Electronic Supplementary Information

Hierarchical Beta zeolites as catalysts in one-pot three-component cascade Prins–Friedel–Crafts reaction

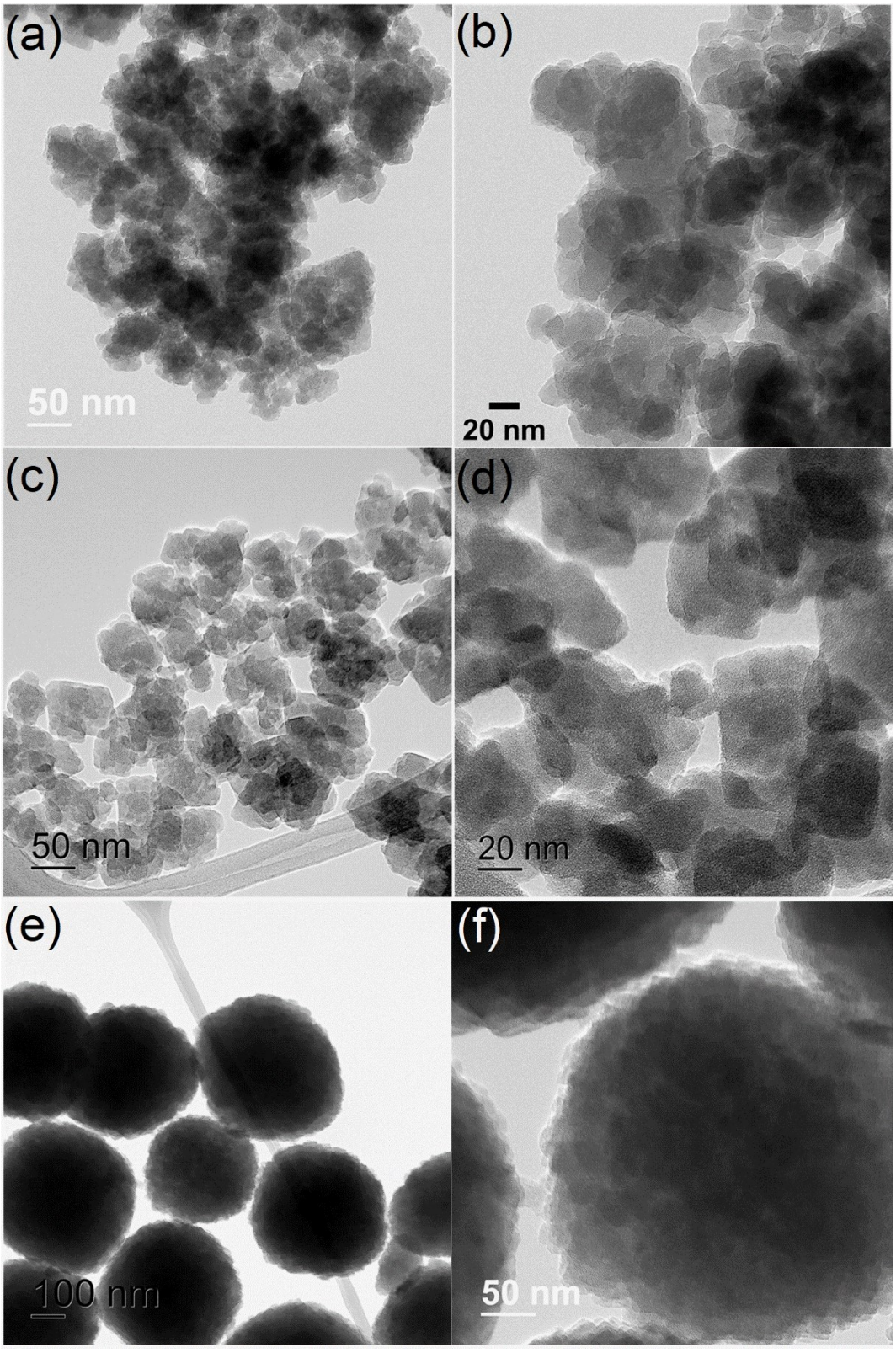

Fig. S1 TEM images of the calcined samples MB-1 (a, b), MB-3 (c, d) and CB-1 (e, f).

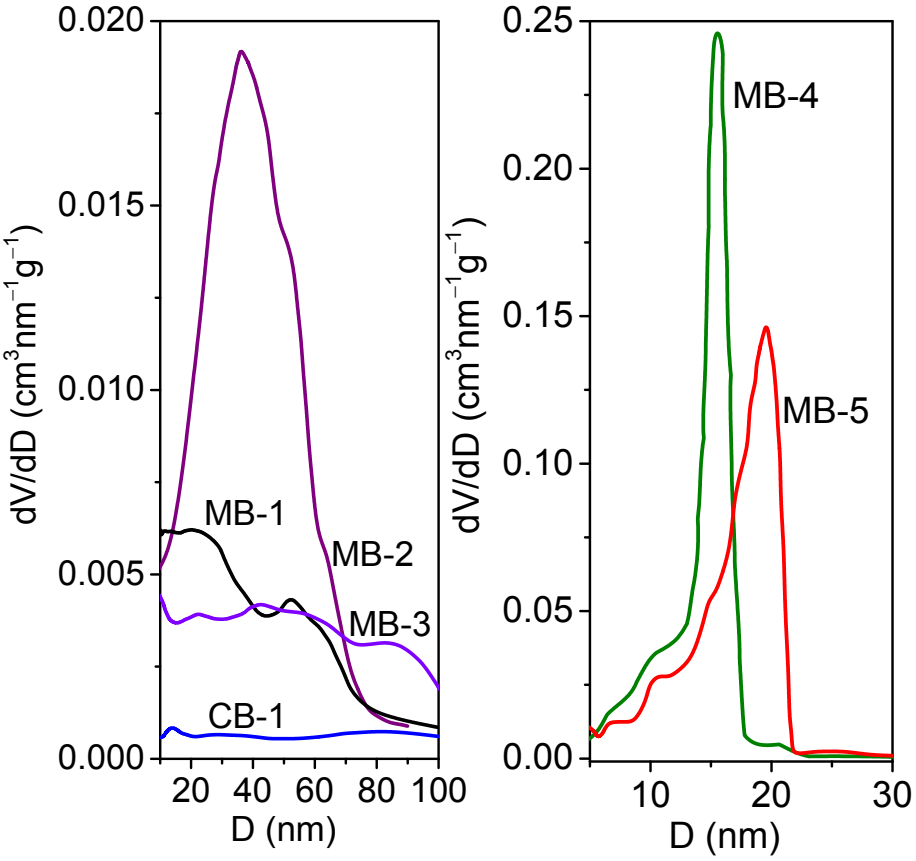

Fig. S2 Mesopore size distribution (from the desorption branch of the nitrogen ad(de)sorption isotherm, –196 °C) curves for the samples MB-1 – 5 and CB-1.

