

Supporting Information

The Adsorbate Structure of Ferrocene inside $[Al(OH)(bdc)]_x$ (MIL-53): A Powder X-ray Diffraction Study.

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Experimental Procedures, Methods and Materials.

All manipulations were carried out under an inert atmosphere. MIL-53(Al) synthesis was performed according to the literature.¹⁵

Elemental Analysis/AAS. For determination of the Al and Fe contents an AAS apparatus by Vario of type 6 (1998) was employed; C and H analyses were carried out using a Vario CHNSO EL (1998) instrument.

FTIR-spectra were measured with an ATR setup using a Bruker Alpha FT-IR instrument. *Solid-state NMR* spectra were measured with a Bruker DSX 400 MHz instrument under MAS conditions in 2.5 mm ZrO₂ rotors with a sample volume of 12 μ L (rotation frequency 20 kHz). For the ¹H-NMR a ZG4PM pulse program was used. The ¹³C-CP-NMR were carried out with the pulse program CP4C and referenced to adamantane at 38.56 ppm.

N₂-Adsorption. Nitrogen adsorption experiments were carried out with a Quantachrome Autosorb-1 MP. The specific surface areas were calculated by fitting the measured type I isotherms to the Langmuir surface model in a pressure range of $p/p^0 = 0.1-0.3$ at $T = 77.36$ K.

FTIR and ^{13}C MAS NMR Spectra of **1 and **2**.** The IR spectrum of **1** exhibits additional bands for C-C vibration of the Cp-Ring at 850 and 875 cm^{-1} in comparison to the empty matrix (Figure 1S). The two characteristic vibrational bands of carboxylate groups of bdc, which are coordinated to Al, exist in both spectra (1604 cm^{-1} and 1503 cm^{-1}). These absorptions can be assigned to asymmetric CO_2 stretching mode of the carboxylic groups. The spectra show no additional bands at 1700 cm^{-1} which would be attributed to free bdc. The O-H band is shifted by 40 cm^{-1} from 3616 cm^{-1} to 3654 cm^{-1} . This may indicate some interaction between the bridging O-H group of the framework and the Fc guest molecule. On the other hand there are no short contacts in the crystal structure (see below). The origin of the shift of the OH vibrational band as observed in the IR spectrum is not obvious and is difficult to correlate with the obtained structure. One possible explanation of this phenomenon is steric confinement of the OH groups by the guest molecule. Also, in the ^1H MAS NMR spectra of **1** and **2**, the OH resonance is missing in contrast to the parent host material. The ^{13}C MAS NMR data of **1** and **2** are as expected without unusual features.

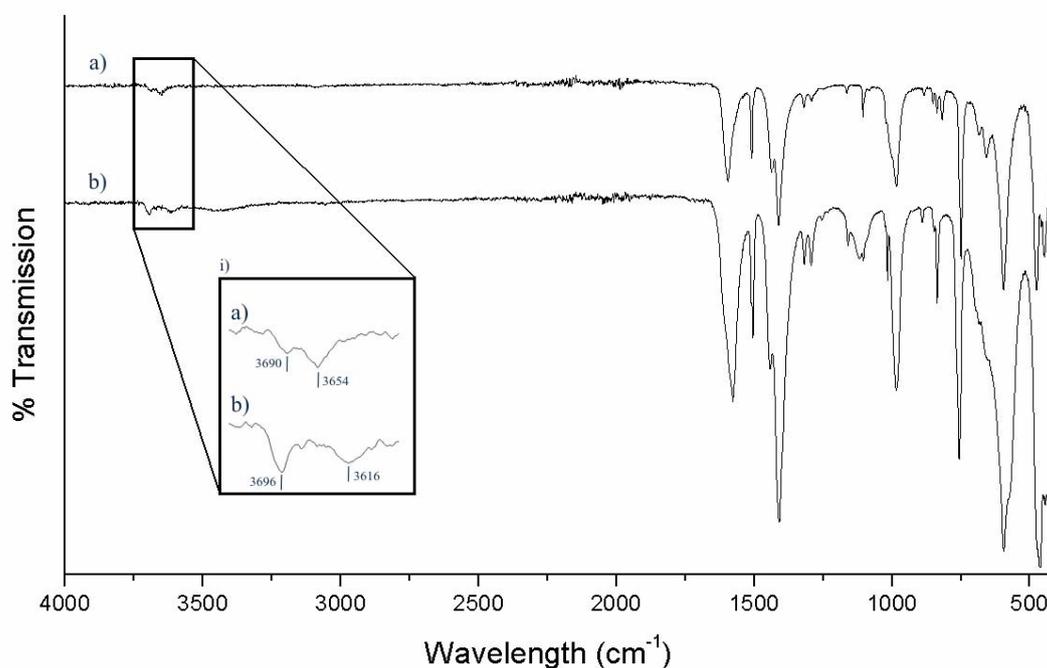


Figure 1S. a) FTIR spectrum of **1**. b) FTIR spectrum of MIL-53(Al). The insert shows an enlargement of O-H band region.

