Supporting Information for

Exploiting Synthetic Conditions to Promote Structural Diversity within the Scandium(III) / Pyrimidine-4,6-dicarboxylate System

Javier Cepeda,[a,b] Sonia Pérez-Yáñez,[a] Garikoitz Beobide,[a] Oscar Castillo,[a]* Antonio Luque,[a] Paul A. Wright,[c] Scott Sneddon,[c] and Sharon E. Ashbrook[c]*

[a]Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, E–48080 Bilbao, Spain. [b]Departamento de Ciencia y Tecnología de Polímeros, Facultad de Ciencias Químicas, Universidad del País Vasco, UPV/EHU. [c]EaStCHEM School of Chemistry, University of St Andrews, Purdie Building, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom.

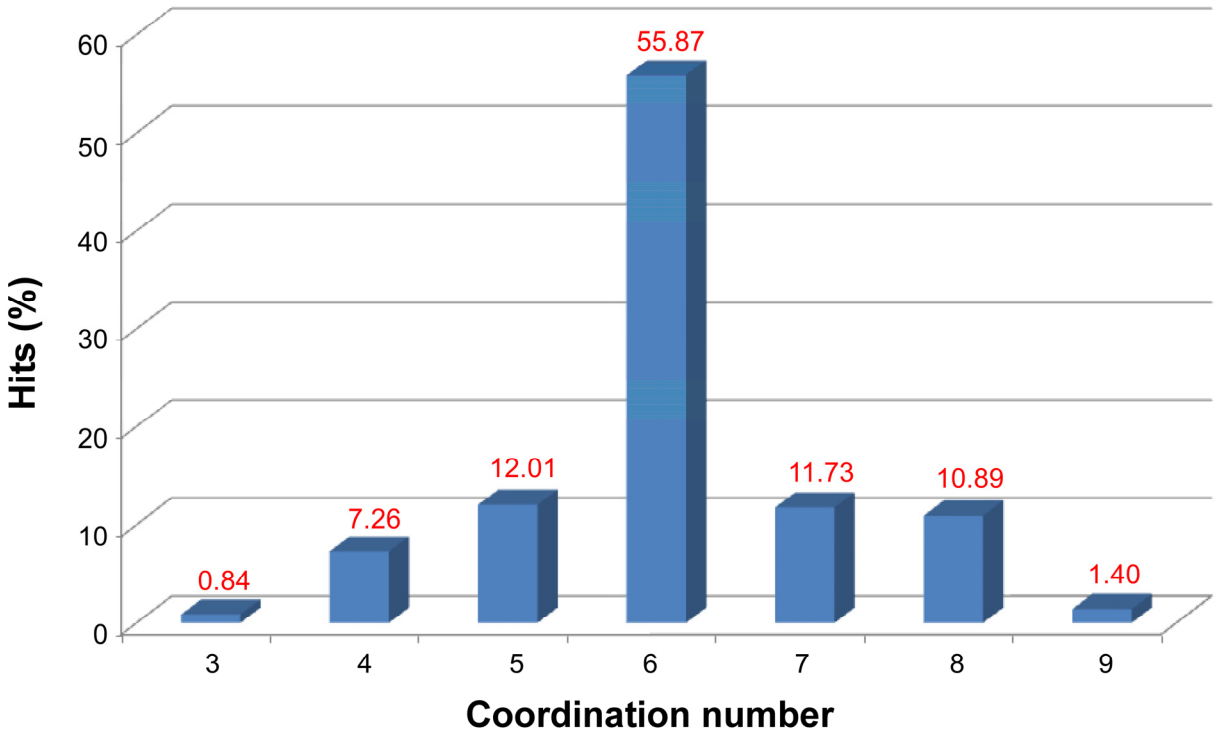
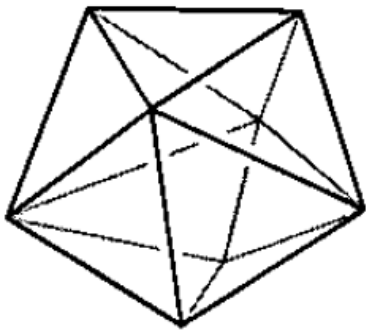
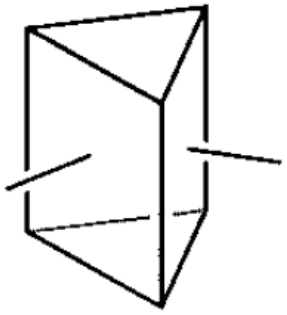


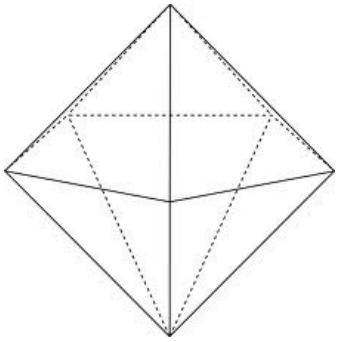
Figure S1. Coordination numbers of Sc(III) atom according to coordination compounds registered in CSD database (obtained from a total number of 358 hits).



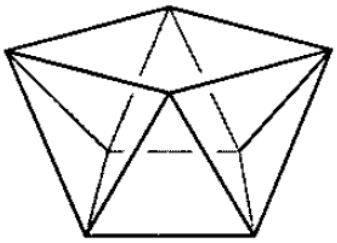
DD / Triangular dodecahedron



SBTP / Spherical biaugmented trigonal prism



PBPY / Pentagonal bipyramid



SAPR / Square antriprism

Figure S2. Ideal shapes found for the reported Sc^{III} compounds (abbreviation / full name).

