Electronic Supplementary Material (ESI) for CrystEngComm.

- Supplementary Information -

Experimental Evidence of Negative Linear Compressibility in the MIL-53 Metal-Organic Framework Family

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Table S1.- The pressure dependent unit cell and structure refinement parameters of MIL-53(Al) using mineral oil as pressure-transmitting medium.

Pressure, GPa	**0**	**1**	**2.9**	**4.38**	**5.97**
Crystal System			Orthorhombic		
Space Group	*Imma*	*Imma*	*Imma*	*Pnma*	*Pnma*
a, Å	6.7(2)	6.69(8)	6.26(4)	5.90(6)	5.48(11)
b, Å	16.6(2)	16.5(6)	17.93(13)	16.1(2)	14.8(4)
c, Å	13.4(1)	13.2(3)	11.10(3)	10.48(6)	9.90(8)
α, (°)	90	90	90	90	90
V, Å^3	1491.2(2)	1461.1(1)	1246.1(2)	1013.1(8)	801.2(5)
2θ$_{interval}$ (°)	1.5–25	1.7–25	1.8–25	1.8–25	1.8–25
R$_p$^{i}, R$_{wp}$^{ii}	0.021, 0.026	0.050, 0.062	0.023, 0.029	0.027, 0.027	0.063, 0.069
R$_B$^{iii}	0.065	0.041	0.055	0.034	0.051

$^{i}\ R_P = \sum_i |y_{i,0} - y_{i,c}| / \sum_i |y_{i,0}|$; $^{ii}\ R_{wp} = \left[\sum_i w_i (y_{i,o} - y_{i,c})^2 / \sum_i w_i (y_{i,o})^2\right]^{1/2}$; $^{iii}\ R_B = \sum_n ||I_{n.o}| - |I_{n,c}|| / \sum_i |I_{n,o}|$

Table S2.- The pressure dependent unit cell and structure refinement parameters of MIL-53(Al) using ethanol as pressure-transmitting medium.

Pressure, GPa	**0**	**0.7**	**2.6**	**4.8**
Crystal System		Orthorhombic		
Space Group	*Imma*	*Imma*	*Imma*	*Pnma*
a, Å	6.751(7)	6.72(3)	6.32(4)	4.102(16)
b, Å	16.58(3)	17.30(9)	17.4(3)	12.02(6)
c, Å	14.91(3)	12.47(3)	11.73(12)	8.351(14)
α, (°)	90	90	90	90
V, Å^3	1669.5(5)	1450(11)	1288(27)	412(3)
2θ$_{interval}$ (°)	5–50	1.7–25	1.7–25	1.7–25
R$_p$^{i}, R$_{wp}$^{ii}	0.035, 0.042	0.045, 0.066	0.041, 0.069	0.027, 0.034
R$_B$^{iii}	0.020	0.014	0.016	0.012

$^{i}\ R_P = \sum_i |y_{i,0} - y_{i,c}| / \sum_i |y_{i,0}|$; $^{ii}\ R_{wp} = \left[\sum_i w_i (y_{i,o} - y_{i,c})^2 / \sum_i w_i (y_{i,o})^2\right]^{1/2}$; $^{iii}\ R_B = \sum_n ||I_{n.o}| - |I_{n,c}|| / \sum_i |I_{n,o}|$

Table S3.- The pressure dependent unit cell and structure refinement parameters of NH_2-MIL-53(Al) using mineral oil as pressure-transmitting medium.

Pressure, GPa	**0**	**0.59**	**1.61**	**2.37**	**4.38**	**7.02**	**11.26**
Crystal System				Orthorhombic			
Space Group	*Imma*	*Imma*	*Imma*	*Imma*	*Imma*	*Imma*	*Imma*
a, Å	6.9(8)	6.4(8)	5.8(3)	6.7(3)	6.4(9)	6.3(8)	6.3(3)
b, Å	16.0(6)	16.6(6)	16.7(8)	15.7(9)	15.1(6)	14.7(5)	14.4(4)
c, Å	13.0(3)	12.2(3)	11.4(4)	10.8(4)	10.7(2)	10.5(2)	10.1(3)
α, (°)	90	90	90	90	90	90	90
V, Å^3	1433(8)	1291(7)	1117(5)	1044(2)	1022(5)	962(3)	914(4)
2θ$_{interval}$ (°)	1.7–25	1.7–25	1.7–25	1.7–25	1.7–25	1.7–25	1.7–25
R_p^{i}, R_{wp}^{ii}	0.038, 0.043	0.077, 0.101	0.078, 0.089	0.074, 0.084	0.025, 0.028	0.041, 0.049	0.067, 0.079
R_B^{iii}	0.033	0.085	0.096	0.076	0.080	0.058	0.034