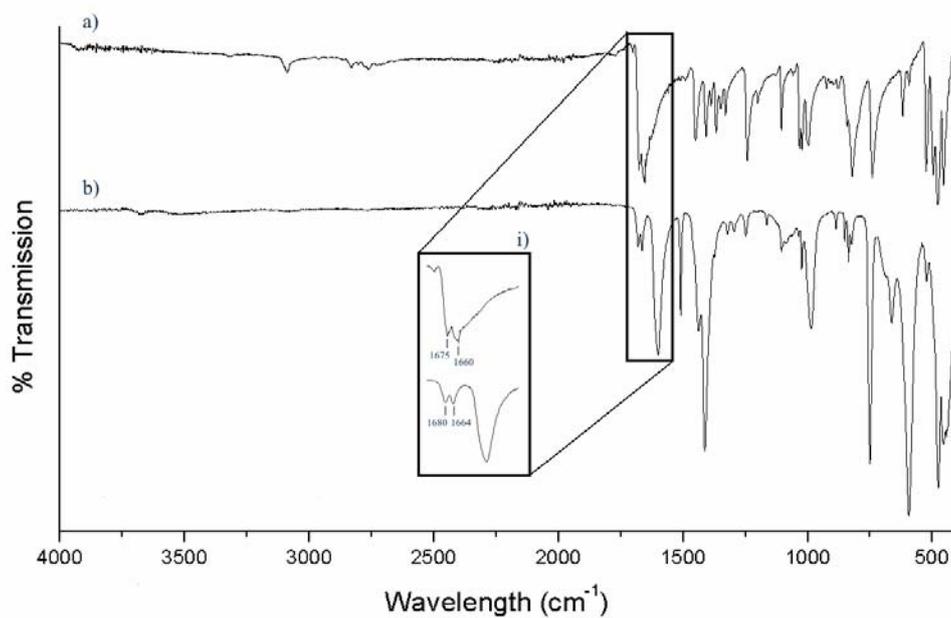


Figure 2S. a) IR spectrum of 1-ferrocenealdehyde; b) IR spectrum of **2**; i) enlargement of C=O band of the aldehyde group.

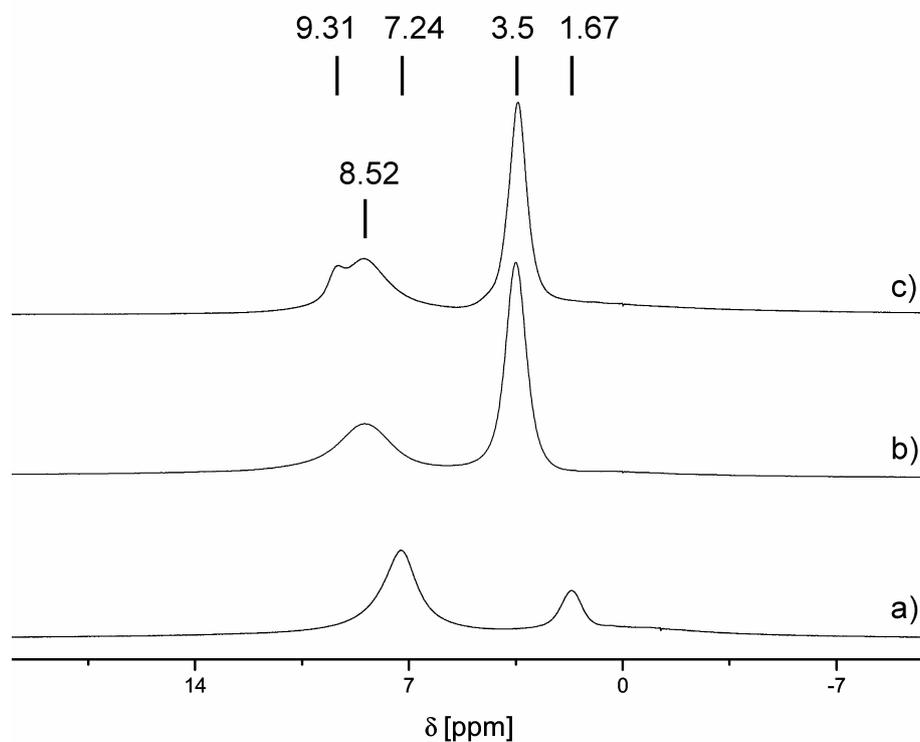


Figure 3S. a) ^1H -MAS-NMR of MIL-53(Al)_{ht}, δ_{H} /ppm: 7.24 (bdc), 1.67 (Al-OH); b) **1**, δ_{H} /ppm: 8.52 (bdc), 3.50 (C_5H_5); c) **2**, δ_{H} /ppm: 9.31 (s, CHO), 8.52 (bdc), 3.50 (C_5H_5).