Table S1. Hydrogen bonding interactions (Å, º) in compound **1**.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
O1w–H11w···O182a	0.86	1.89	2.735(2)	170.5
O1w–H12w···O4wb	0.86	1.82	2.675(2)	172.4
O2w–H21w···O5wc	0.85	1.82	2.660(2)	168.7
O2w–H22w···O5wd	0.87	1.88	2.716(2)	159.0
O3w–H31w···O182e	0.91	1.91	2.724(2)	147.6
O3w–H32w···O21	0.89	1.95	2.784(2)	155.7
O4w–H41w···O3wg	0.85	1.96	2.805(2)	170.5
O4w–H42w···O172d	0.86	2.01	2.853(2)	167.7
O5w–H51w···O3w	0.85	1.84	2.673(2)	167.6
O5w–H52w···O23	0.87	1.93	2.774(2)	162.4

[a] Symmetry codes: (a) –x + 1, –y, –z; (b) x, –y, z – 1/2; (c) x, –y + 1, z – 1/2; (d) –x + 1, y, –z + 1/2; (e) x, y + 1, z; (f) –x + 3/2, –y + 1/2, –z + 1. [b] D: donor. A: acceptor.

Table S2. Hydrogen bonding interactions (Å, º) in compound **2**.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
O1w–H11w···O182a	0.86	1.91	2.755(2)	166.3
O1w–H12w···O171b	0.86	1.92	2.769(2)	174.6
O2w–H21w···O172a	0.85	1.85	2.692(2)	171.0
O2w–H22w···O182c	0.88	1.92	2.759(2)	160.1

[a] Symmetry codes: (a) x, –y + 1/2, z – 1/2; (b) –x + 1, –y, –z + 1; (c) –x + 1, –y + 1, –z + 1. [b] D: donor. A: acceptor.

Table S3. Selected bond lengths for compound **3**.[a]

Sc1–O11	2.244(6)	Sc1–O14	2.336(7)
Sc1–O11a	2.244(6)	Sc1–O14a	2.336(7)
Sc1–O11b	2.244(6)	Sc1–O14b	2.336(7)
Sc1–O11c	2.244(6)	Sc1–O14c	2.336(7)

[a] Symmetries: (a) –x - 1, –y, z; (b) x – y, –y, –z; (c) –x + y – 1, y, –z.

Table S4. Selected bond lengths for compound **4**.[a]

Sc1–O11	2.077(1)	K2–O13	2.677(1)
Sc1–O11a	2.077(1)	K2–O13f	2.677(1)
Sc1–O21b	2.093(1)	K2–O23	2.668(1)
Sc1–O21c	2.093(1)	K2–O23f	2.668(1)
Sc1–O31d	2.094(1)	K2–O33	2.702(1)
Sc1–O31e	2.094(1)	K2–O33f	2.702(1)

[a] Symmetries: (a) –x + 4, –y, –z + 1; (b) x, y + 1, z; (c) –x + 4, –y – 1, –z + 1; (d) x + 1/2, –y – 1/2, z – 1/2; (e) –x + 7/2, y + 1/2, –z + 3/2; (f) –x + 3, –y – 1, –z + 1.

FTIR analysis

Spectra of **1**, **2**, and **5** share many similarities as a result of the coordination of the pmdc ligand. The characteristic bands could be assigned for these compounds except for **1**, given the simultaneous presence of oxalate ligand whose bands are overlapped. The remaining spectra exhibit a broad and intense band around 3530 cm^{-1} that corresponds to the vibration of the O–H bond of free water, followed by weak bands between 3215 and 3085 cm^{-1} corresponding to the C–H vibrations of the pyrimidinic ring of the pmdc. The intense vibrations in the 1670–1520 cm^{-1} region are attributed to both the asymmetric stretching vibrations of the carboxylate groups and the aromatic C–C and C–N bonds, while the symmetric stretching vibrations of the carboxylate groups appear in the lower range of 1405–1285 cm^{-1}. At lower frequencies, the remaining bands are attributed to the distortions originated in the aromatic ring and the carboxylate groups of the pmdc ligand. The vibration bands of the M–O and M–N bonds are observed below 530 cm^{-1}.

Concerning the spectra of **3** and **4**, they show typical vibration bands corresponding to oxalate and formate ligands. In particular, spectrum of **3** shows the presence of a broad and strong band at 1630 cm^{-1} for asymmetric stretching vibration, and narrower bands at 1350 and 1330 cm^{-1} for the symmetric vibration. In compound **4** these bands are at 1605 cm^{-1}, and 1385 and 1375 cm^{-1}, respectively. On the other hand, weak peaks around 3405 and 3110 cm^{-1} are observable, which have been assigned to N–H vibrations of ammonium cations; whereas tetramethylammonium cations generate weak C–H vibrations at 3100, 3030, and 2900 cm^{-1}.