$^{i}\ R_P = \sum_i |y_{i,0} - y_{i,c}| / \sum_i |y_{i,0}|$; $^{ii}\ R_{wp} = \left[\sum_i w_i (y_{i,o} - y_{i,c})^2 / \sum_i w_i (y_{i,o})^2\right]^{1/2}$; $^{iii}\ R_B = \sum_n ||I_{n.o}| - |I_{n,c}|| / \sum_i |I_{n,o}|$

Table S4.- The pressure dependent unit cell and structure refinement parameters of NH_2-MIL-53(Al) using ethanol as pressure-transmitting medium.

Pressure, GPa	**0**	**0.57**	**3.05**	**4.06**	**5.59**	**8.32**
Crystal System				Orthorhombic		
Space Group	*Imma*	*Imma*	*Imma*	*Imma*	*Imma*	*Imma*
a, Å	6.653(8)	6.66(9)	6.41(6)	6.42(7)	6.58(3)	6.6(2)
b, Å	16.515(12)	16.21(7)	16.08(9)	16.03(1)	15.55(17)	17.0(2)
c, Å	14.178(10)	13.72(6)	13.91(7)	13.89(9)	13.67(4)	12.0(6)
α, (°)	90	90	90	90	90	90
V, Å^3	1558(3)	1481(16)	1434(7)	1430(2)	1398(4)	1343(8)
2θ$_{interval}$ (°)		1.7–25.6	2.0–25.6	2.0–25.6	2.0–25.6	2.0–25.6
R_p^{i}, R_{wp}^{ii}	0.035, 0.042	0.024, 0.033	0.021, 0.027	0.027, 0.032	0.026, 0.033	0.020, 0.032
R_B^{iii}	0.056	0.046	0.032	0.050	0.065	0.064

$^{i}\ R_P = \sum_i |y_{i,0} - y_{i,c}| / \sum_i |y_{i,0}|$; $^{ii}\ R_{wp} = \left[\sum_i w_i (y_{i,o} - y_{i,c})^2 / \sum_i w_i (y_{i,o})^2\right]^{1/2}$; $^{iii}\ R_B = \sum_n ||I_{n.o}| - |I_{n,c}|| / \sum_i |I_{n,o}|$

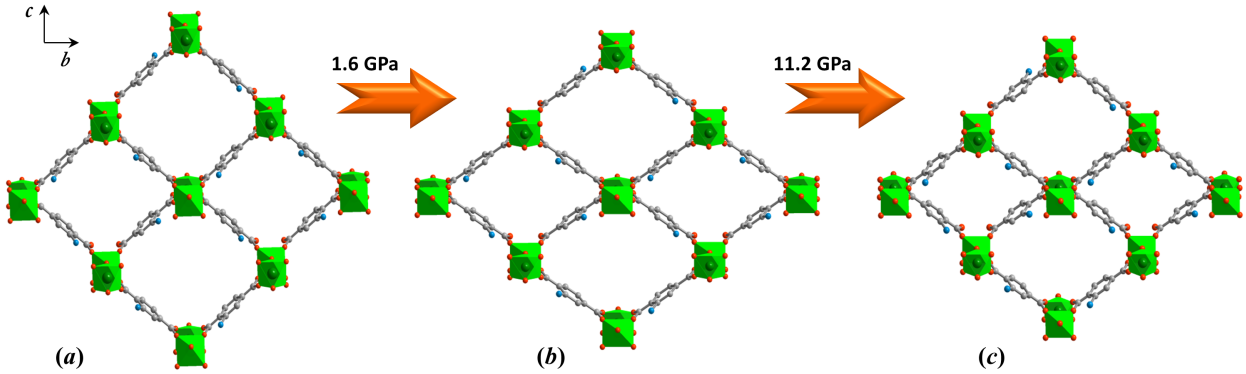

Figure S1.- The structural changes of NH_2-MIL-53(Al) being exposed to 0 GPa (*a*), 1.6 GPa (*b*) and 11.6 GPa (*c*) using mineral oil as pressurization medium.