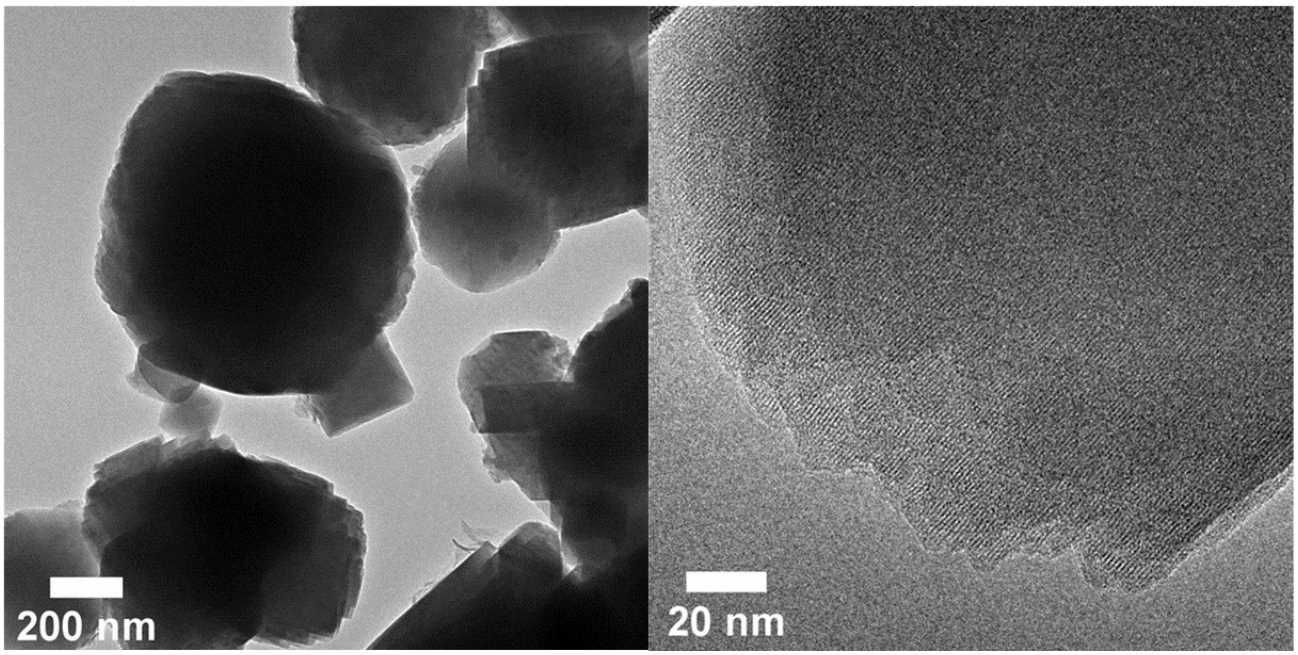

Fig. S3 TEM images of the calcined sample MB-7.

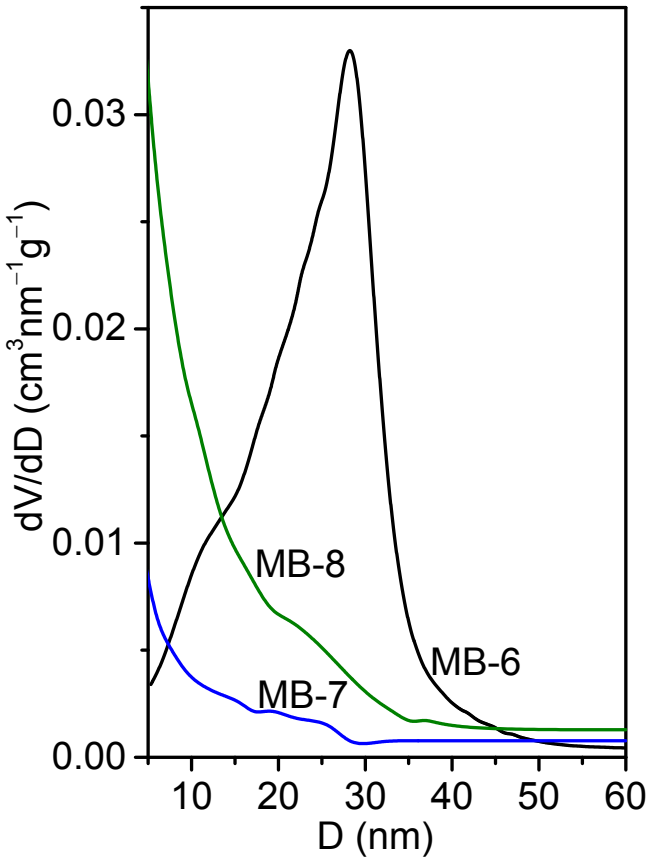

Fig. S4 Mesopore size distribution (from the desorption branch of the nitrogen ad(de)sorption isotherm, –196 °C) curves for the samples MB-6 – MB-8.

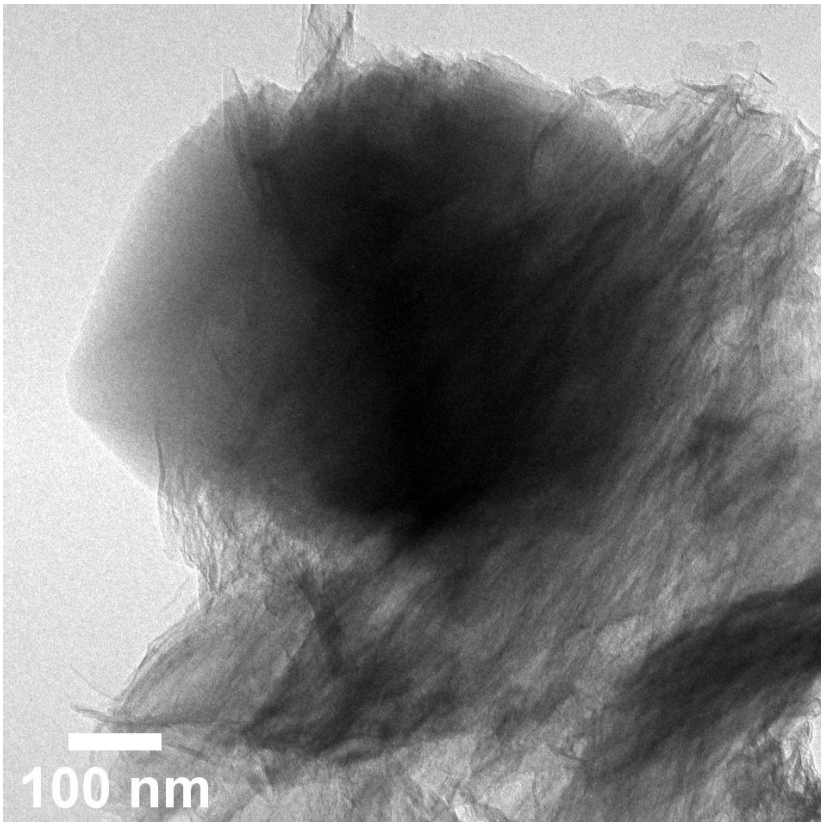

Fig. S5 TEM image of the calcined sample MB-8.