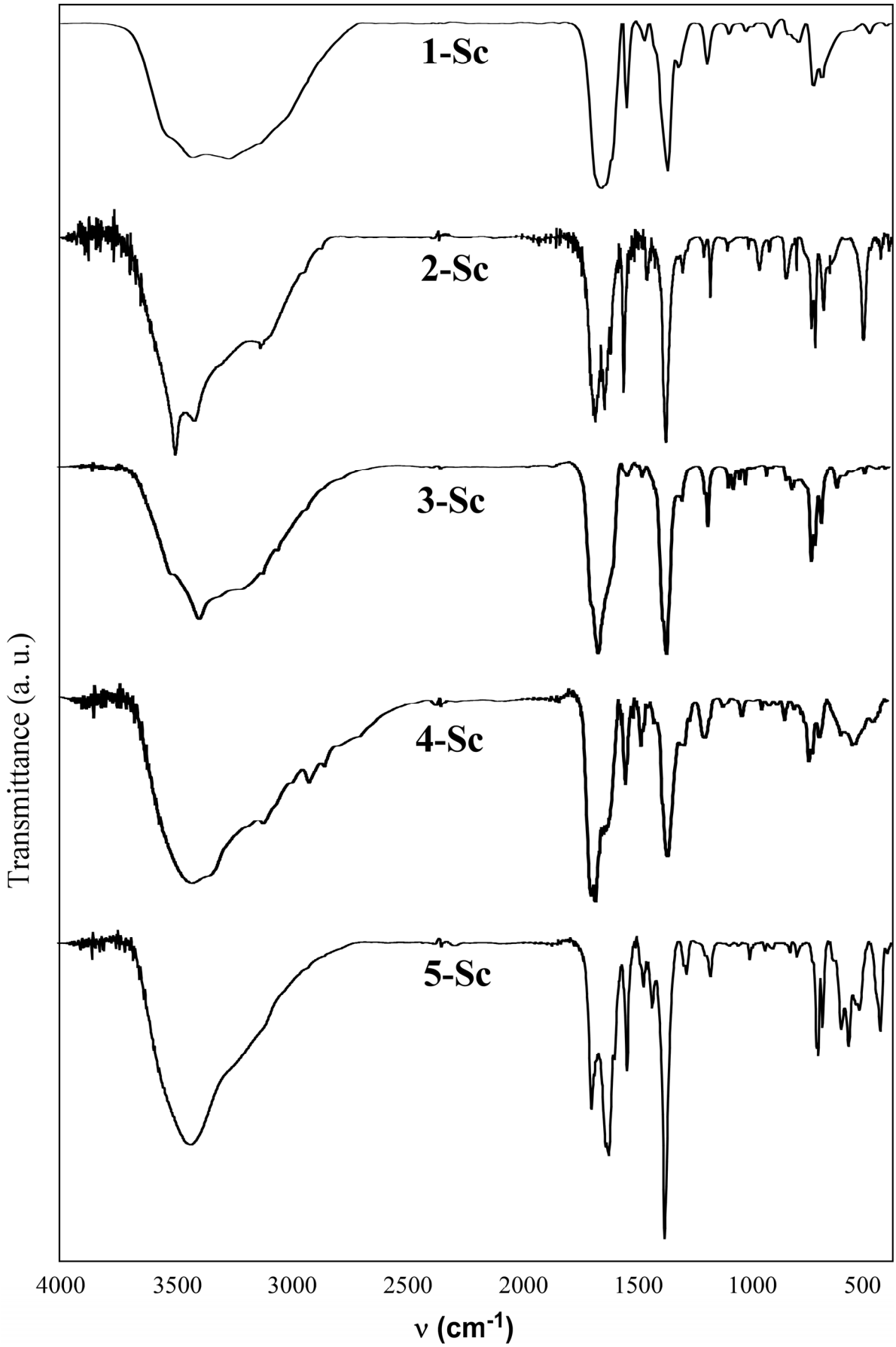


Figure S3. FTIR spectra of all compounds.

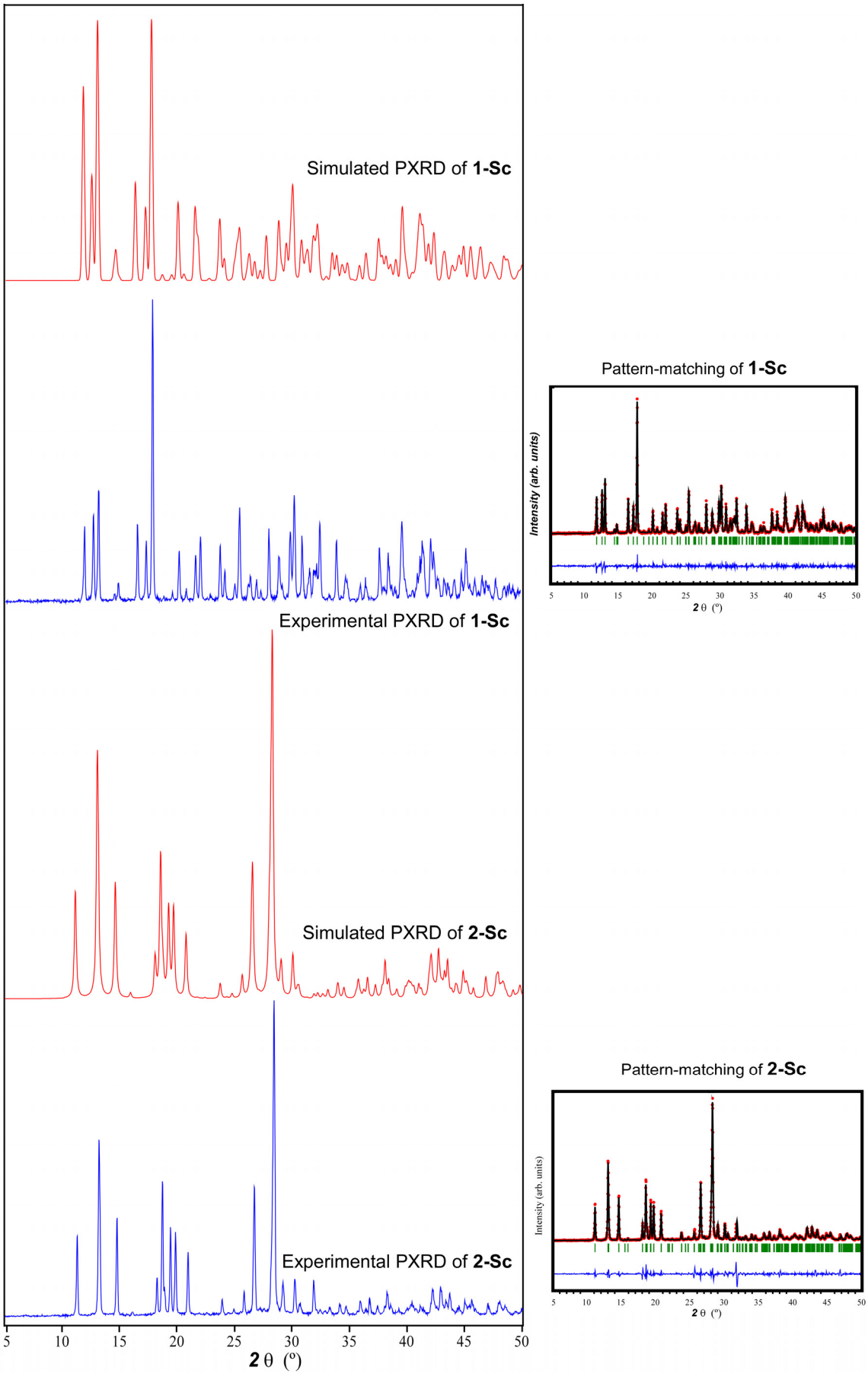


Figure S4. PXRD data and pattern-matching analysis of **1-Sc** and **2-Sc** compounds.

