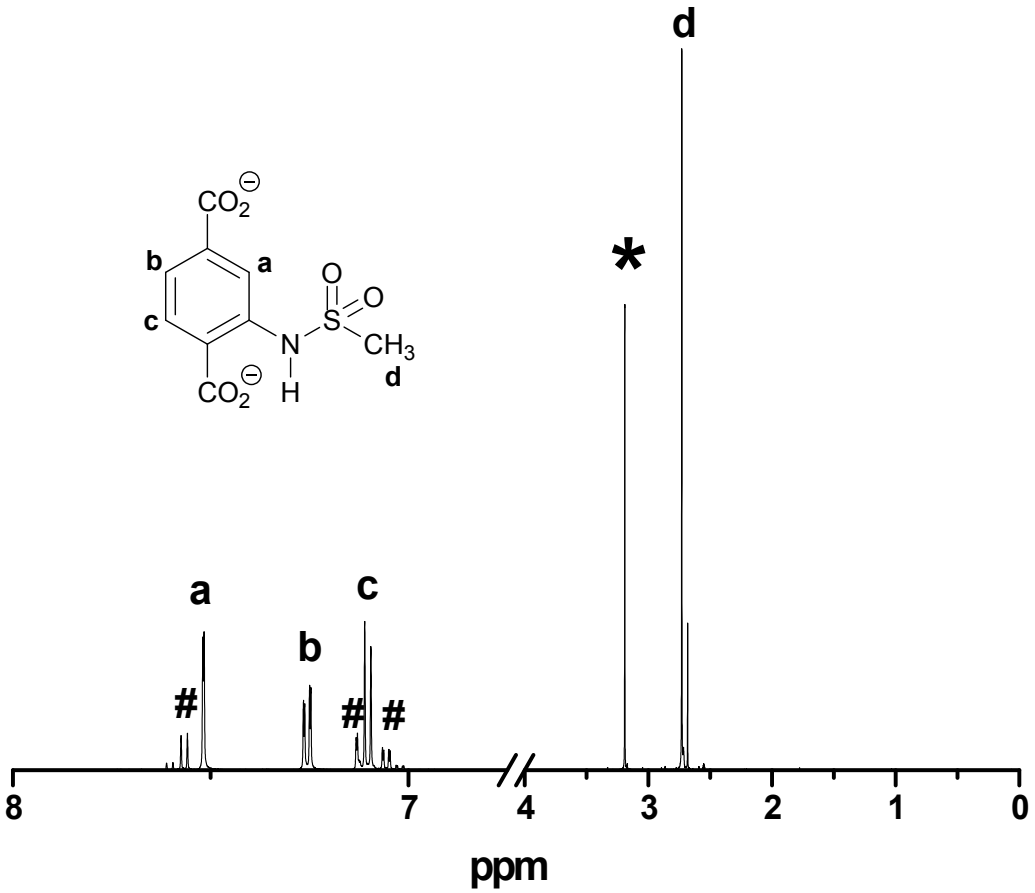


Fig. S29. ^{1}H-NMR spectrum of the digested CAU-1-NHSO$_2$Me **5** (500 MHz, 5 % NaOD in D$_2$O): (**a-c**) terephthalic protons, (**d**) methyl protons, (#) amino terephthalic acid from starting material **4**, (*) methanol.