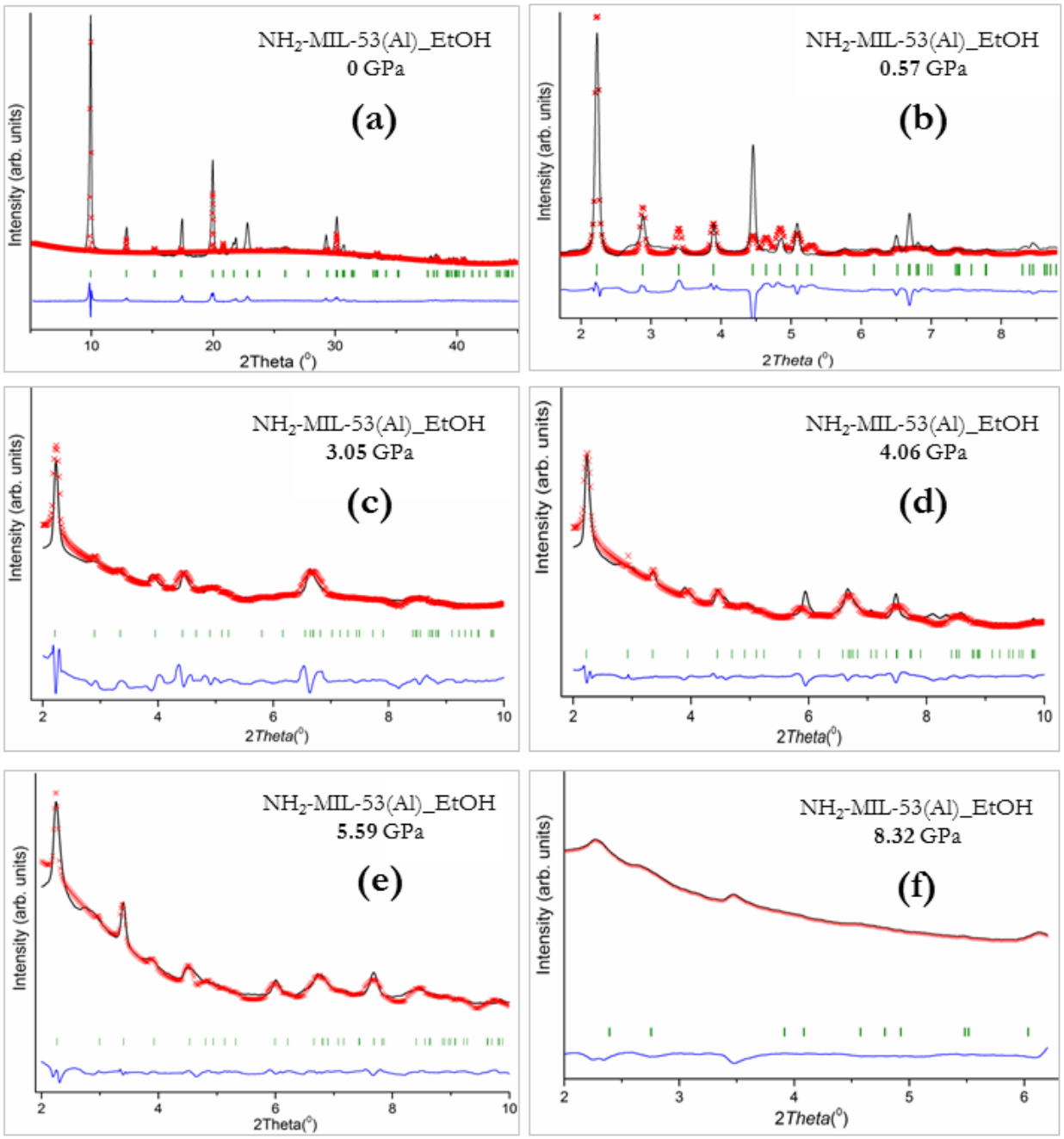

Figure S2.- Rietveld refinement plots for NH_2-MIL-53(Al) using ethanol as pressurization medium at 0 GPa (*a*), 0.57 GPa (*b*), 3.05 GPa (*c*), 4.06 GPa (*d*), 5.59 GPa (*e*) and 8.32 GPa (*f*). The experimental data are presented as a black solid line, calculated one by red crosses and difference between them as a blue solid line. The Bragg positions of the peaks are represented as green sticks.