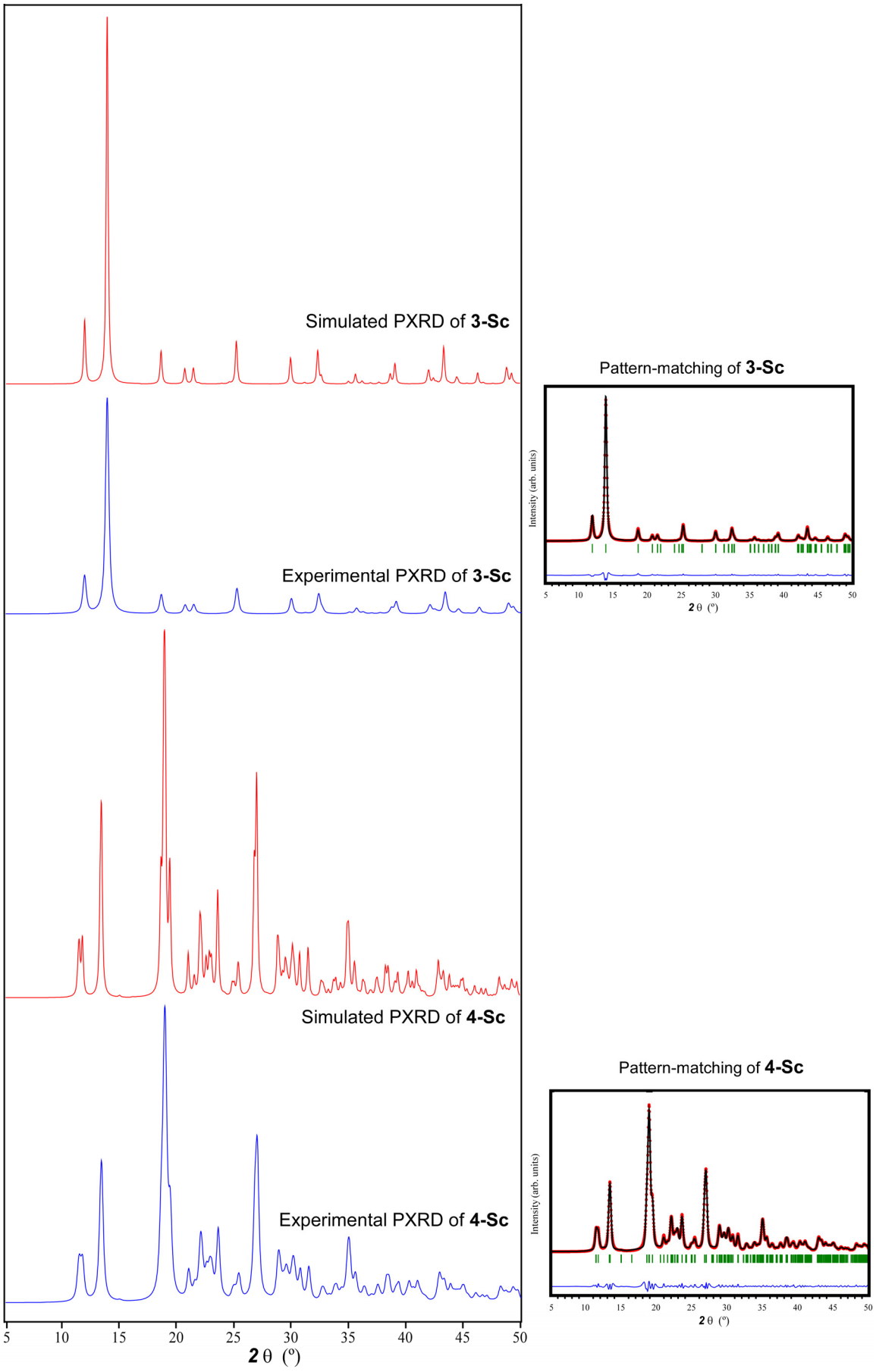
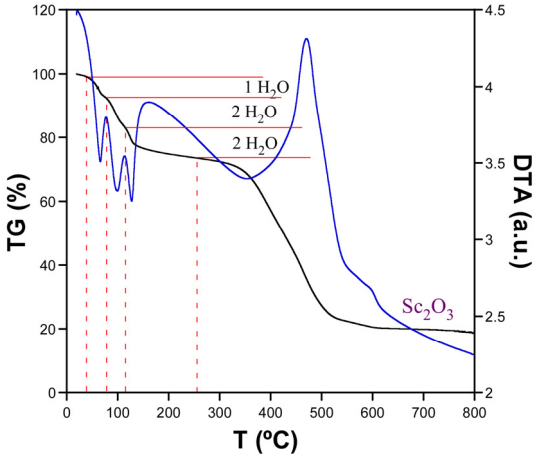


Figure S5. PXRD data and pattern-matching analysis of **3-Sc** and **4-Sc** compounds.

Table S5. Elemental analysis and TG/DTA curves for compound **1**.

$C_7H_{12}N_2O_{11}Sc$		
Ti–Tf	**ΣΔm(%)**	**ΣΔm(%)$_{teor}$**
30–77	5.4	5.2 (–1H_2O)
77–114	16.1	15.5 (–2H_2O)
114–250	25.8	25.8 (–2H_2O)
315–620	79.9	80.2 (Sc_2O_3)



Elemental analysis

Anal. Calc.: C, 24.35; H, 3.48; N, 8.11; Sc, 13.04%.

Found: C, 24.14; H, 3.65; N, 8.03; Sc, 13.26%.