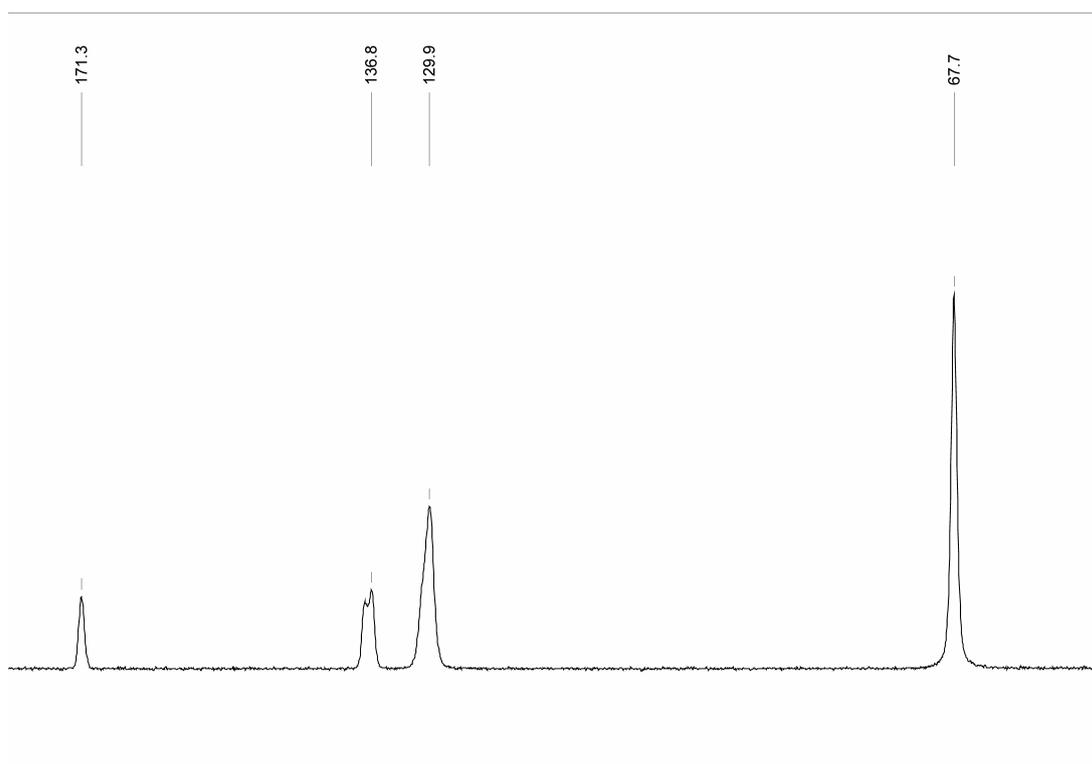


Figure 4S. ^{13}C -CP-MAS-NMR of **1**. ^{13}C -CP-MAS-NMR, $\delta_{\text{C}}/\text{ppm}$: 171.3 (O_2C^-), 136.8 ($\text{O}_2\text{CC}^{\text{bdc}}$), 129.9 (HC^{bdc}), 67.7 (C_5H_5)

