Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

An energy-efficient route to the rapid synthesis of organically-modified SBA-15 via ultrasonic template removal

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Structural characterisation

Thermal analysis

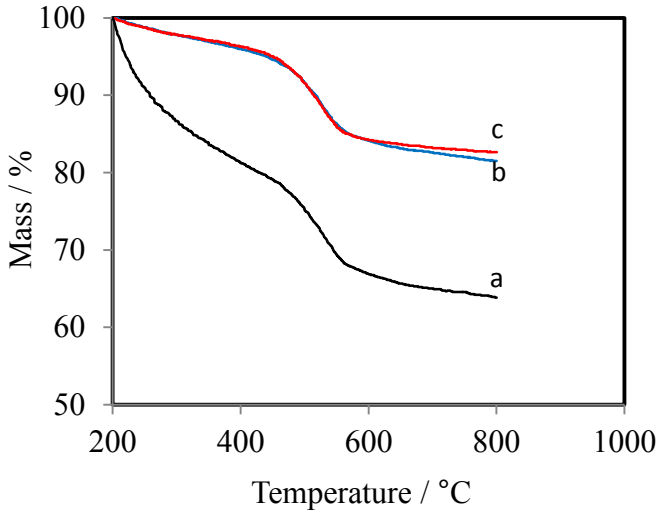


Fig. S1 Thermogravimetric analysis (TGA) profiles of $PrSO_3H$-SBA-15: (a) as-synthesised (unextracted); (b) extracted by MeOH reflux (2 x 50 cm^3); and (c) extracted by 5 min MeOH ultrasonication

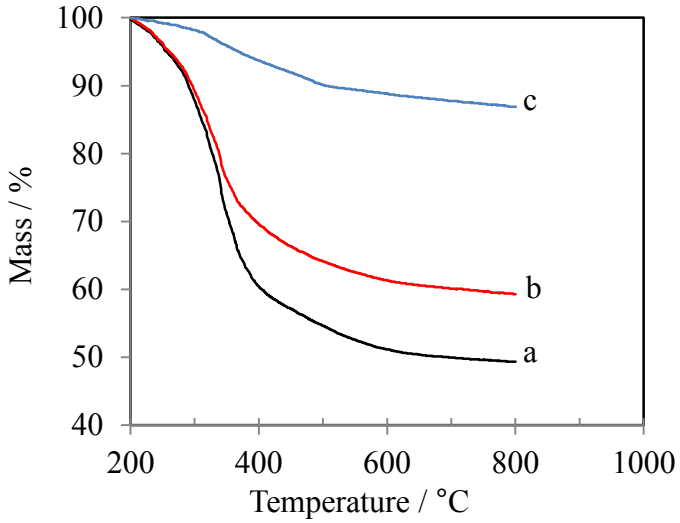


Fig. S2 Thermogravimetric analysis (TGA) profiles of SBA-15: (a) as-synthesised (unextracted); (b) extracted by 5 min MeOH ultrasonication; and (c) extracted by MeOH reflux (2 x 50 cm^3)

NB. The greater mass losses in the SBA-15 sample extracted by ultrasonication compared to that extracted with MeOH may reflect the requirement for thermal activation to overcome H-bonding interactions between the P123 template and isolated silanol groups (c.f. DRIFT spectra in Fig. 5).