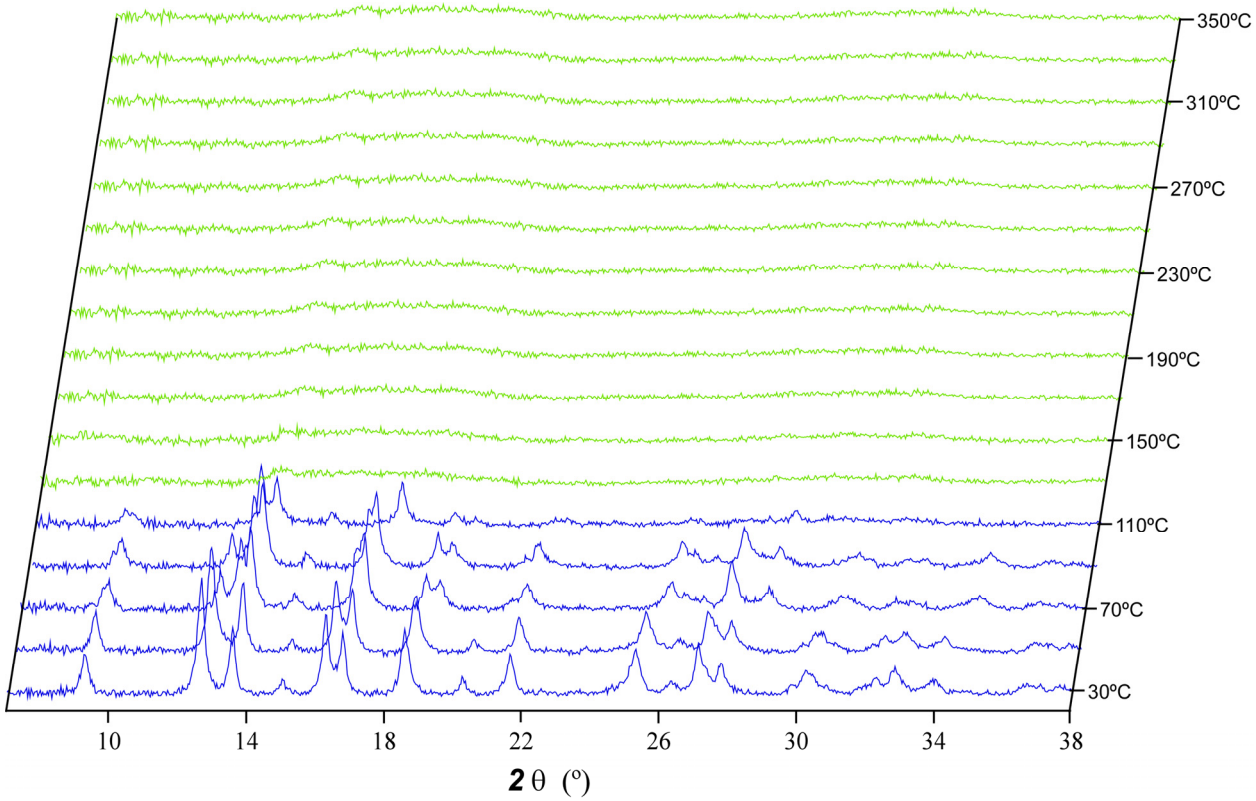


Figure S6. Thermodiffractometric data for compound **1**.

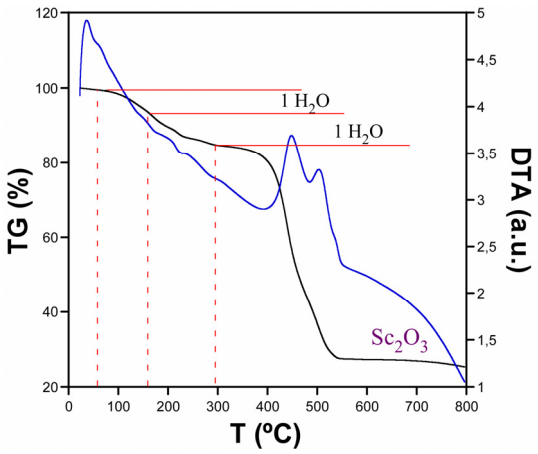
Table S6. Elemental analysis and TG/DTA curves for compound **2**.

$C_6H_7N_2O_7Sc$		
Ti–Tf	**ΣΔm(%)**	**ΣΔm(%)$_{teor}$**
70–165	7.3	7.1 (–1H_2O)
165–300	15.1	14.2 (–1H_2O)
390–560	72.9	72.9 (Sc_2O_3)

Elemental analysis

Anal. Calc.: C, 27.27; H, 2.65; N, 10.61; Sc, 17.05%.

Found: C, 26.98; H, 2.75; N, 10.03; Sc, 17.14%.