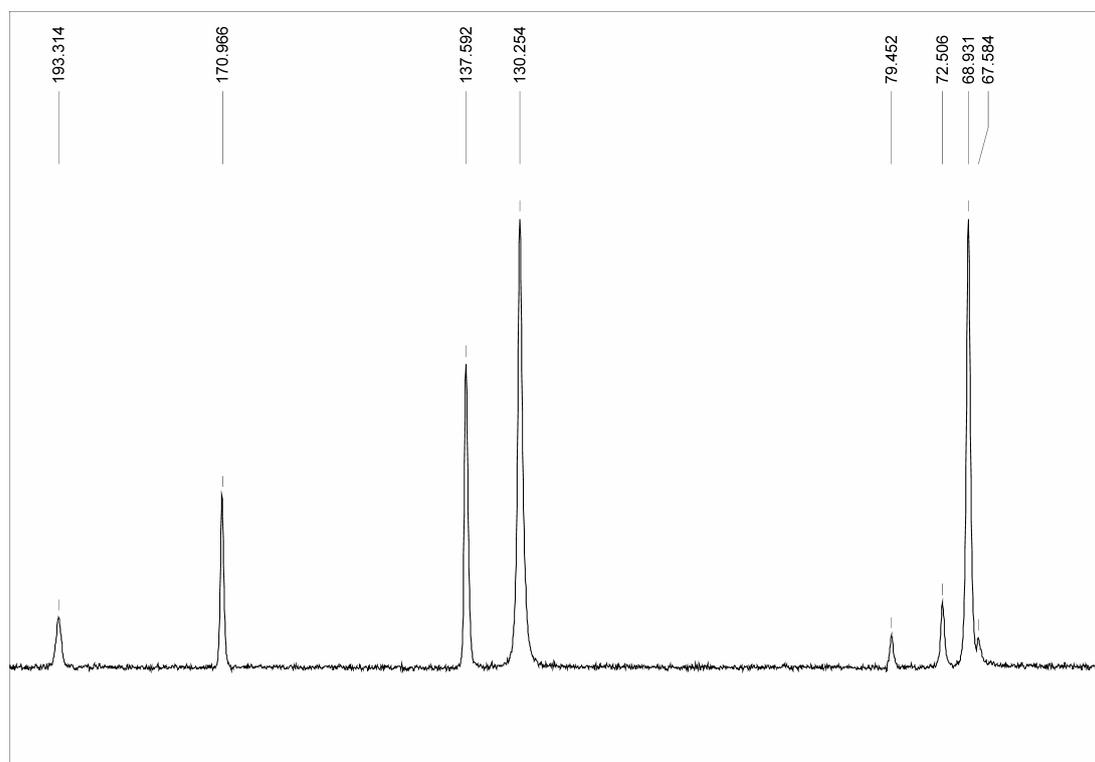


Figure 5S. ^{13}C -CP-MAS-NMR of **2**. ^{13}C -CP-MAS-NMR, $\delta_{\text{C}}/\text{ppm}$: 193.3 ($\text{HOC}^{\text{aldehyde}}$), 171.0 ($\text{O}_2\text{C}^{\text{bdc}}$), 137.6 ($\text{O}_2\text{CC}^{\text{bdc}}$), 130.3 (HC^{bdc}), 79.5 ($\text{C}_5\text{H}_4\text{CHO}$), 72.5 ($\text{C}_5\text{H}_4\text{CHO}$), 68.9 (C_5H_5), 67.6 ($\text{C}_5\text{H}_4\text{CHO}$).

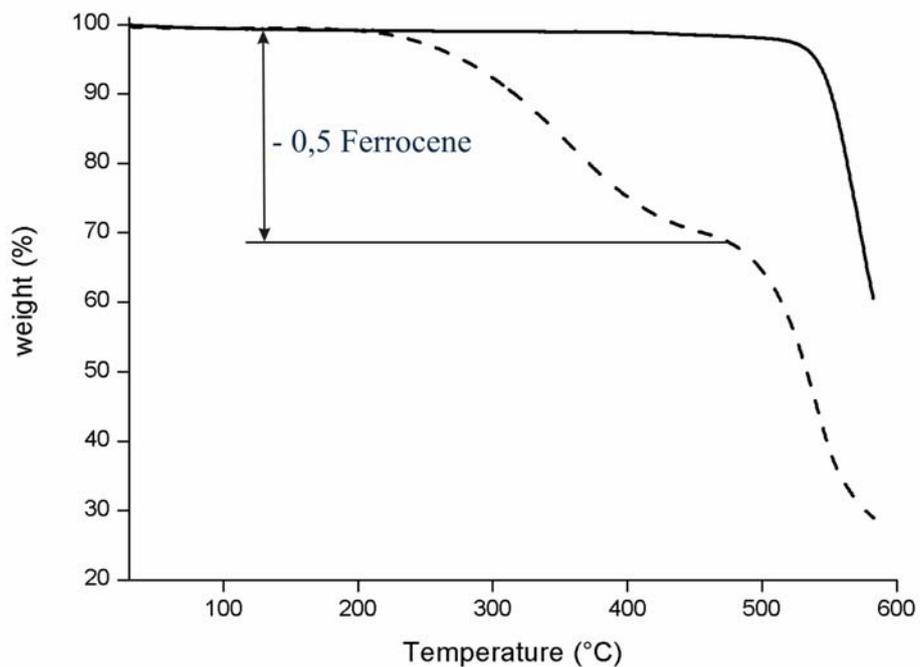


Figure 6S. Thermal analysis of **1** (firm line: TG of MIL-53_ht; dotted line: TG of **1**).