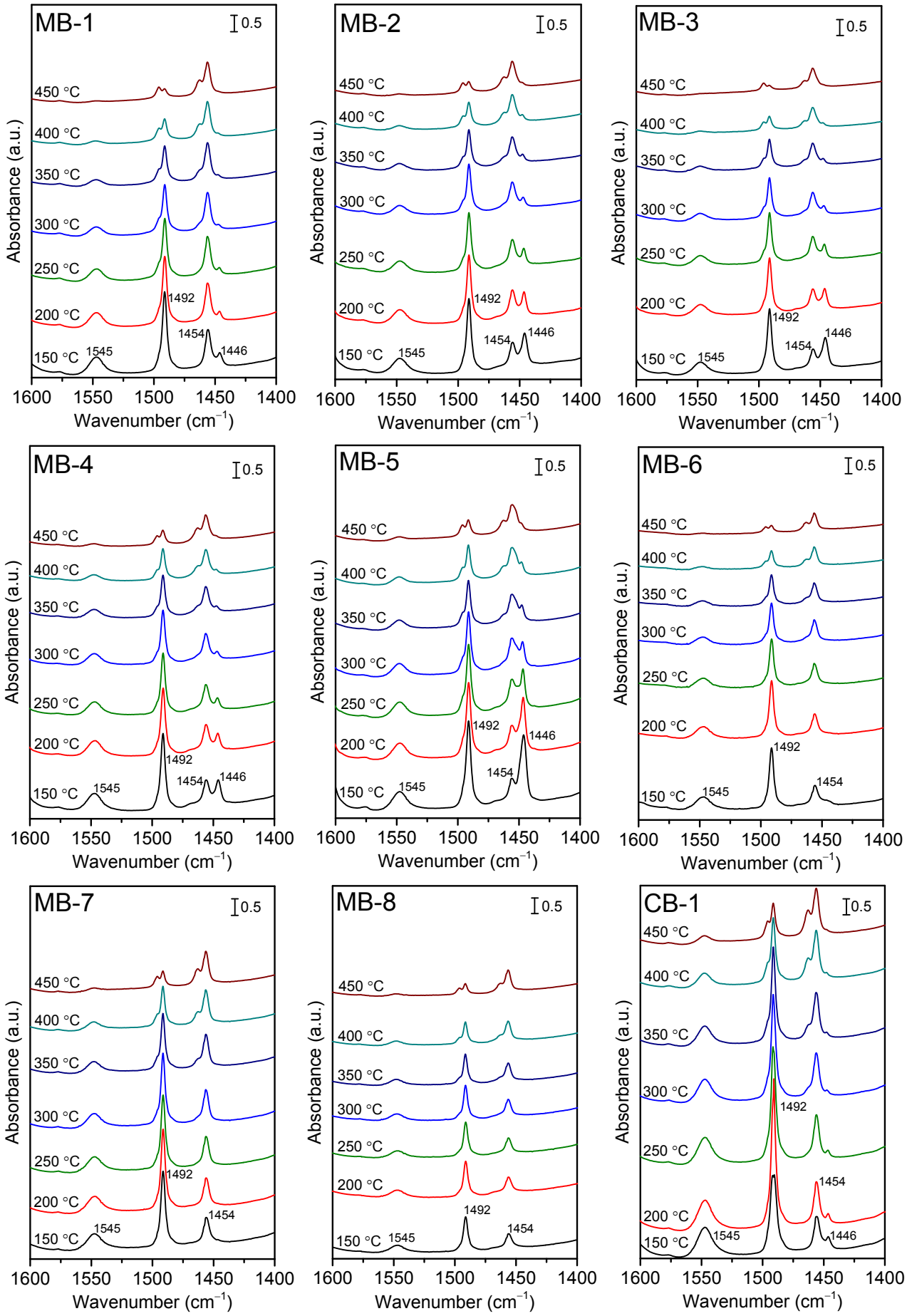

Fig. S6. FTIR spectra of the samples MB-1 – 8 and CB-1 (in the region of 1600 – 1400 cm^{-1}) recorded after adsorption of pyridine and its desorption at 150 – 450 °C.

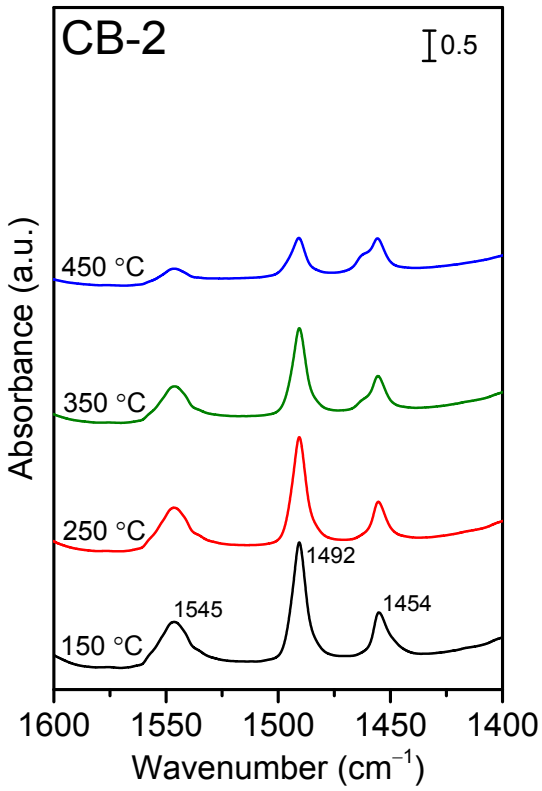

Fig. S7. FTIR spectra of the sample CB-2 (in the region of 1600 – 1400 cm^{-1}) recorded after adsorption of pyridine and its desorption at 150 – 450 °C.