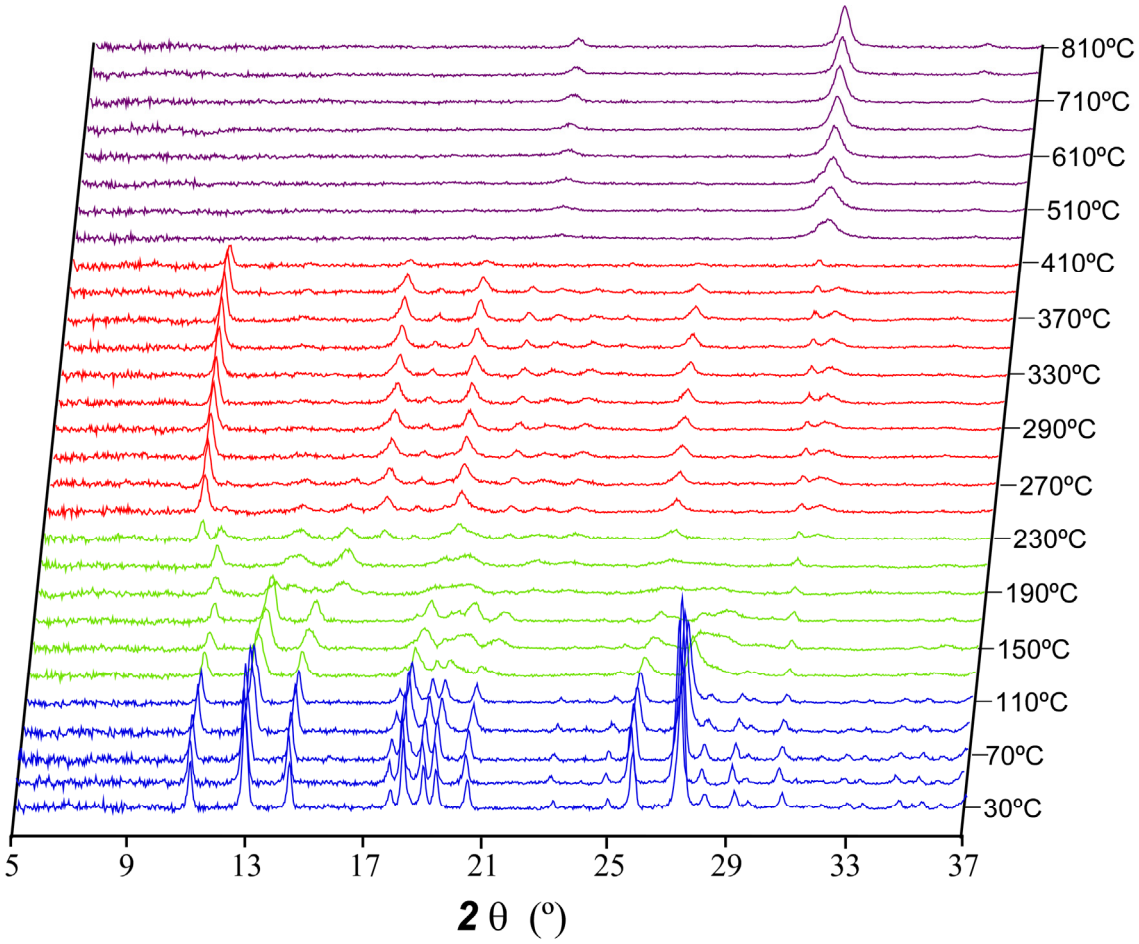


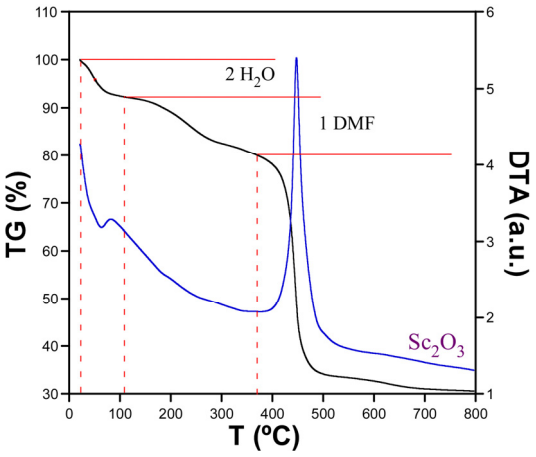
Figure S7. Variable temperature PXRD data for compound **2**.

Table S7. Elemental analysis and TG/DTA curves for compound **5**.

$C_9H_{16}ClN_3O_{10}Sc_2$		
Ti–Tf	**ΣΔm(%)**	**ΣΔm(%)$_{teor}$**
30–85	7.6	8.0 (–2H_2O)
85–380	22.8	24.1 (–1DMF)
380–680	69.2	69.4 (Sc_2O_3)

Elemental analysis

Anal. Calc.: C, 23.95; H, 3.55; Cl, 7.76; N, 9.31; Sc, 19.96%. Found: C, 23.88; H, 3.75; Cl, 7.58; N, 9.13; Sc, 20.14%.