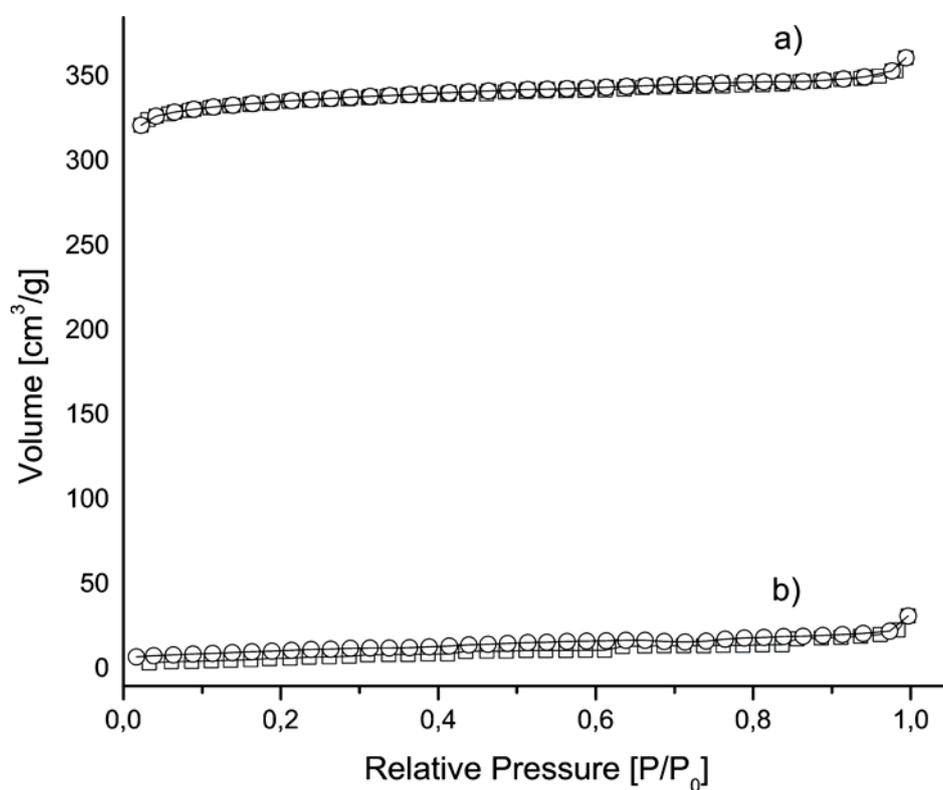


Figure 7S. a) N₂ adsorption data of MIL-53(Al)_ht (Langmuir surface area of 1476 m²/g);
b) N₂ adsorption data of **1** (Langmuir surface area of 33 m²/g).

Powder X-ray Diffraction (PXRD) and Rietveld Structure Refinement of 1 and 2. A D8-Advance Bruker AXS diffractometer with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$) operating at 25 °C was employed; Göbel mirror; Θ -2 Θ scan; $2\Theta = 7 - 60^\circ$; step size = 0.0142 (2Θ); scan speed = 10 second/step; position sensitive detector; α -Al $_2$ O $_3$ as external standard. The samples were filled (glove-box) into standard capillaries (0.7-mm diameter) and measured in Debye-Scherrer geometry. The phase purity was verified by the match search in the International Centre for Diffraction Data (ICDD, PDF-2 Release 2004) database and by comparison with original data on MIL-53(Al) provided by G. Férey et al.¹⁵ The pattern matching was carried out using the software PowderCell 2.4. with an interpolated background and refining the zero shift, peak shape parameters for the pseudo-Voigt function, and cell parameters.³⁵ Crystal data for **1** are as follows: space group *Imma* (no. 74), $a = 6.619(2)$, $b = 16.883(3)$, $c = 12.579(2)$ \AA , $Z = 4$, $V = 1405.6 \text{ \AA}^3$, $R_f/R_{fw} = 0.095/0.071$, GooF = 1.50. Initial positions of the Fc molecules were obtained by global optimisation in the direct space using parallel tempering algorithm of the FOX software starting from rigid “empty” MIL-53(Al) and Fc as building blocks.³⁶ The modelling of diffractograms of **1** using FOX was based on the assumption that the interactions between the guest molecules and the host MIL-53(Al) framework are weak. Herewith, the geometries of the individual molecules and framework remain relatively unchanged during the formation of the inclusion complex. In this case, FOX is particularly robust because individual molecules can be added as mathematical objects in the form of a Fenske–Hall Z-matrix, thus retaining their geometry for the optimisation algorithm. The Monte Carlo optimisation, in which the parameters of the Fc Z-matrix were fixed (i.e., the guest molecule was treated as a rigid body),^{15,25} was launched in FOX and the initial location of the crystallographically independent Fc complexes were found after nearly $2 \cdot 10^6$ movements (calculated R factor were about 0.30), whereas the atomic coordinates of MIL-53(Al) framework were fixed. Finally, the obtained model was refined by the Rietveld method with Jana2000 software.³⁷ For this refinement, bond distances and angle restrains for the host MIL-53(Al) and the guest Fc were taken from pure “host” and “guest” structures. Isotropic parameters values (U_{iso}) were fixed as 0.038 \AA^{-2} for all atoms. The next parameters were refined step by step: (i) zero shift, background’s function, profile (pseudo-Voigt function) and cell parameters; (ii) structural parameters of the “guest” molecules; (iii) structural parameters of the “host” framework; (iv) all parameters together to give the final R_p , R_{wp} , R_f , R_{fw} factors. [Additional references for PXRD and Rietveld. ³⁵ W. Kraus, G. Nolze, *J. Appl. Cryst.* **1996**, *29*, 301-303. ³⁶ V. Favre-Nicolin, R. Černý, *J. Appl. Cryst.*, **2002**, *35*, 734-743; <http://objcryst.sourceforge.net>. ³⁷ V. Petříček, M. Dušek, L. Palatinus, *Jana2000. The crystallographic computing system.* **2000**; <http://www-xray.fzu.cz/jana/Jana2000/jana.html>.]