Table S1 Comparison of P123 extraction from SBA-15 vs $PrSO_3H$-SBA-15

Material	Extraction method	Solvent extraction (50 cm^3 per 100 mg)	Duration	P123 / % wt loss[a]	%P123[b] removed
SBA-15	As-synthesised	-	-	49	0
SBA-15	Calcination	-	-	1	98
SBA-15	Reflux	Toluene	24 h	32	35
SBA-15	Reflux	THF	24 h	10	80
SBA-15	Reflux	Acetone	24 h	12	76
SBA-15	Reflux	EtOH	24 h	11.8	76
SBA-15	Reflux	MeOH	24 h	10	80
SBA-15	Reflux[c]	MeOH*2	24 h	5	90
SBA-15	Ultrasonication	MeOH	5 min	30	39
SBA-15	Ultrasonication	MeOH	30 min	27	45
SBA-15	Ultrasonication	MeOH	1 h	28	43
$PrSO_3H$-SBA-15	As-synthesised	-	-	35	0
$PrSO_3H$-SBA-15	Reflux	Toluene	24 h	13.4	62
$PrSO_3H$-SBA-15	Reflux	THF	24 h	11	69
$PrSO_3H$-SBA-15	Reflux	Acetone	24 h	11.1	68
$PrSO_3H$-SBA-15	Reflux	EtOH	24 h	9.8	72
$PrSO_3H$-SBA-15	Reflux	MeOH	24 h	9.1	74
$PrSO_3H$-SBA-15	Reflux	MeOH*2	24 h	4	89
$PrSO_3H$-SBA-15	Ultrasonication	MeOH	5 min	3.8	89
$PrSO_3H$-SBA-15	Ultrasonication	MeOH	1 h	3.6	90
$PrSO_3H$-SBA-15	Ultrasonication[d]	MeOH*	5 min	3.6	90

[a]TGA weight loss between 150-350 ºC; [b]Proportion of template removed relative to as-synthesised SBA-15 and as-synthesised $PrSO_3H$-SBA-15; [c]two consecutive 50 cm^3 reflux cycles; [d]10 cm^3 per 100 mg.

Porosimetry

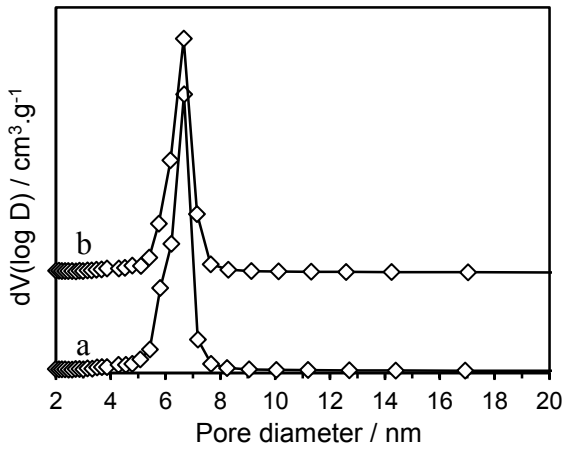


Fig. S3 BJH pore-size distributions of $PrSO_3H$-SBA-15 extracted by: (a) MeOH reflux; and (b) MeOH ultrasonication