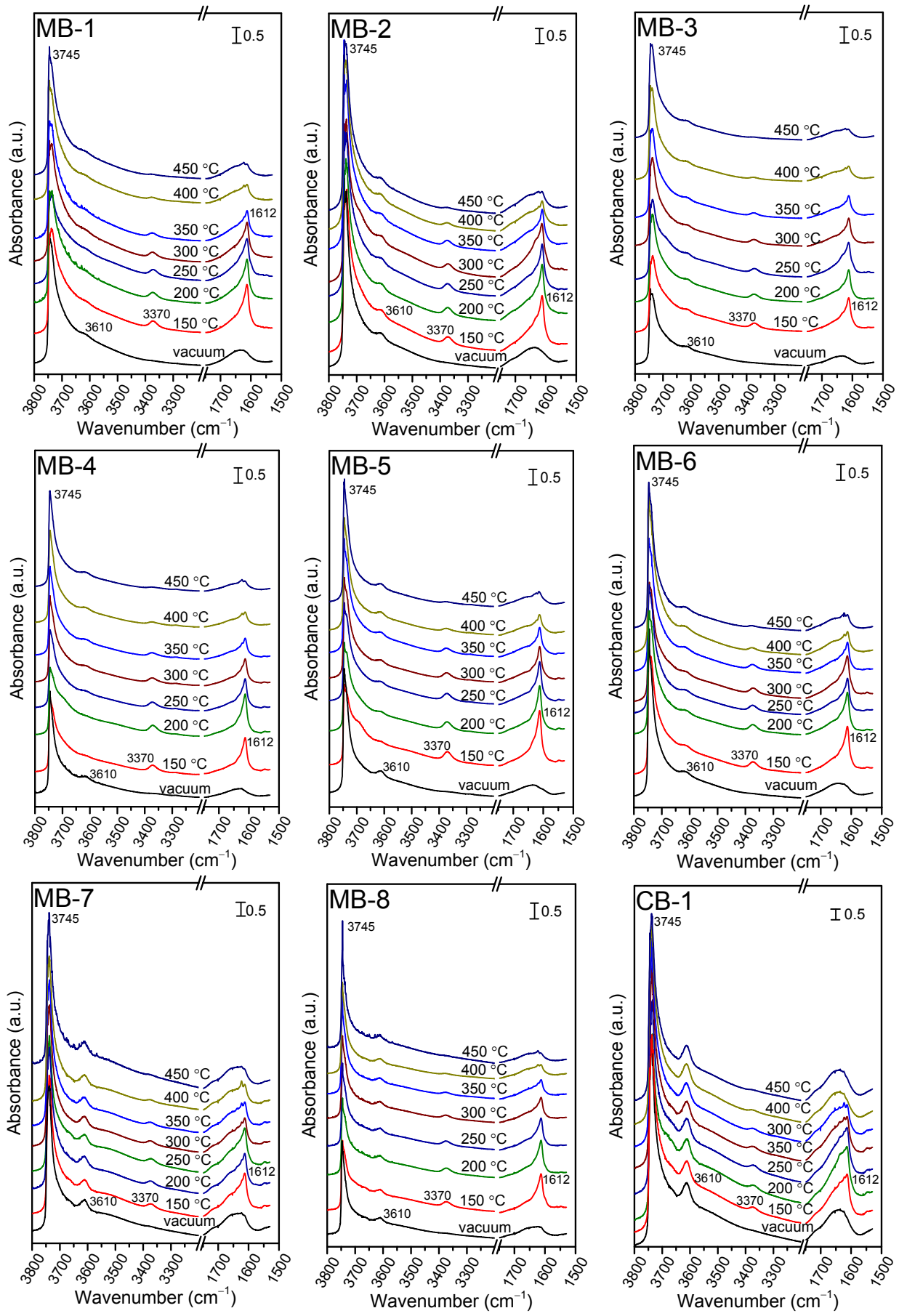

Fig. S8. FTIR spectra of the samples MB-1 – 8 and CB-1 (in the regions of 3800 – 3200 cm^{-1} and 1750 – 1550) recorded after evacuated (P = 1.4 Pa) at 450 °C, adsorption of 2,4,6-tri-tertbutylpyridine and its desorption at 150 – 450 °C.

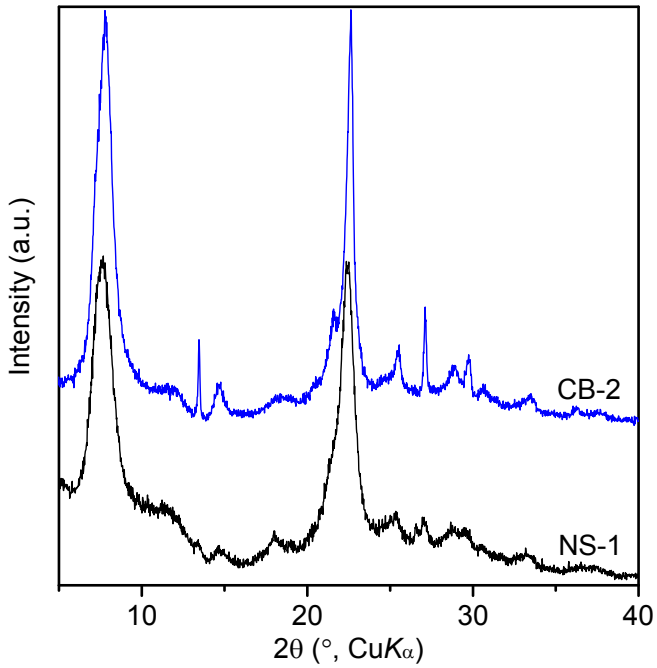

Fig. S9 XRD patterns of the calcined samples NS-1 and CB-2.

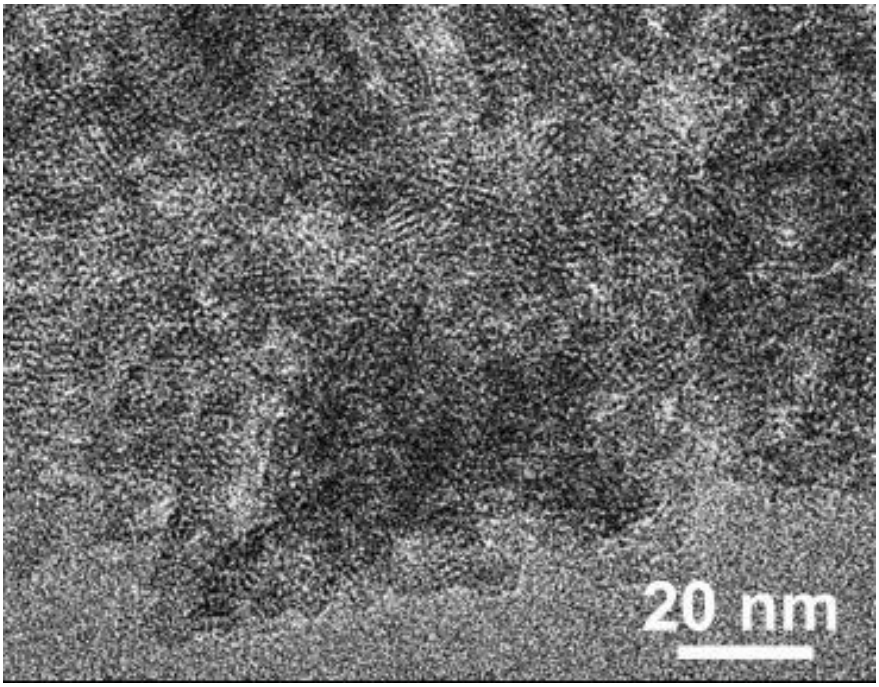

Fig. S10 TEM image of the sample NS-1.