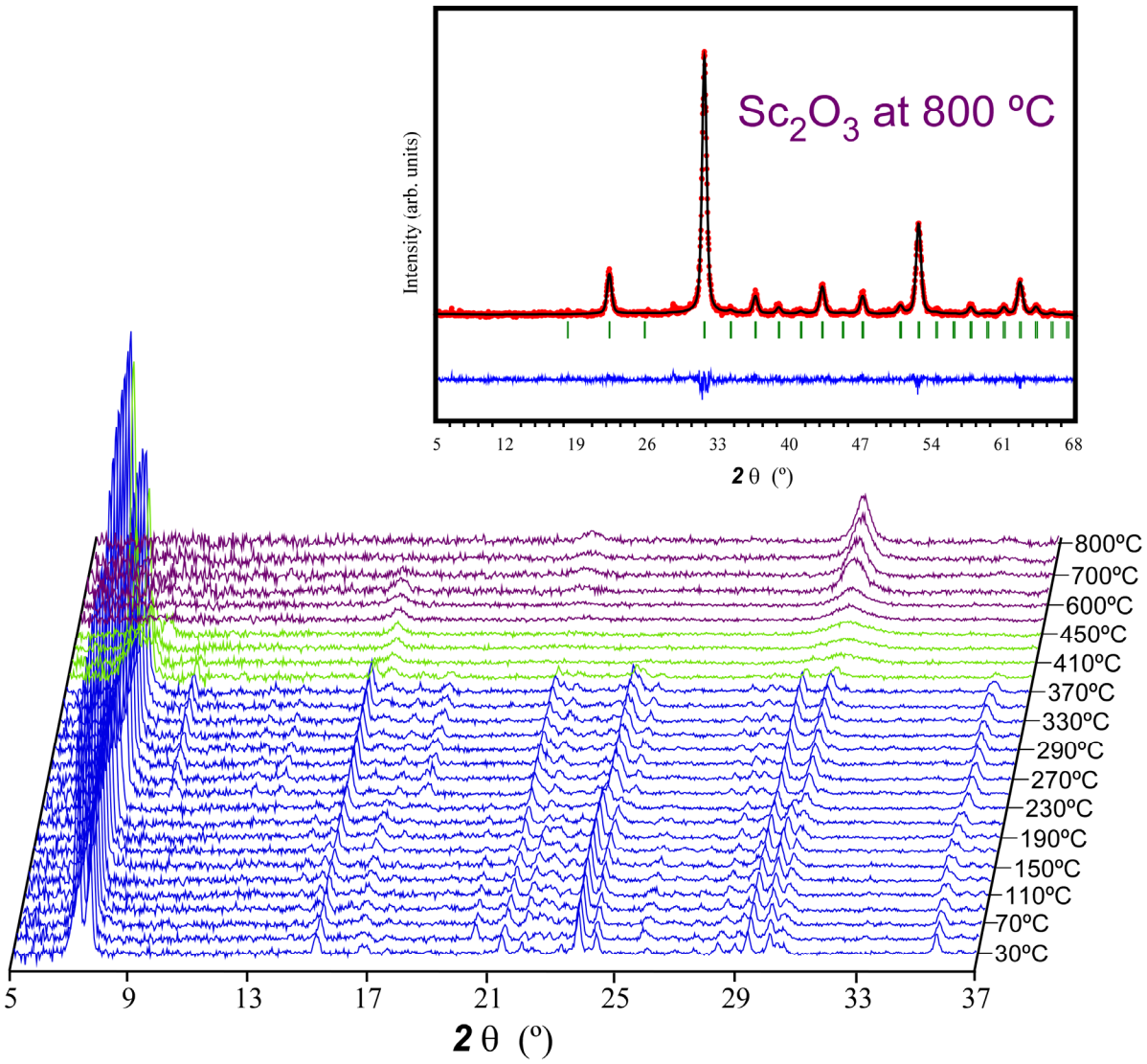


Figure S8. Variable temperature PXRD data and pattern-matching of Sc_2O_3 obtained at 800 ºC for compound **5**.

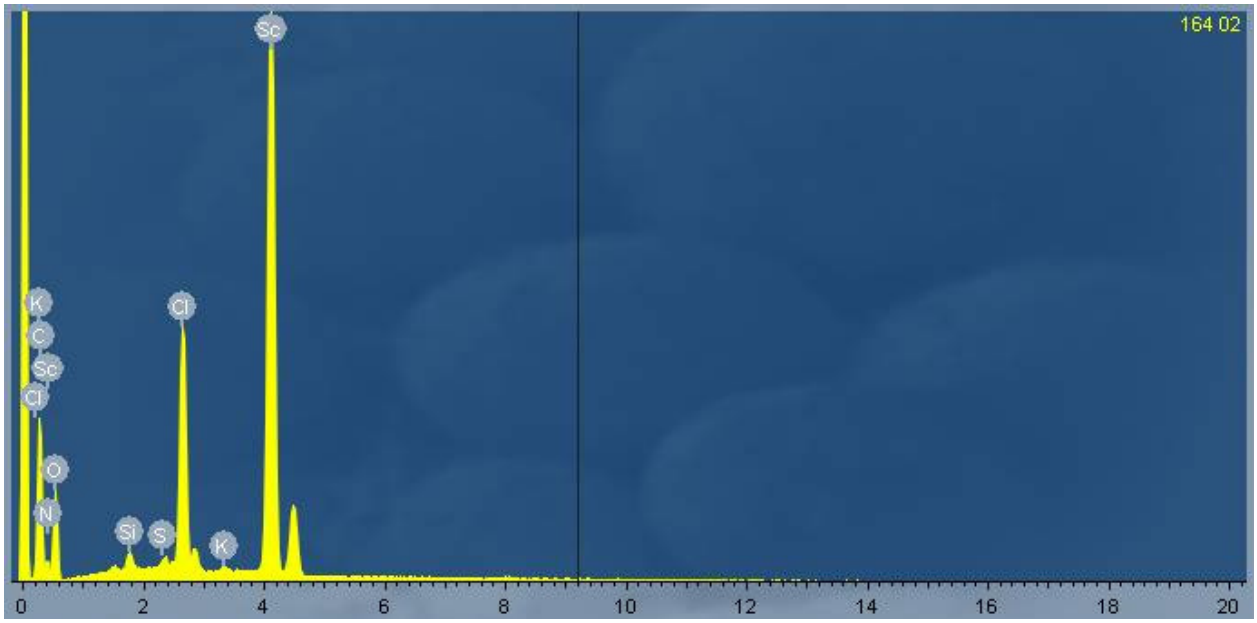


Figure S9. EDX analysis over compound **5**.

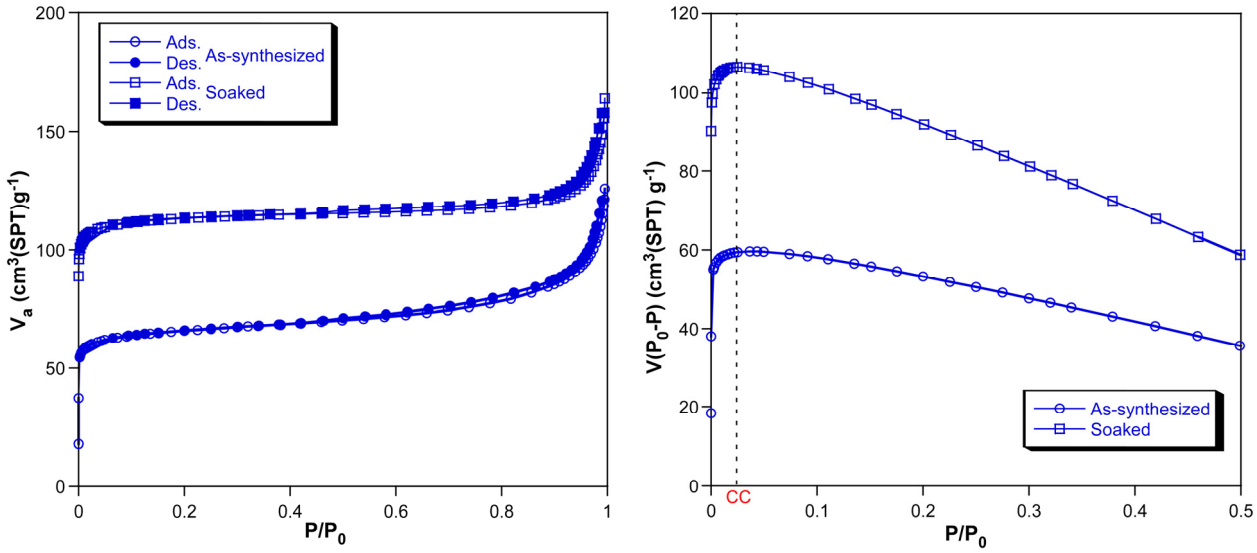


Figure S10. (a) Adsorption (open) and desorption (filled) curves for as-synthesized (o) and methanol soaked (□) **5** samples. **(b)** Consistency plot.