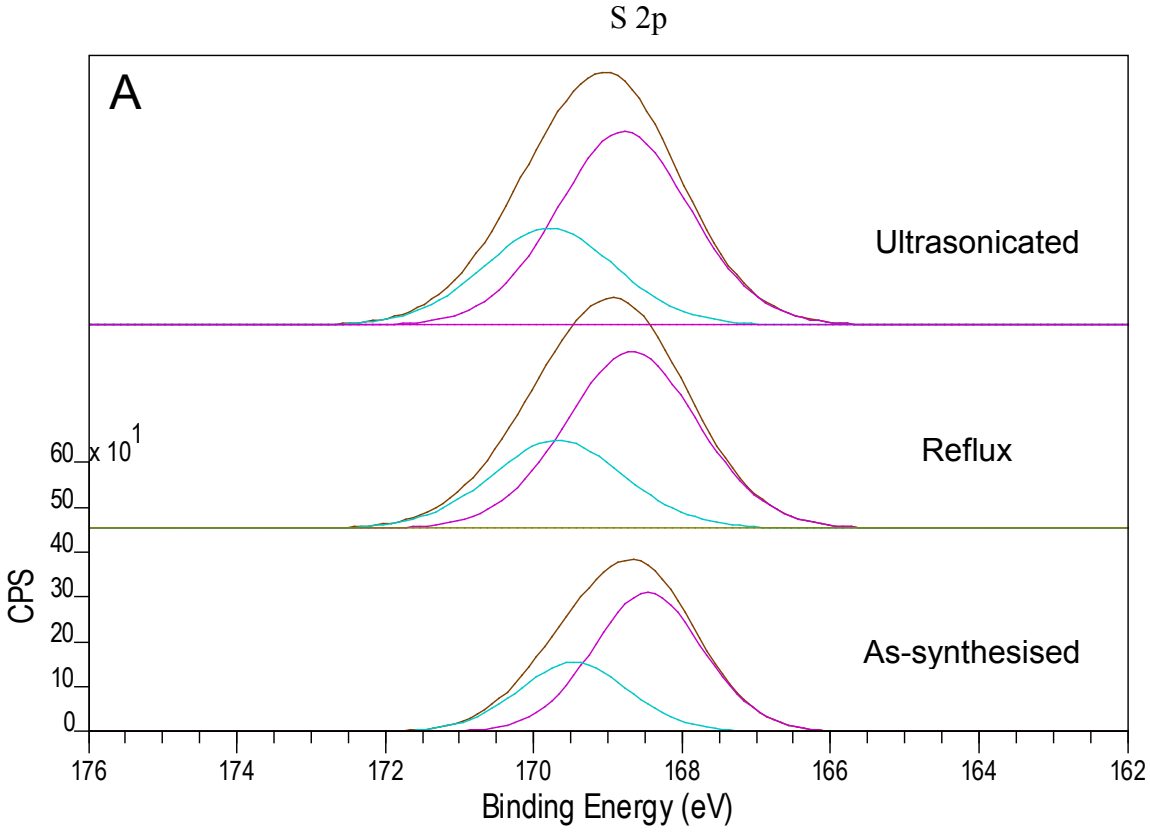
X-ray photoelectron spectroscopy

Elemental quantification was undertaken using the entire element region and associated instrumental response factors are per standard analytical protocols (e.g. for sulfur both S $2p_{1/2}$ and S $2p_{3/2}$ spin-orbit components were utilised to estimate the mass% and wt%). A common Gaussian-Lorentzian lineshape (30% Lorentzian) was adopted for all elements.

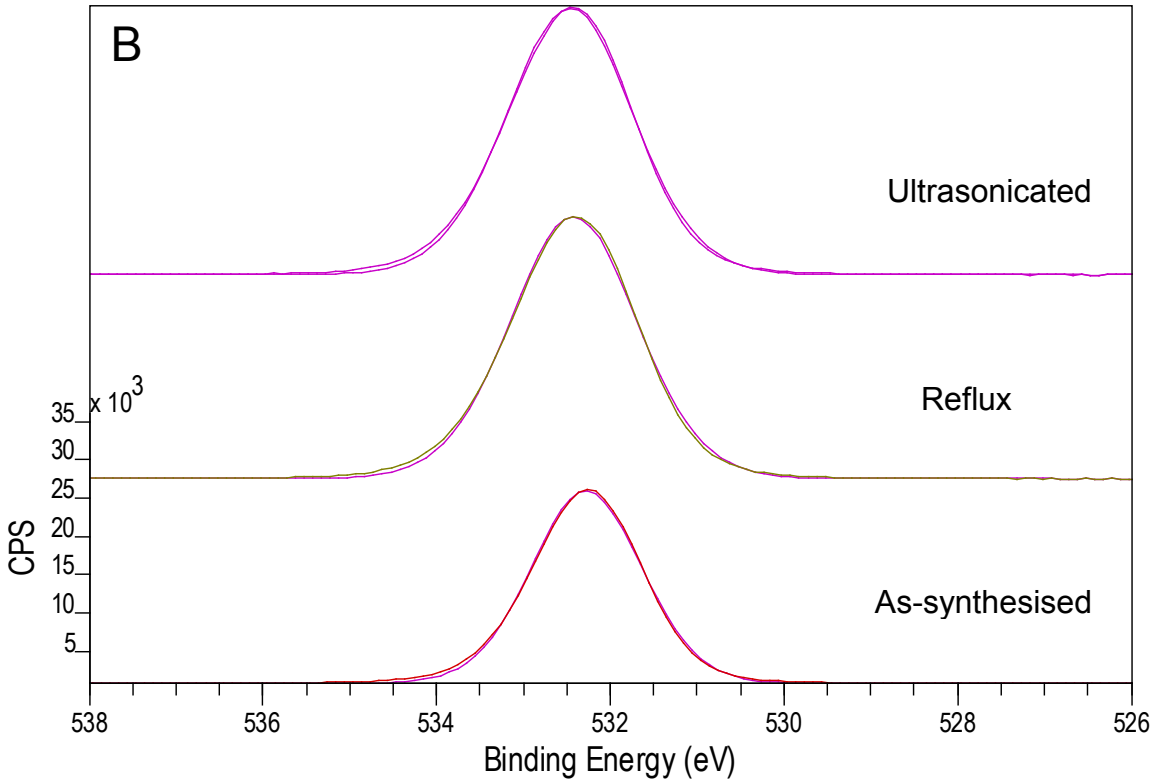
Table S2 Surface elemental analysis of $PrSO_3H$-SBA-15 by XPS