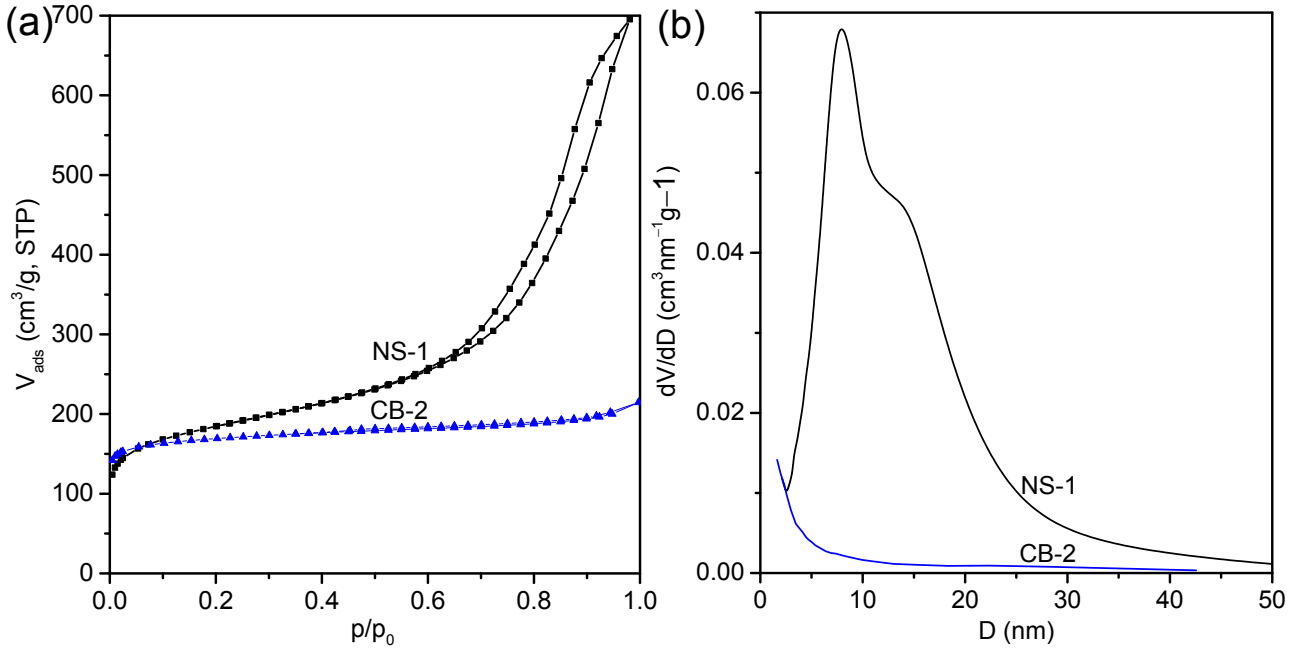

Fig. S11 Nitrogen ad(de)sorption isotherms at –196 °C (a) and mesopore size distribution (from the desorption branch) curves (b) for the samples NS-1 and CB-2.

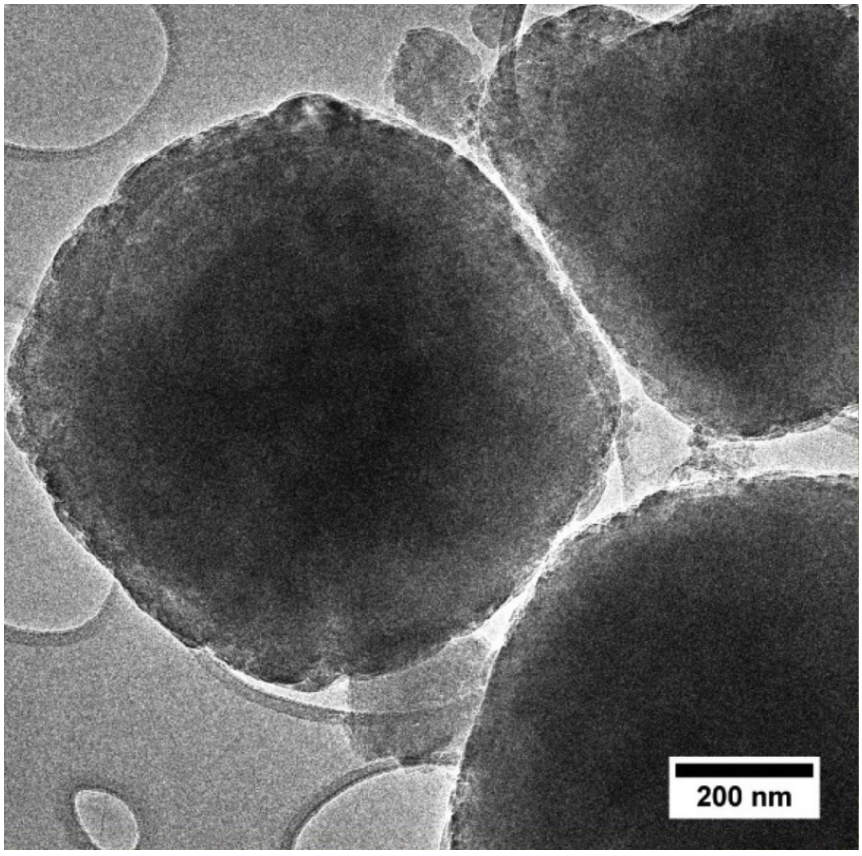

Fig. S12 TEM image of the sample CB-2.

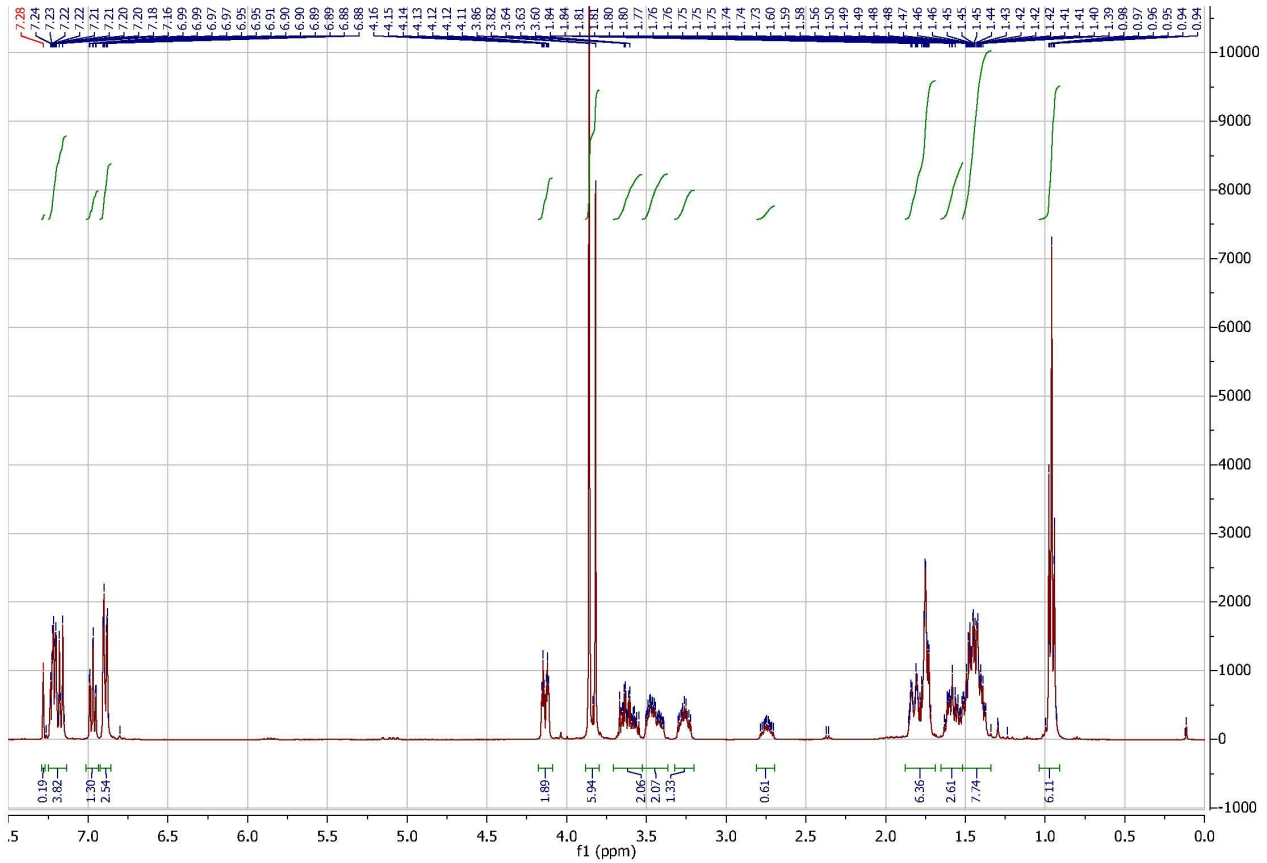

Fig. S13 ^{1}H NMR spectrum of a mixture of *o*-, *p*-isomers of 4-(2(4)-methoxyphenyl)-2-propyltetrahydropyran.