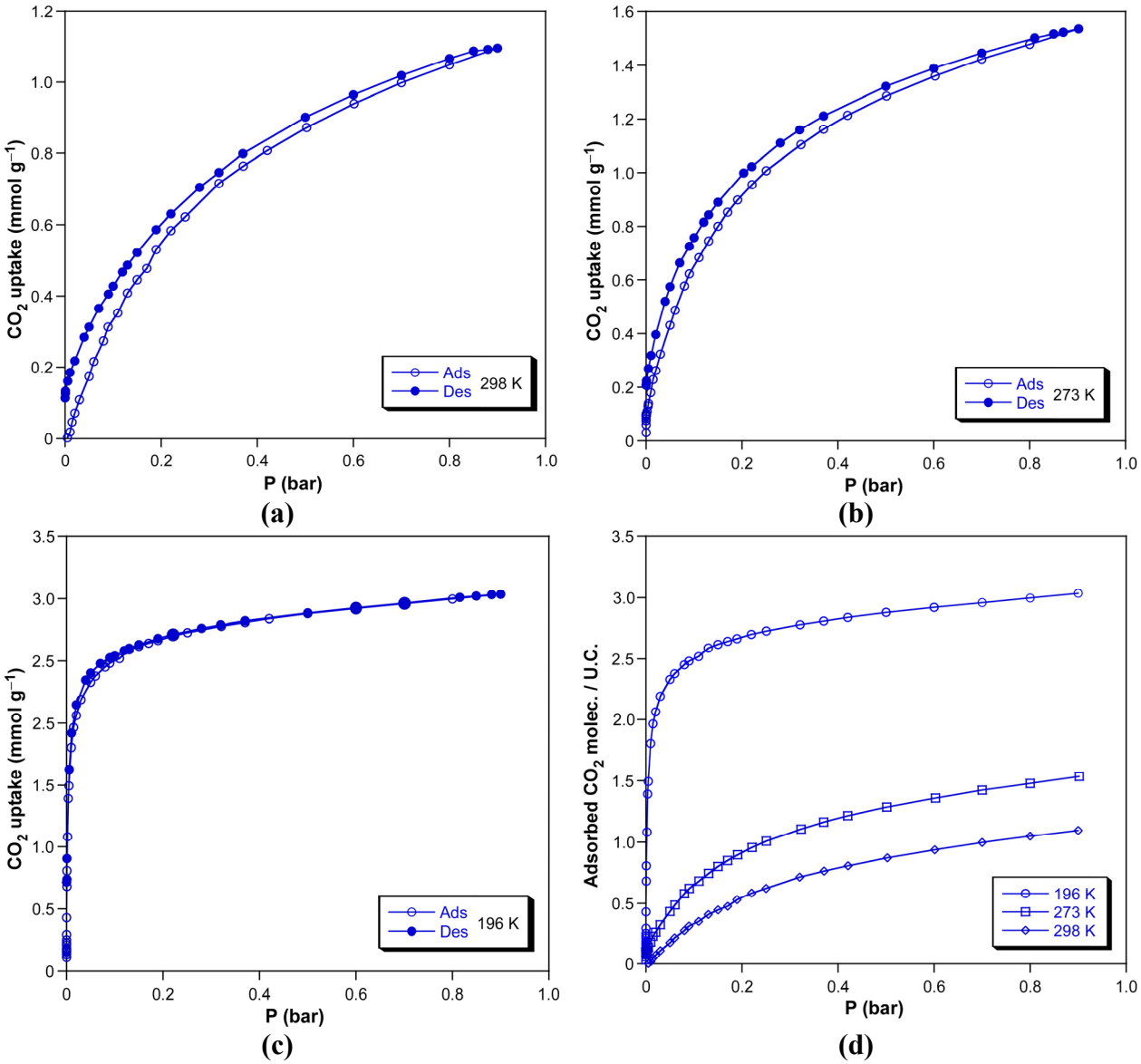


Figure S11. CO_2 adsorption (open) and desorption (filled) curves for simulated **5** compound at **(a)** 298 K, **(b)** 273 K, and **(c)** 196 K. **(d)** Corresponding adsorbed CO_2 molecules per unit cell.

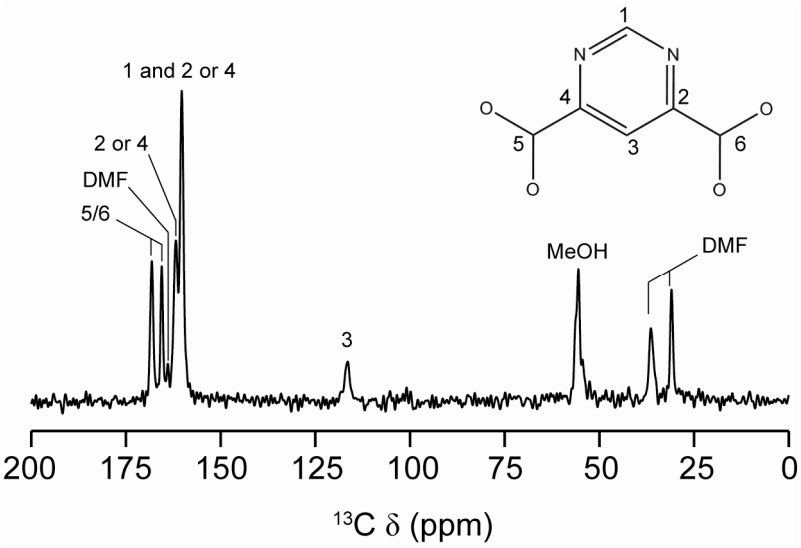


Figure S12. ^{13}C (14.1 T, 16 kHz CP MAS) NMR spectrum of compound **5** with a tentative assignation of the peaks corresponding to the organic linker and solvent molecules. The spectrum is the result of averaging 688 transients using a recycle delay of 3 s. The asterisk indicates the presence of DMF in the sample.