Extraction method	Element	Binding energy[a] / eV	Atom%	Wt%[b]
As-synthesised	**O 1s**	532.3 (1.7)	51.1	48.6
	C 1s	284.5 (1.5)	12.5	8.9
		286.1	19.6	14.0
	S $2p_{3/2}$	168.5 (2.1)	1.4	2.6
	Si $2p_{3/2}$	102.9 (1.5)	15.5	25.9
Reflux	**O 1s**	532.4 (1.7)	62.9	55.0
	C 1s	284.5 (1.5)	7.6	5.0
		285.7 (1.5)	4.3	2.8
		286.7 (1.5)	2.1	1.4
	S $2p_{3/2}$	168.7 (2.1)	1.7	3.0
	Si $2p_{3/2}$	103.0 (1.5)	21.4	32.8
Ultrasonication	**O 1s**	532.5 (1.7)	63.0	54.9
	C 1s	284.5 (1.5)	8.0	5.2
		285.6 (1.5)	4.2	2.8
		286.6 (1.5)	2.1	1.4
	S $2p_{3/2}$	168.8 (2.1)	1.9	3.1
	Si $2p_{3/2}$	103.1 (1.5)	21.7	33.2

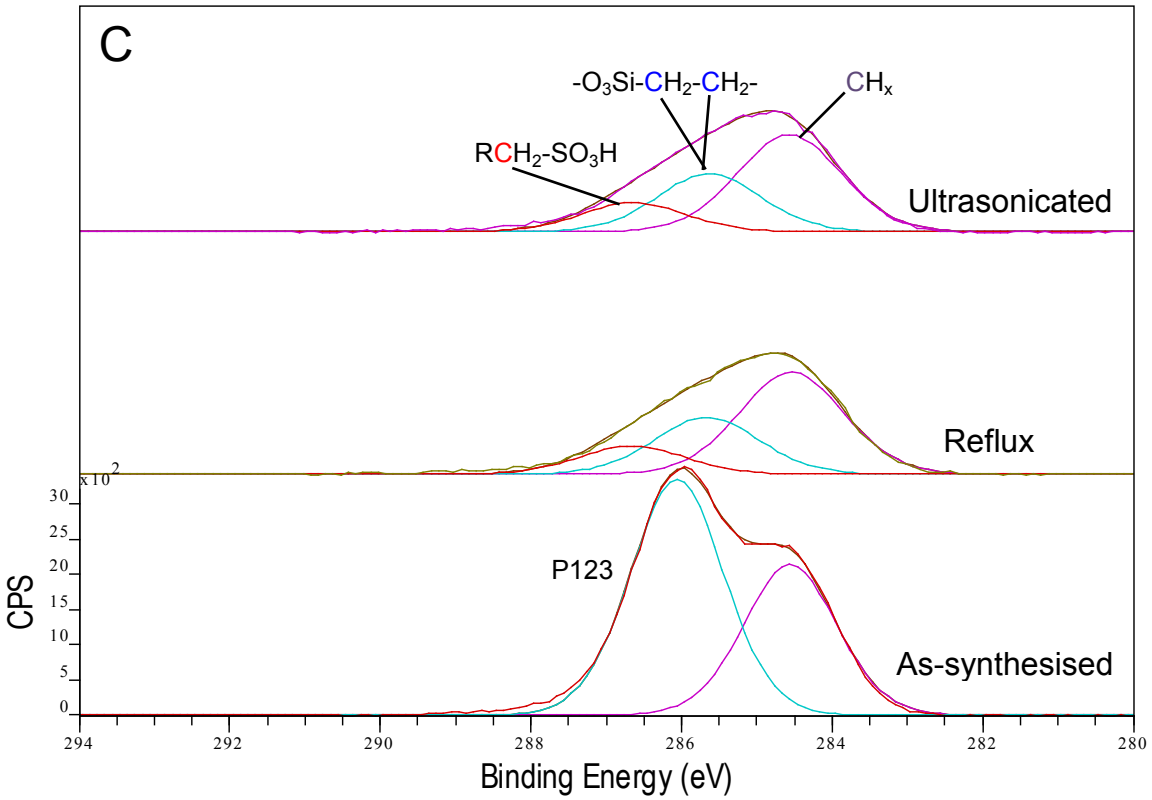
[a]FWHM shown in parentheses; [b]for element A, $wt\%^A = (mass\%^A \times RMM^A) / \sum_{i=A,B,C..} mass\%^i \times RMM^i$ where i=A, B, C.. etc. for all elements in material.