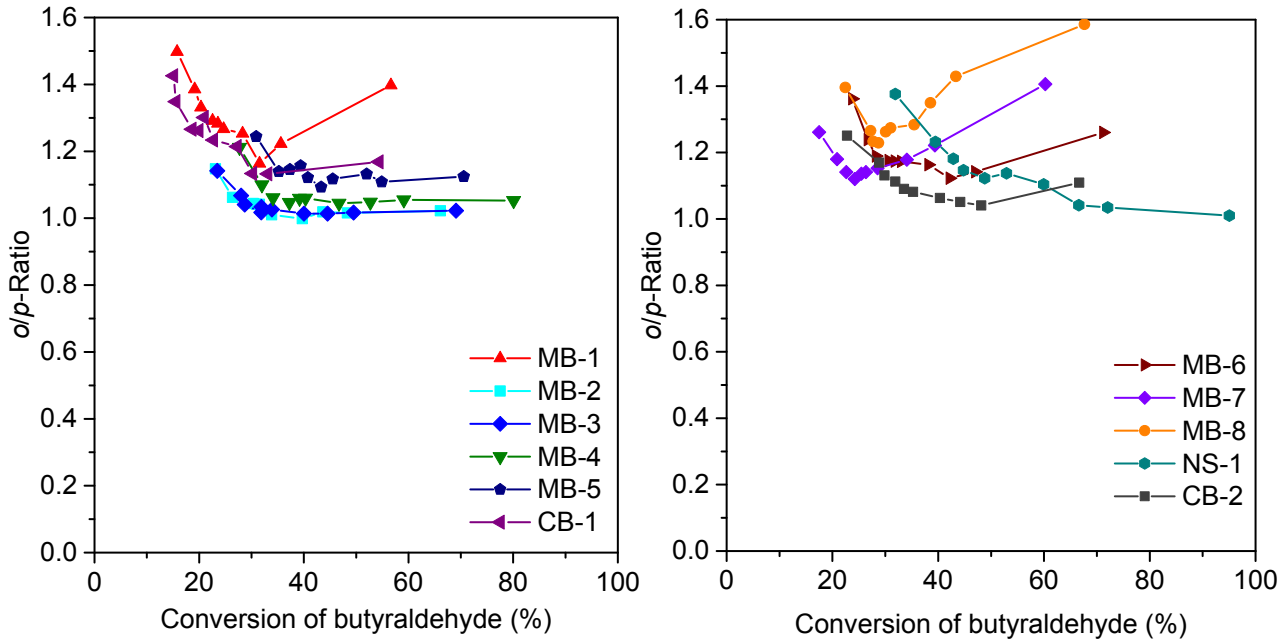

Fig. S14 *o*/*p*-4-Aryltetrahydropyrans ratio versus conversion of butyraldehyde in Prins–Friedel–Crafts reaction over the obtained and reference samples.

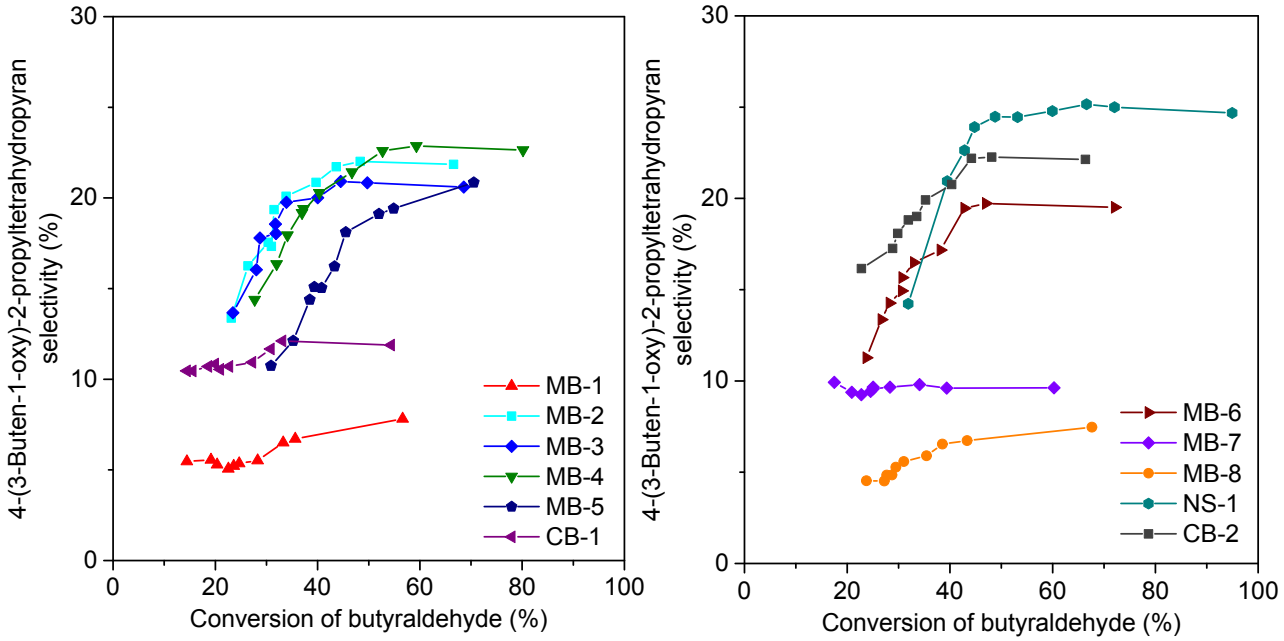

Fig. S15 4-(3-Buten-1-oxy)-2-propyltetrahydropyran **4** selectivity versus conversion of butyraldehyde in Prins–Friedel–Crafts reaction over the obtained and reference samples.