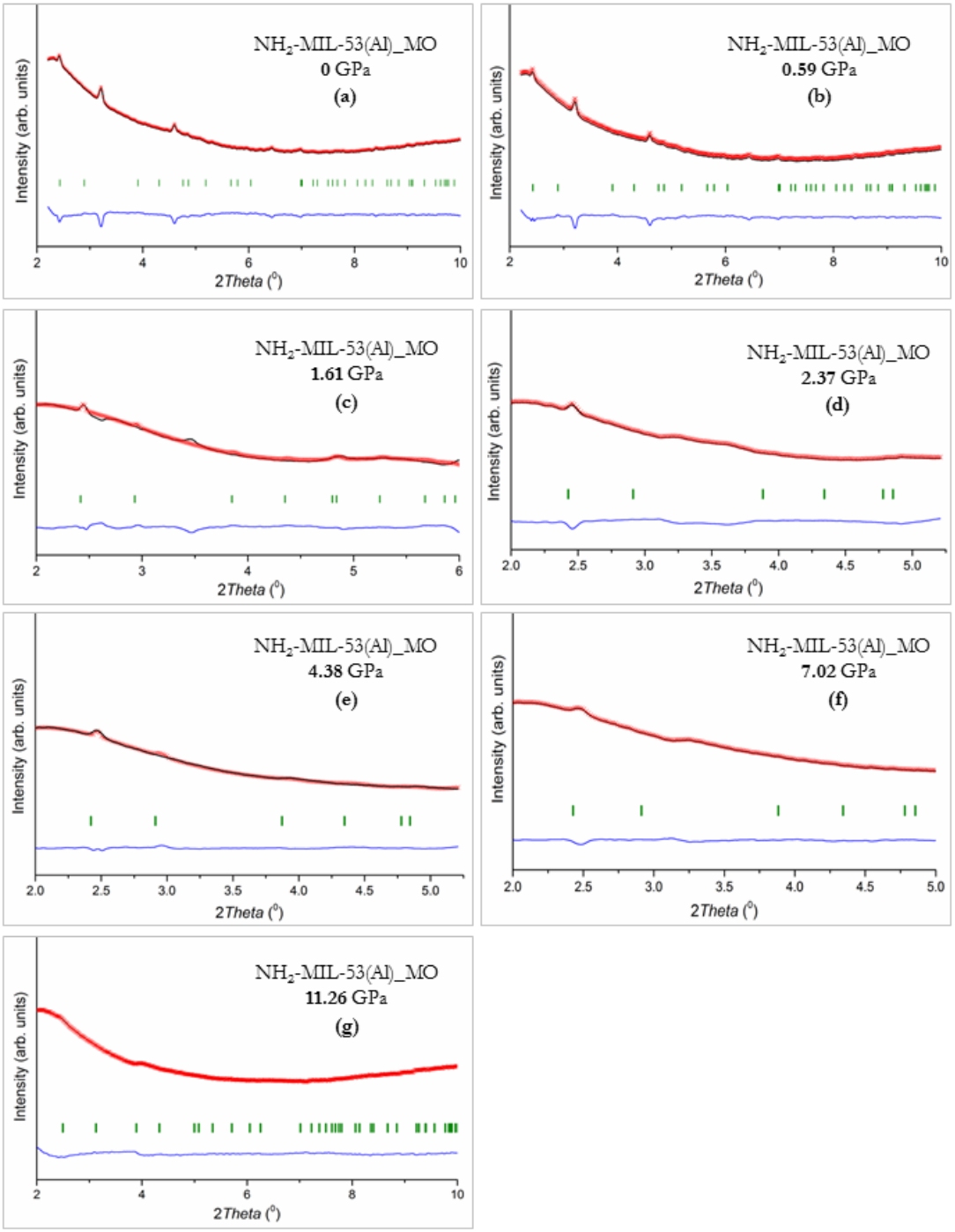

Figure S3.- Rietveld refinement plots for NH_2-MIL-53(Al) using mineral oil as pressurization medium at 0 GPa (*a*), 0.59 GPa (*b*), 1.61 GPa (*c*), 2.37 GPa (*d*), 4.38 GPa (*e*), 7.02 GPa (*f*) and 11.26 GPa (*g*). The experimental data are presented as a black solid line, calculated one by red crosses and difference between them as a blue solid line. The Bragg positions of the peaks are represented as green sticks.