O 1s



C 1s



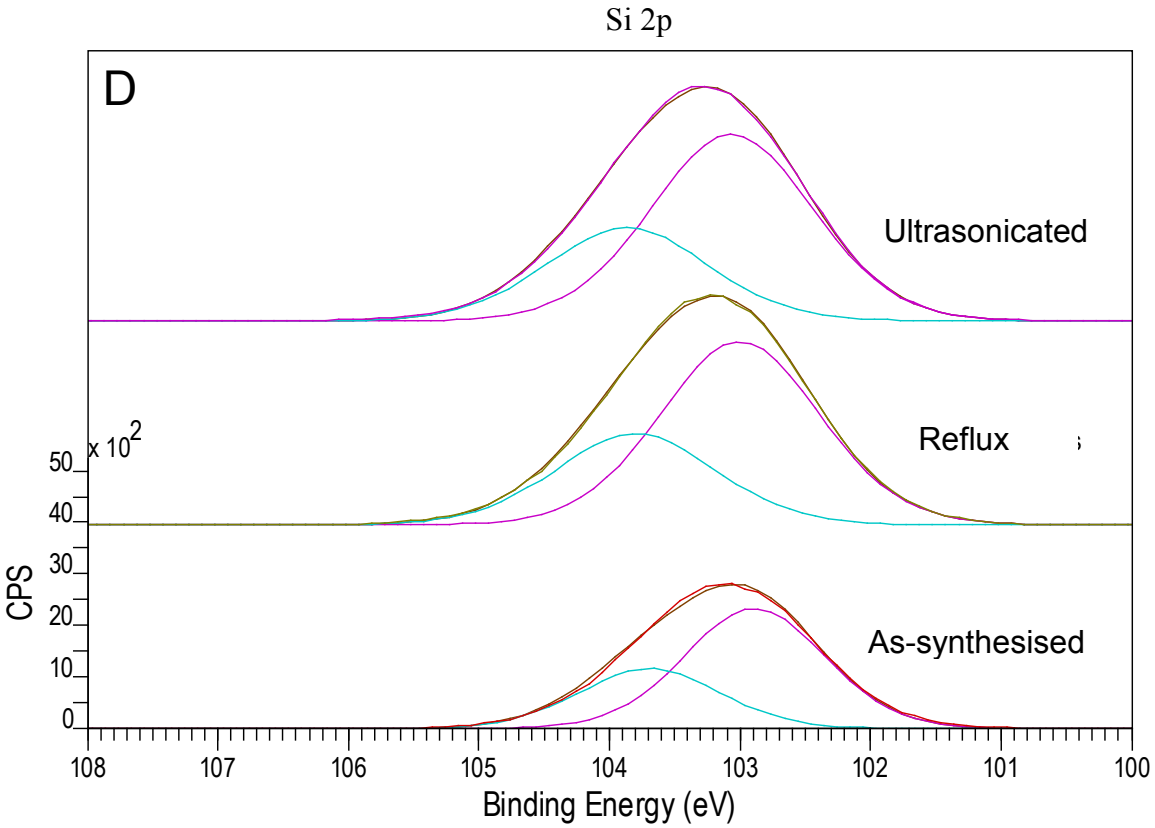


Fig. S4A-D Background-subtracted, fitted XP spectra of as-synthesised $PrSO_3H$-SBA-15 and after extraction by MeOH reflux (2 x 50cm^3) or 5 min MeOH ultrasonication