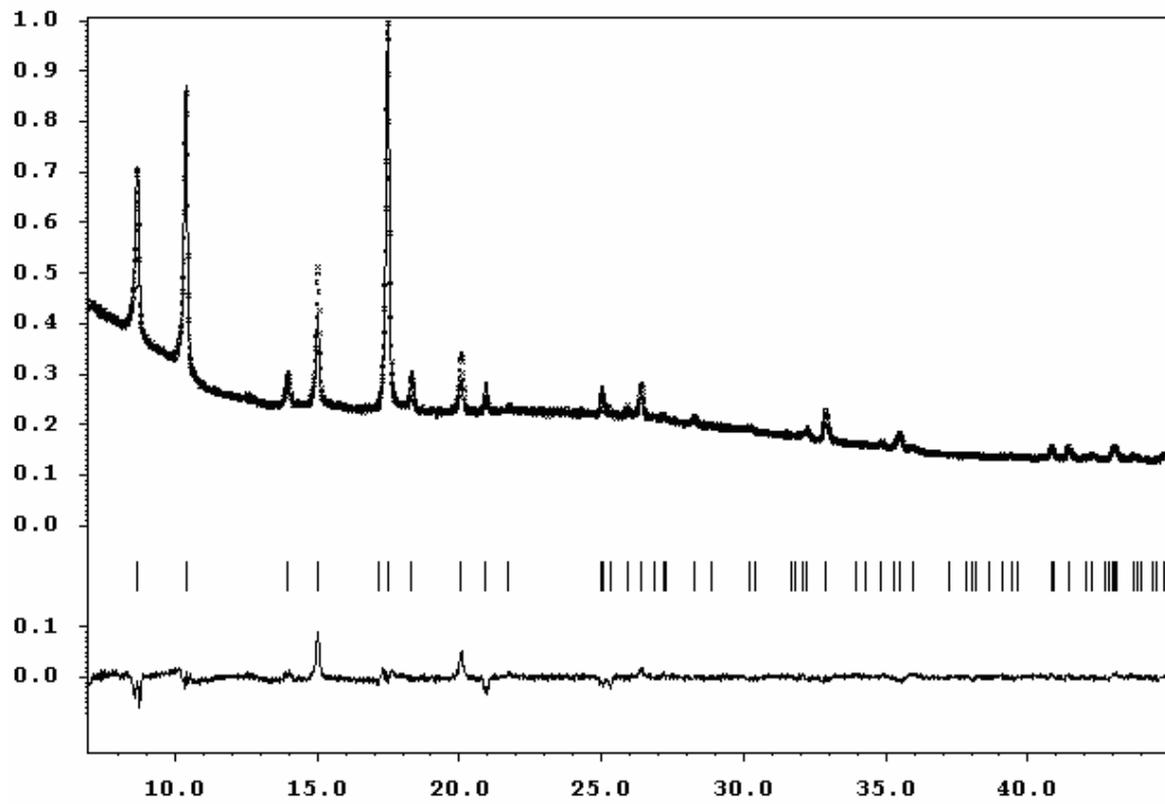


Figure 8S: Graphical plot of the final Rietveld refinement cycle for **1**.