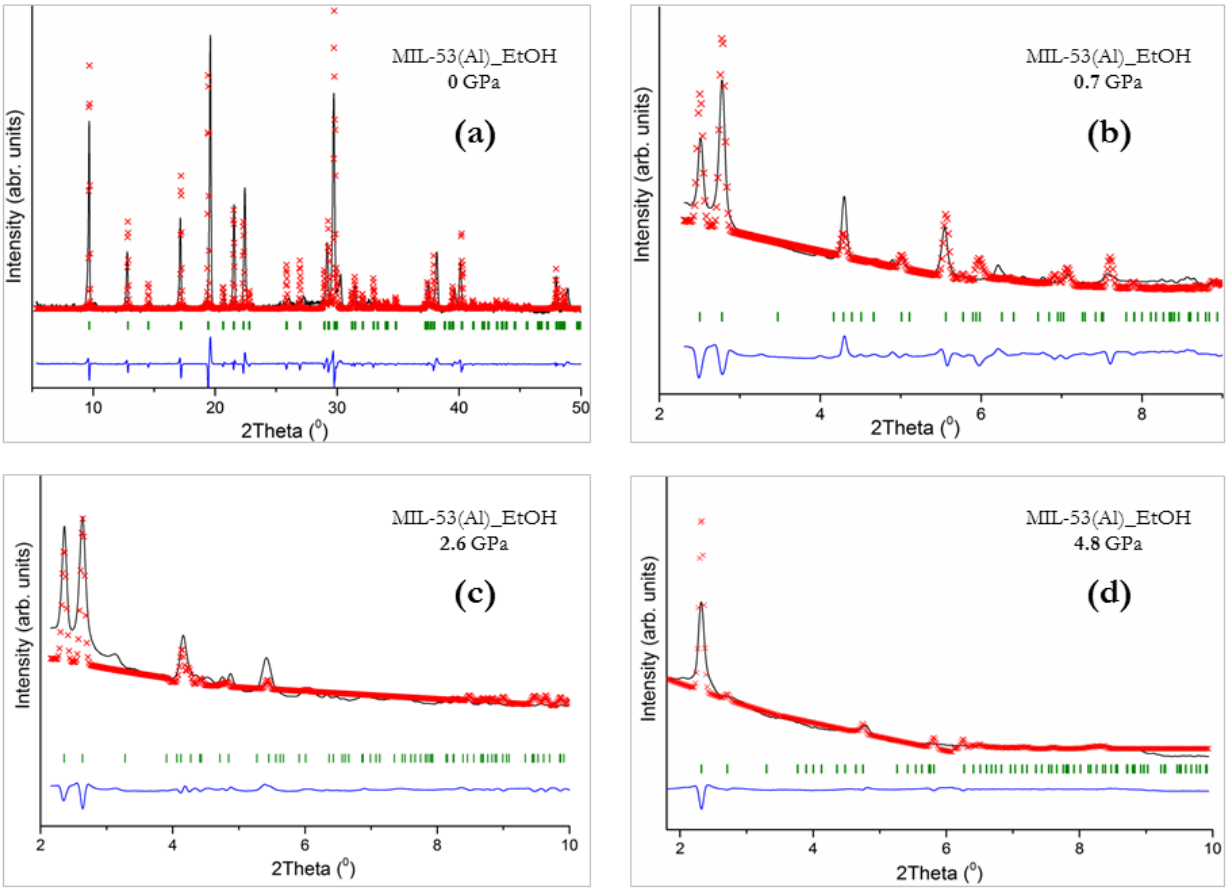

Figure S4.- Rietveld refinement plots for MIL-53(Al) using ethanol as pressurization medium at 0 GPa (*a*), 0.7 GPa (*b*), 2.6 GPa (*c*) and 4.8 GPa (*d*). The experimental data are presented as a black solid line, calculated one by red crosses and difference between them as a blue solid line. The Bragg positions of the peaks are represented as green sticks.