Transmission electron microscopy

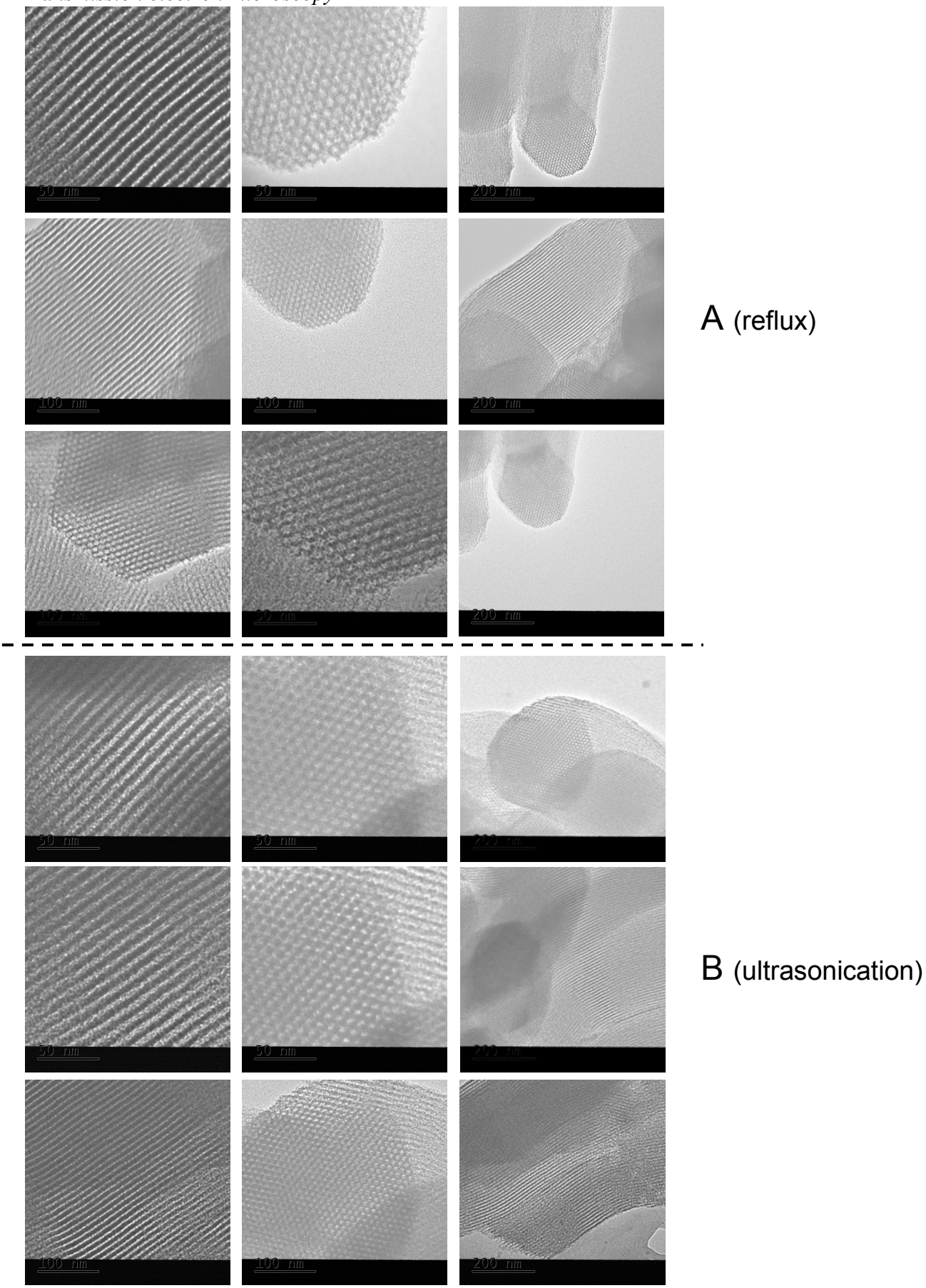