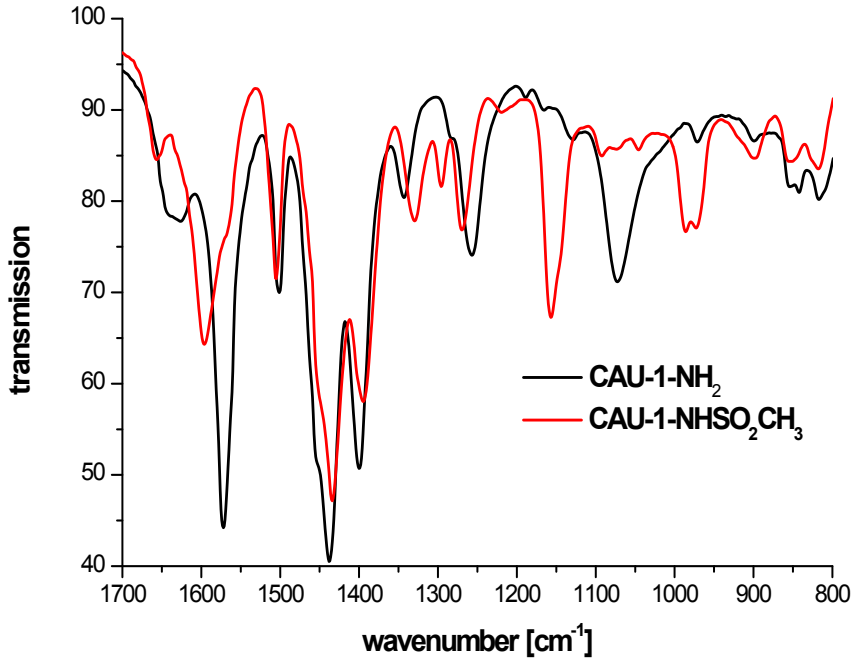


Fig. S30. FT-IR spectra of the starting material CAU-1-NH$_2$ **4** (**black**) and CAU-1-NHSO$_2$Me **5** (**red**). Characteristical frequencies: 1330 cm^{-1} (CH$_3$), 1296 cm^{-1}, 1157 cm^{-1}(sulfonamides).

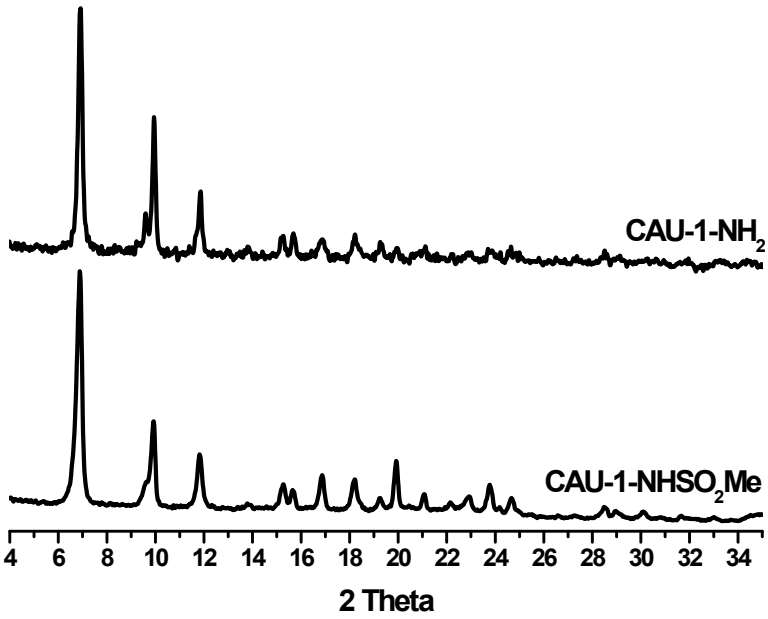


Fig. S31. PXRD PATTERN of the starting material CAU-1-NH_2 **4** (top) and CAU-1-$NHSO_2Me$ **5** (bottom).