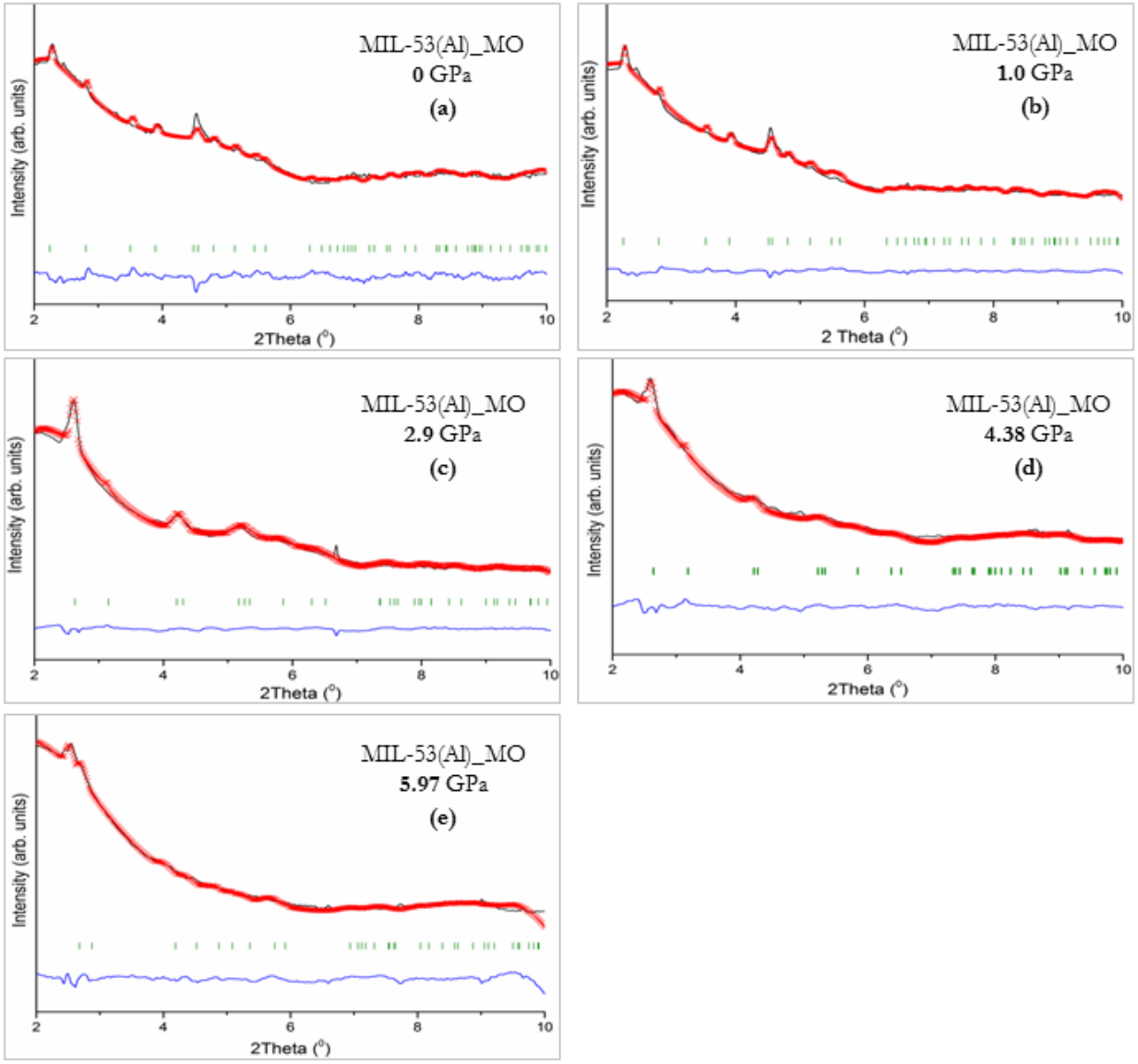

Figure S5.- Rietveld refinement plots for MIL-53(Al) using mineral oil as pressurization medium at 0 GPa (*a*), 1.0 GPa (*b*), 2.9 GPa (*c*), 4.38 GPa (*d*) and 5.97 GPa (*e*). The experimental data are presented as a black solid line, calculated one by red crosses and difference between them as a blue solid line. The Bragg positions of the peaks are represented as green sticks.