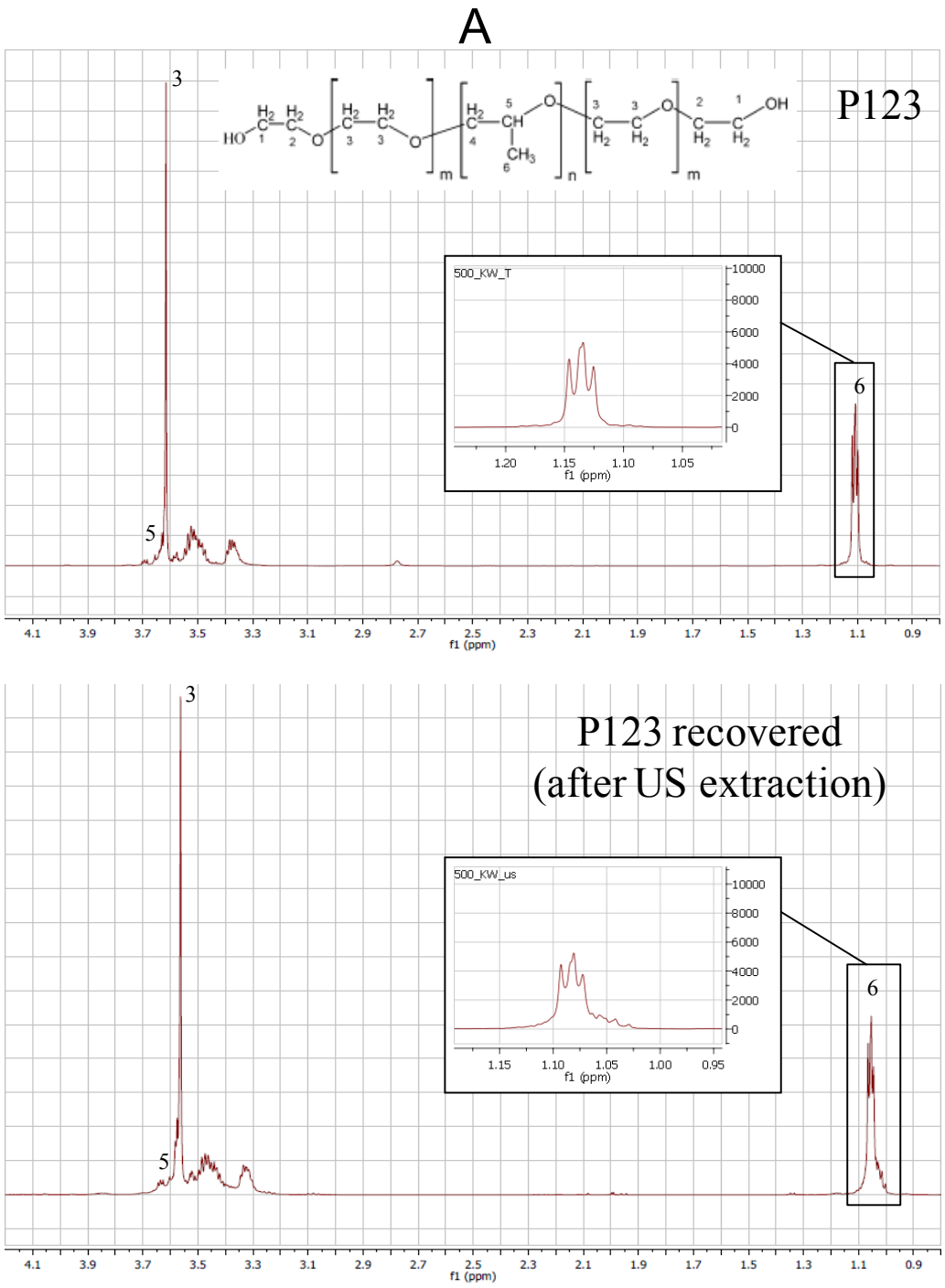