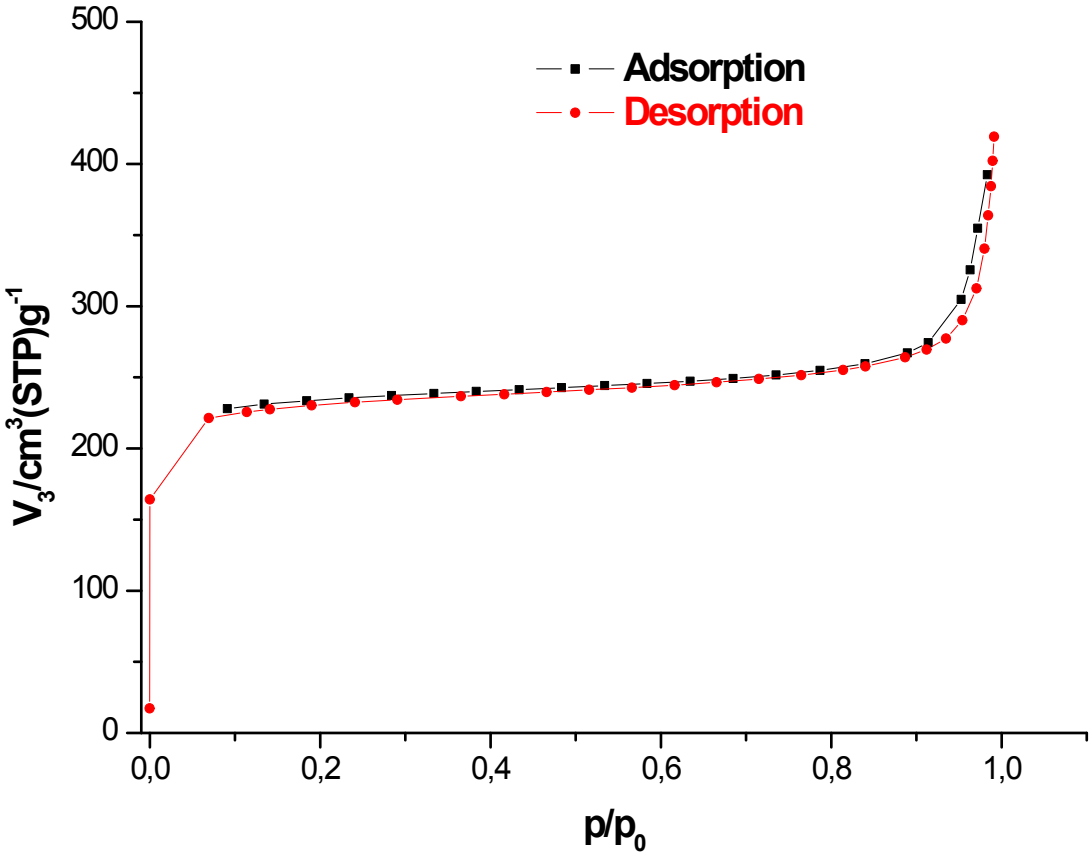
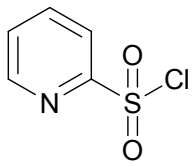


Fig. S32. N_2 adsorption isotherm (77 K) of CAU-1-$NHSO_2Me$ **5**: $a_{s,BET}$ = 900 m^2/g, total pore volume = 0.372 cm^3/g (starting material **1**: $a_{s,BET}$ = 1480 m^2/g, total pore volume = 0.610 cm^3/g). Recorded with a BELSORP-mini apparatus (BEL JAPAN INC.).

3.3 Synthesis and characterization of CAU-1-NHSO$_2$Py (6)

3.3.1 Synthesis of pyridine-2-sulfonyl chloride[3]



A solution of 1.00 g (9.00 mmol) of 2-mercaptopyridine in 25 mL of conc. sulfuric acid was cooled to 0 °C and treated carefully with 60 mL of sodium hypochlorite acid (10 - 15 % available chlorine). After stirring for additional 60 min at this temperature, the mixture was treated with 50 mL of ice cold water. The aqueous phase was extracted three times using 50 mL of ice cold dichloromethane. The organic phase was dried with magnesium sulfate and filtered. After removing the solvent in vacuo, a slightly yellow oil was obtained. Due to the instability of this compound, the crude product (1.12 g) was stored at – 18 °C and used without further purification.

^{1}H-NMR (600 MHz, CDCl$_3$): δ = 8.83 (d, 1H, ^3J = 4.6 Hz, Py-*H*-6), 8.12 (d, 1H, ^3J = 7.8 Hz, Py-*H*-3), 8.06 (td, 1H, ^3J = 7.8 Hz, Py-*H*-4), 7.70 (ddd, 1H, ^3J = 7.8 Hz, ^3J = 4.6 Hz, Py-*H*-5) ppm.