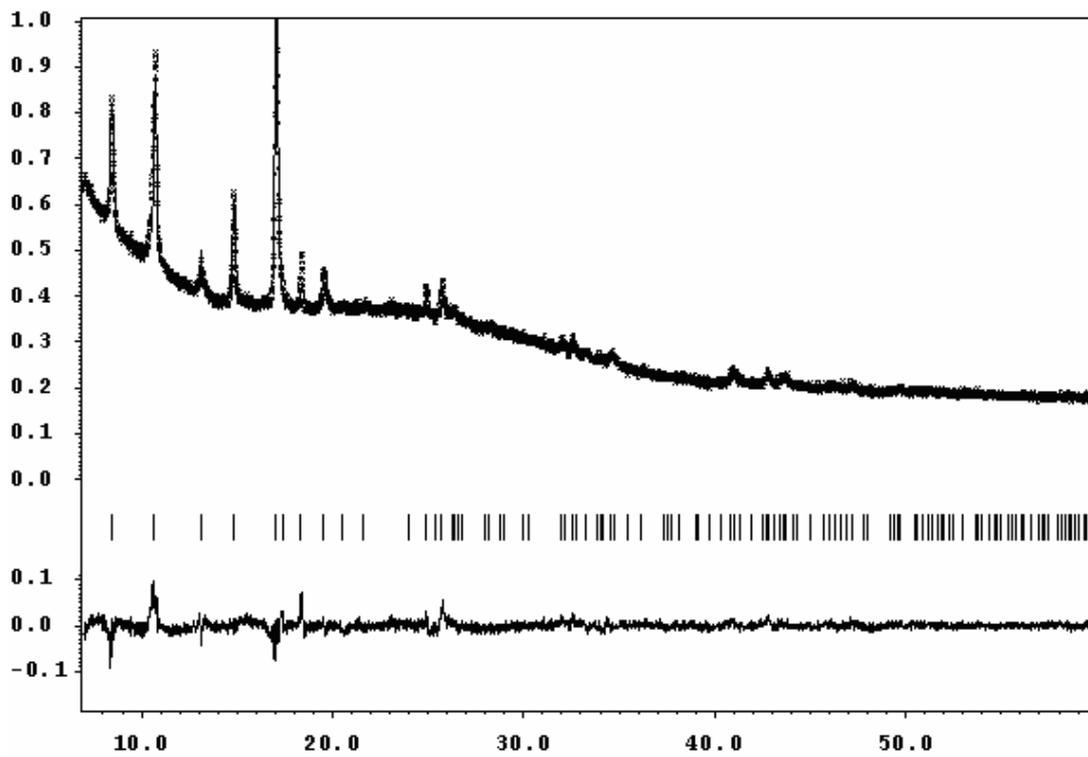


Figure 9S: Graphical plot of the final Rietveld refinement cycle for **2**.

Table 1S. Crystallographic data for **1** and **2**.

	0	1	2
	MIL-53Al_ht	Fc@MIL-53	FeA@MIL-53
Composition	AlO ₅ C ₈ H ₅	AlO ₅ C ₁₃ H ₁₀ Fe _{0.5}	AlO _{5.33} C _{11.67} H _{8.33} Fe _{0.33}
Colour	colourless	yellow	red
space group	Imma (No 74)	Imma (No 74)	Imma (No 74)
a (Å)	6.608(1)	6.619(2)	6.654(2)
b (Å)	16.675(3)	16.883(3)	16.448(3)
c (Å)	12.813(2)	12.579(2)	13.375(2)
V (Å ³)	1419.6	1405.6	1463.7
Z	4	4	4
data points, y _{i,0}	—	3728	3728
reflections	—	134	134
restraints	—	28	28
positional parameters	—	19	23
Profile parameters	—	8	8
R _p / R _{wp}	—	0.022 / 0.031	0.021 / 0.029
R _f / R _{fw}	—	0.095 / 0.071	0.082 / 0.068
goodness of fit	—	1.50	1.63
Fe—C	—	1.94	1.96
C—C	—	1.51	1.49

Table 2S. Atomic coordinates for **1**.

Atom	x/a	y/b	z/c	occupancy
Al1	0.25	0.25	0.75	1
O1	0	0.25	0.69297(13)	1
O2	0.15590(17)	0.16690(12)	0.84182(12)	1
C1	0	0.05987(19)	0.95711(15)	1
C2	0	0.12911(14)	0.88311(15)	1
C3	-0.1958(4)	0.0361(2)	0.97409(15)	1
Fe1	0.25	0.25	0.25	½
C4	0.080(10)	0.2934(13)	0.363(5)	½
C5	0.287(9)	0.3234(17)	0.365(2)	½
C6	0.425(11)	0.25	0.370(6)	½