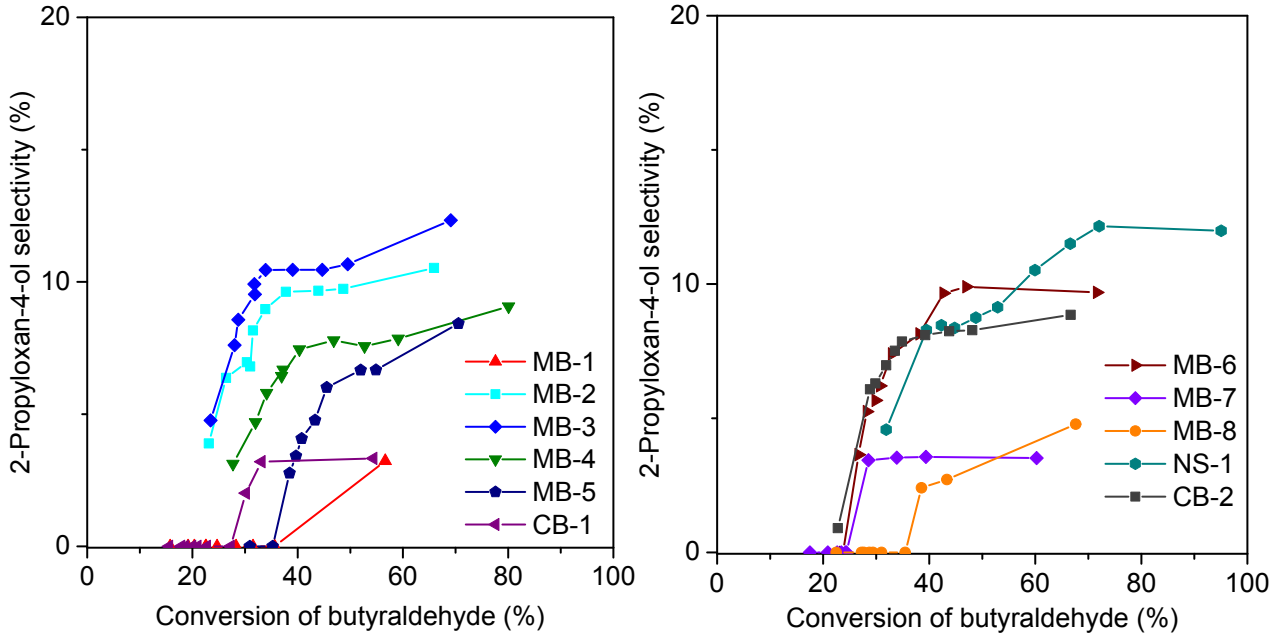

Fig. S16 2-Propyloxan-4-ol **5** selectivity versus conversion of butyraldehyde in Prins–Friedel–Crafts reaction over the obtained and reference samples.

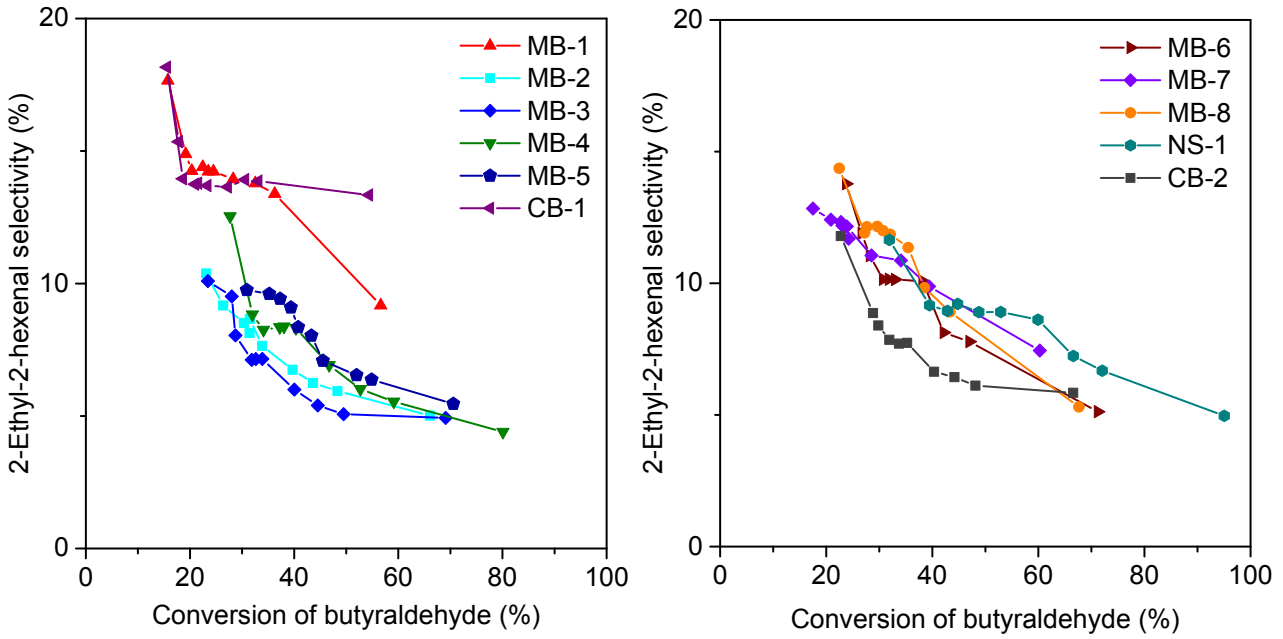

Fig. S17 2-Ethyl-2-hexenal **6** selectivity versus conversion of butyraldehyde in Prins–Friedel–Crafts reaction over the obtained and reference samples.

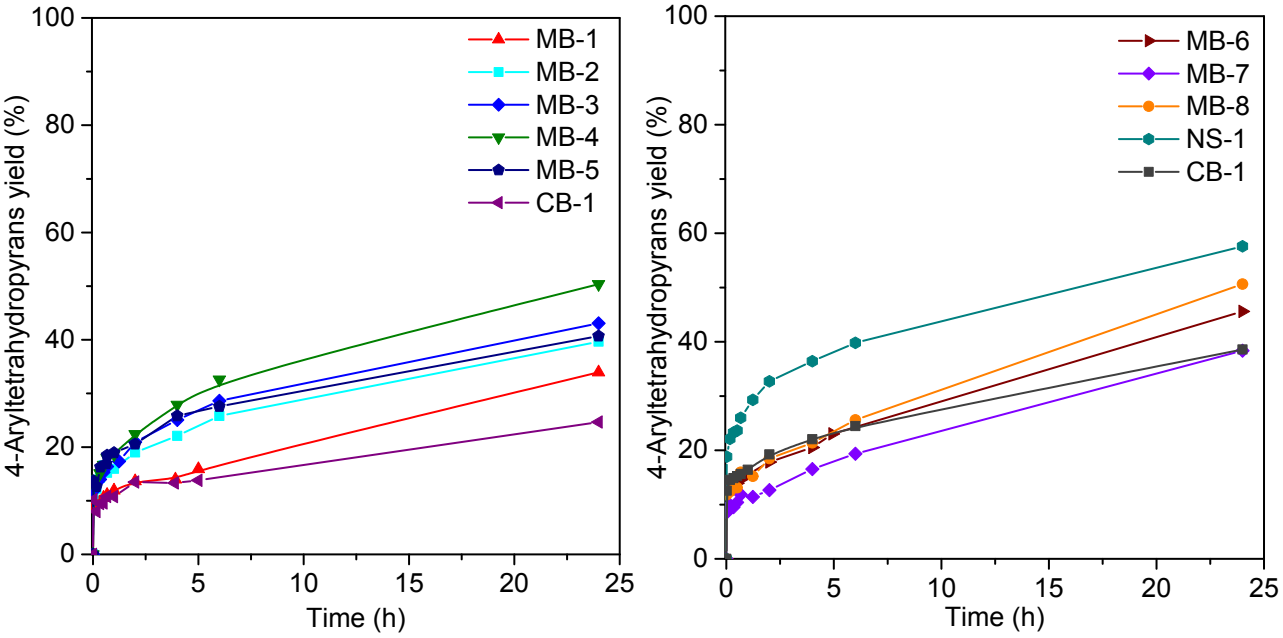

Fig. S18 Yield of 4-aryltetrahydropyrans as a function of reaction time in Prins–Friedel–Crafts reaction over the obtained and reference samples. Reaction conditions: 2.5 mmol of butyraldehyde, 5 mmol of 3-buten-1-ol, 10 ml of anisole (also as a solvent), 0.2 g of *n*-dodecane (internal standard), 50 mg of catalyst, 60 °C.