^{13}C-NMR (150 MHz, CDCl$_3$): δ = 159.21 (s, Py-*C*-2), 150.69 (d, Py-*C*-6), 139.02 (Py-*C*-4), 129.05 (d, Py-*C*-5), 121.91 (Py-*C*-3) ppm.

3.3.2 Synthesis of CAU-1-NHSO$_2$Py (6)

A Schlenck tube was loaded with 40 mg of CAU-1-NH$_2$ and cooled down to 0 °C. After addition of 1.0 mL of solution of pyridine-2-sulfonylchloride pyridine (crude product from the previous step, max. 2 mmol) in dry tetrahydrofurane, the sample was allowed to warm to room temperature and stirred overnight. The precipitate was collected by centrifugation and washed using dichloromethane (2 mL, 2 x 15 min), methanol (2 mL, 3 x 15 min) and water (2 mL, 3 x 15 min). The sample was dried in vacuo at 60 °C for 12 h.

For ^{1}H-NMR analysis, the sample was digested in 5 % deuterated sodium hydroxide in deuterated water.

3.3.2 Characterization

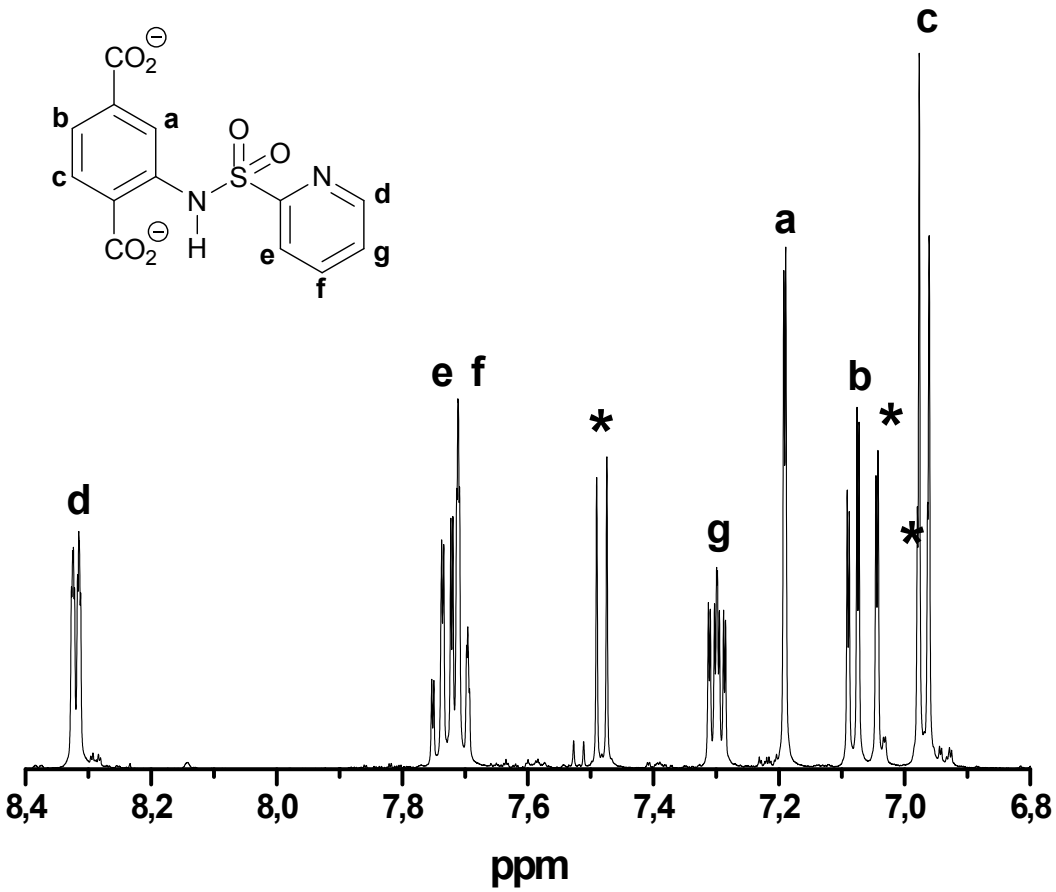


Fig. S33. ^{1}H-NMR spectrum of the digested CAU-1-NHSO$_2$Py **6** (500 MHz, 5 % NaOD in D$_2$O): (**a-c**) terephthalic protons, (**d-g**) pyridine protons, (*) amino terephthalic acid from starting material **4**.

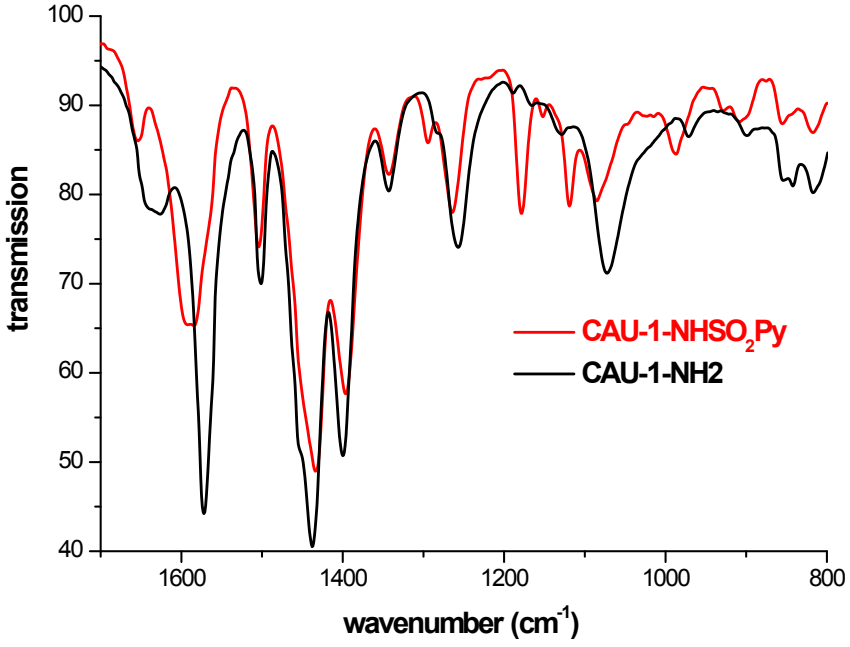


Fig. S34. FT-IR spectra of the starting material CAU-1-NH$_2$ **4** (**black**) and CAU-1-NHSO$_2$Py **5** (**red**). Characteristical frequencies: 1294 cm^{-1}, 1178 cm^{-1}(sulfonamides), 1119 cm^{-1} (S=O).

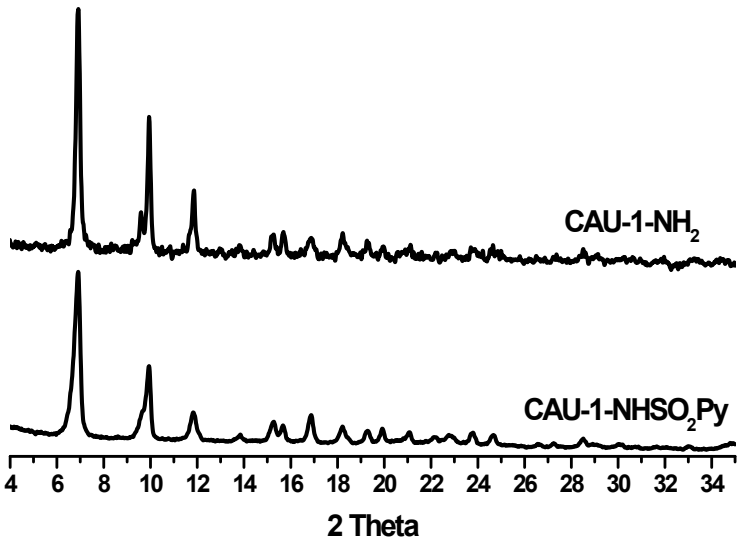


Fig. S35. PXRD PATTERN of the starting material CAU-1-NH_2 **4** (top) and CAU-1-$NHSO_2Py$ **6** (bottom).