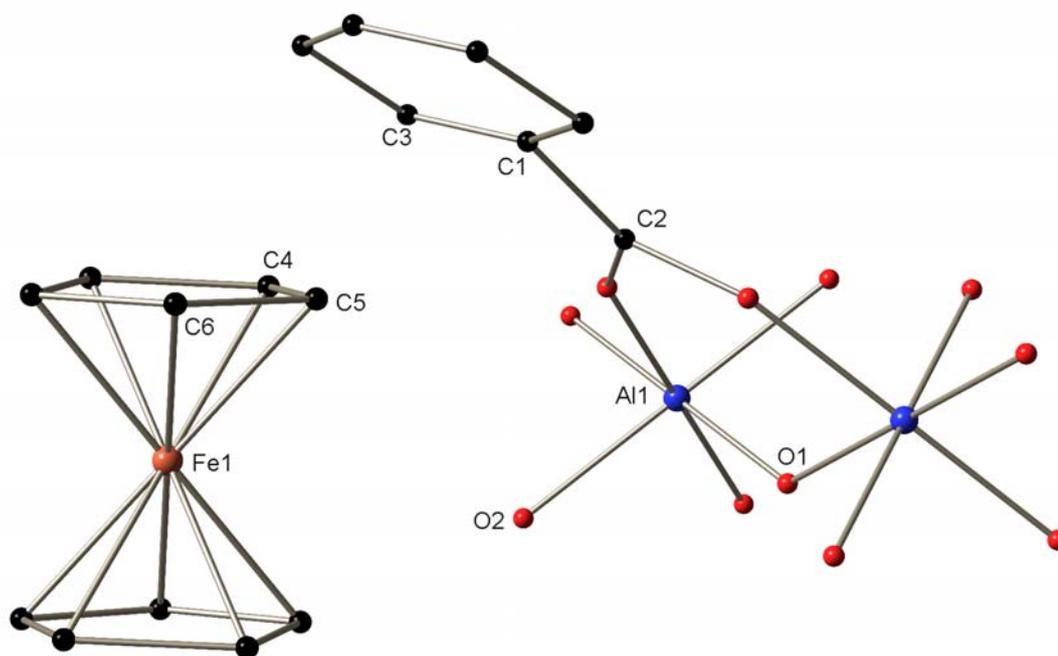
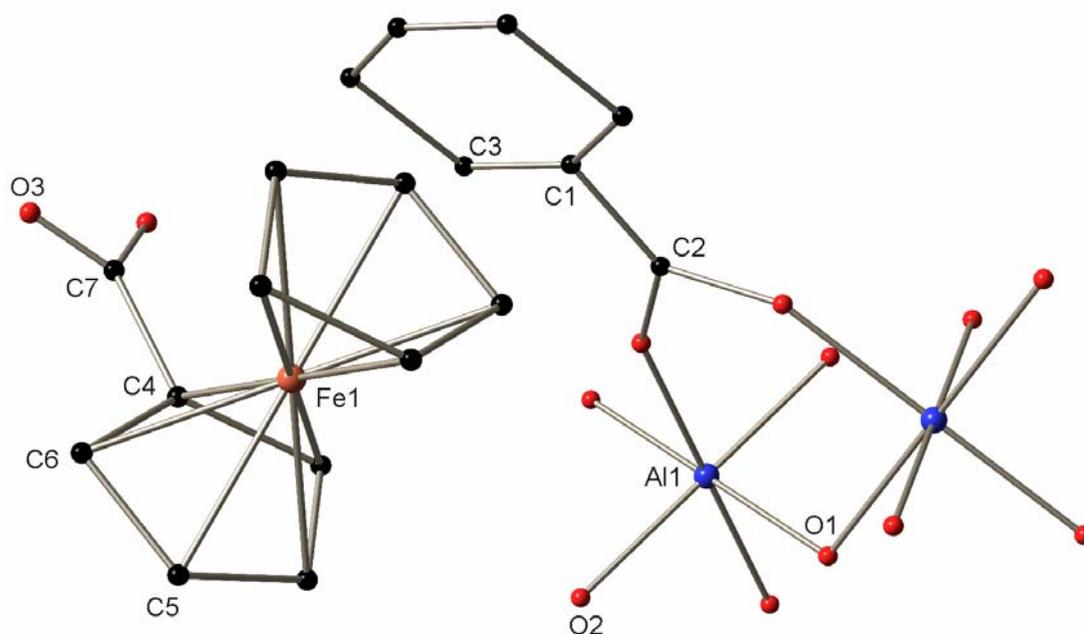
**Figure 10S:** Asymmetric unit and atom labelling scheme of **1**.

Table 3S. Atomic coordinates for **2**.

Atom	x/a	y/b	z/c	occupancy
Al1	0.25	0.25	0.75	1
O1	0	0.25	0.667(6)	1
O2	0.157(2)	0.1686(13)	0.8412(14)	1
C1	-0.178(6)	0.0426(12)	0.9702(9)	1
C2	0	0.0644(12)	0.9548(10)	1
C3	0	0.1307(12)	0.8827(14)	1
Fe1	0.25	0.25	0.25	1/3
C4	0.5	0.25	0.260(6)	1/3
C5	0.386(18)	0.2956(18)	0.124(5)	1/3
C6	0.454(8)	0.335(2)	0.212(6)	1/3
C7	0.623(12)	0.25	0.362(10)	1/6
O4	0.672(17)	0.208(3)	0.405(12)	1/12

**Figure 11S:** Asymmetric unit and atom labelling scheme of **2**.