Fig. S5 Bright-field TEM images of $PrSO_3H$-SBA-15 after (**A**) 48 h extraction by MeOH reflux (2 x 50cm^3) or (**B**) 5 min MeOH ultrasonication

Solution NMR spectra of extract after MeOH vacuum removal

^{1}H and ^{13}C NMR spectra were recorded using a Bruker 500 Advance III Spectrometer. Typically, 128 scans were employed for ^{1}H experiments and 512 scans for ^{13}C [^{1}H] experiments. P123 template, and the organic residue extracted from $PrSO_3H$-SBA-15 by 5 min ultrasonication in MeOH, were dissolved in $CDCl_3$.

^{1}H NMR



^{13}C NMR

B

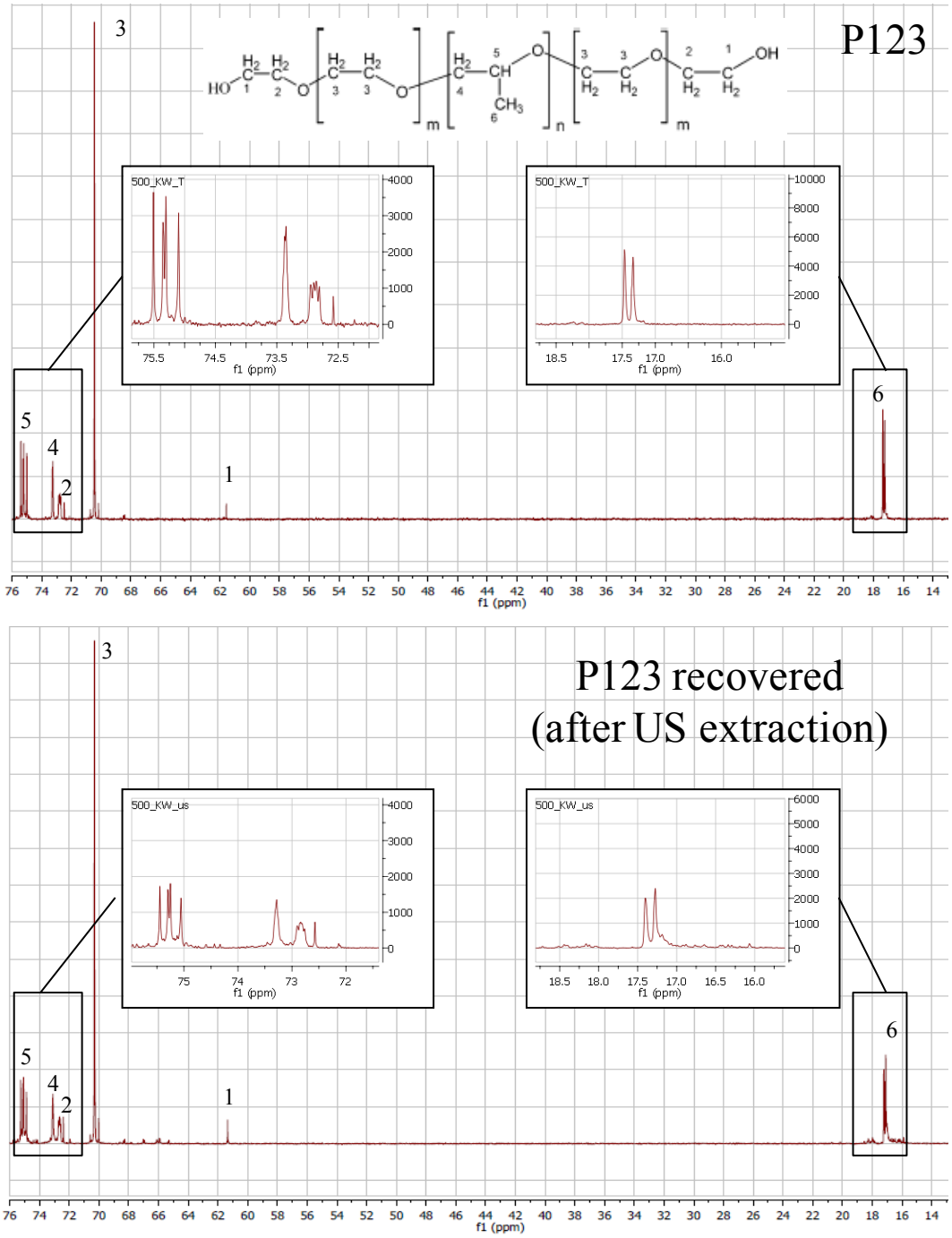


Fig. S6 Solution state (**A**) ^{1}H NMR and (**B**) ^{13}C NMR of pure P123 and the organic extract from $PrSO_3H$-SBA-15 after 5 min MeOH ultrasonication