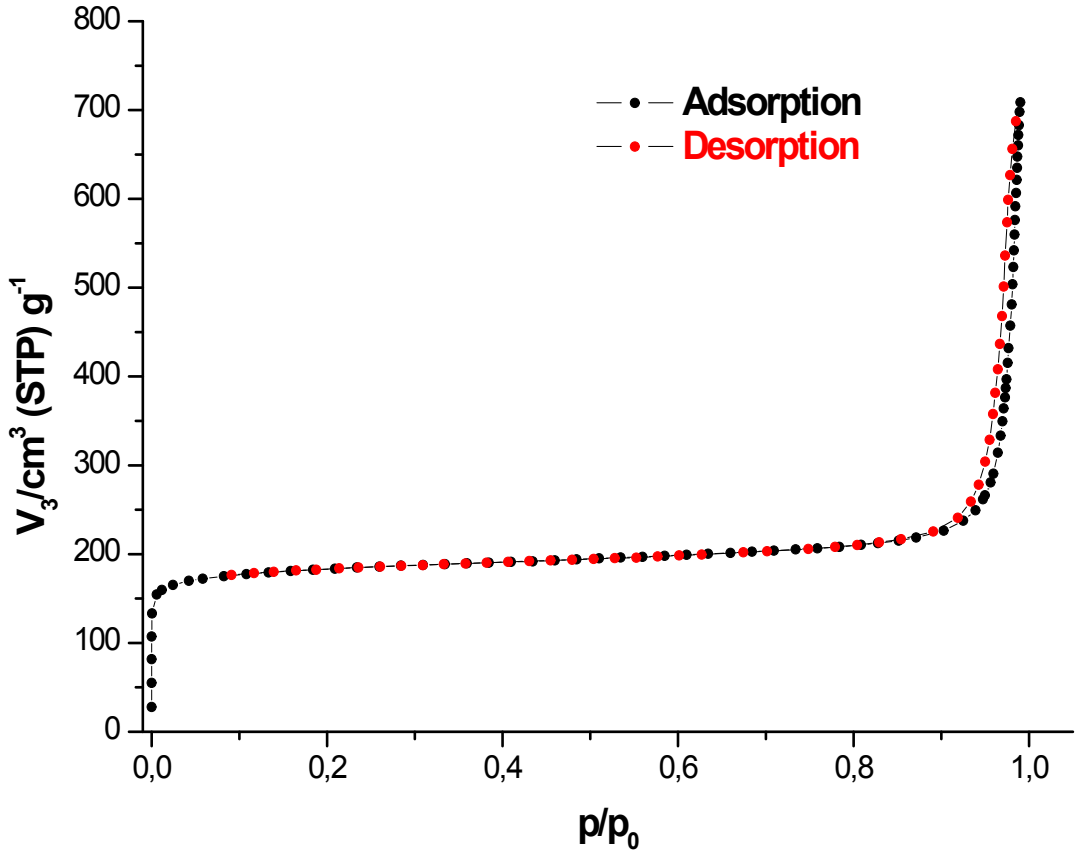


Fig. S36. N_2 adsorption isotherm (77 K) of CAU-1-$NHSO_2Py$ **6**: $a_{s,BET}$ = 720 m^2/g, V_m = 0.294 cm^3/g (starting material **4**: $a_{s,BET}$ = 1480 m^2/g, total pore volume = 0.610 cm^3/g).

4. References

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2. T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker, and N. Stock, *Angew. Chem. Int. Ed.*, 2009, **48**, 5163; *Angew. Chem.*, 2009, **121**, 5265.

3. *US Pat.*, US2007/60623, 2007.