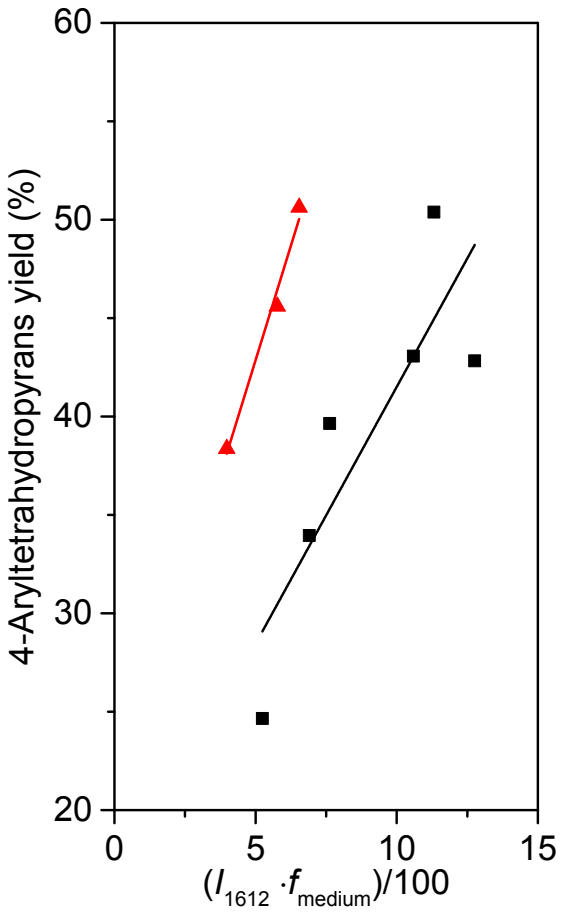

Fig. S19. Correlation of 4-aryltetrahydropyrans yield with relative concentration of the medium-strength Brønsted acid sites on the mesopore surface for the Prins–Friedel–Crafts reaction over Beta samples obtained without CTAB (black line) and with CTAB (red line).

Table S1 Characteristics of porous structure of the samples obtained.

Sample	V_{micro}[a] (cm^3/g)	V_{meso}[b] (cm^3/g)	D_{meso}[c] (nm)	S_{meso}[d] (m^2/g)	S_{BET}[e] (m^2/g)
MB-1	0.24[f]	0.43	50±7.4	110	670
MB-2	0.25	0.69	36±17.2	130	760
MB-3	0.23	0.46	–[g]	85	640
MB-4	0.21	0.81	15±1.0	230	765
MB-5	0.23	0.84	19±2.2	200	780
MB-6	0.23	0.85	29±6.6	155	720
MB-7	0.23	0.14	–[g]	65	640
MB-8	0.11	0.56	–[g]	325	600
CB-1	0.25	0.06	–[g]	20[h]	645
NS-1	0.13	0.93	8±3.0	355	645
CB-2	0.22	0.10	–[g]	100[h]	585

[a] V_{micro}, micropore volume. [b] V_{meso}, mesopore volume. [c] D_{meso}, average mesopore diameter and deviation from this value. [d] S_{meso}, mesopore surface area. [e] S_{BET}, total specific surface area. [f] Micropore diameter for the samples given in Table S1 is 0.65 nm. [g] Mesopore size distribution without maximum. [h] The external surface area of Beta zeolite.

Table S2 Si/Al molar ratio in the obtained samples and their acidity by pyridine ad(de)sorption with IR-spectral analysis.

Sample	Si/Al	Brønsted acid sites concentration (μmol/g)				Lewis acid sites concentration (μmol/g)	Total acid sites concentration (μmol/g)
		Weak[a]	Medium	Strong	Total		
MB-1	27	35	37	35	107	73	180
MB-2	31	36	40	48	124	62	186
MB-3	29	28	38	37	103	49	152
MB-4	26	37	38	63	138	64	202
MB-5	19	25	36	53	114	53	167
MB-6	22	37	36	37	110	50	160
MB-7	23	9	34	60	103	42	145
MB-8	18	1	11	42	54	34	88
CB-1	20	36	66	156	258	87	345
CB-2	19	30	60	230	320	110	430

[a] Weak acid sites – pyridine is desorbed in the range of 150 – 250 °C, medium acid sites – pyridine is desorbed in the range of 250 – 350 °C, strong acid sites – pyridine remains after desorption at 350 °C.

Table S3 Acidity of the obtained samples by temperature-programmed desorption of ammonia.

Sample	Acidity by TPDA	
	T_{max}[a] (°C)	C[b] (μmol/g)
MB-1	220	94
	355	133
MB-2	200	178
	355	251
MB-3	200	137
	340	240
MB-4	200	205
	335	295
MB-5	190	378
	345	245
MB-6	210	27
	325	65
MB-7	195	155
	335	481
MB-8	185	185
	335	259
CB-1	180	211
	325	380

[a] T_{max}, temperature of the maximum of ammonia desorption. [b] C, concentration of acid sites.

Table S4 The integral intensity of the absorption band at 3370 cm^{-1} in FTIR spectra of the samples after 2,4,6-tri-*tert*-butylpyridine adsorption (at a temperature of 150 °C) and its desorption at 150 – 450 °C.

Sample	Integral intensity						
	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
MB-1	1.28[a]	1.15	1.01	0.89	0.63	0.25	0.07
MB-2	1.20	1.18	1.10	1.05	0.86	0.39	0.10
MB-3	1.60	1.41	1.33	1.19	0.84	0.35	0.07
MB-4	2.39	2.14	1.97	1.62	1.32	0.84	0.50
MB-5	2.63	2.26	2.15	1.53	1.43	0.89	0.39
MB-6	1.19	1.14	0.98	0.95	0.72	0.47	0.19
MB-7	0.68	0.61	0.51	0.48	0.37	0.24	0.11
MB-8	1.30	1.28	1.12	0.80	0.50	0.18	0
CB-1	0.39	0.32	0.31	0.30	0.19	0.10	0

[a] The intensities are normalized per weight of the sample

Table S5 The integral intensity of the absorption band at 1612 cm^{-1} in FTIR spectra of the samples after 2,4,6-tri-*tert*-butylpyridine adsorption (at a temperature of 150 °C) and its desorption at 150 – 450 °C.

Sample	Integral intensity						
	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
MB-1	6.91[a]	6.18	5.61	5.15	3.17	0	0
MB-2	7.62	6.87	6.01	5.85	2.99	1.88	0.22
MB-3	10.59	9.05	8.69	7.19	4.77	2.32	0.99
MB-4	11.32	9.52	7.57	5.37	3.73	1.97	0.63
MB-5	12.76	9.43	7.98	6.14	4.68	1.83	0.59
MB-6	5.77	5.55	4.77	3.83	2.80	2.12	0.55
MB-7	3.98	3.38	2.41	1.15	0.49	0.16	0
MB-8	6.54	5.91	4.06	1.97	0.67	0	0
CB-1	5.24	3.84	3.07	2.19	1.16	0.30	0

[a] The intensities are normalized per weight of the sample

Table S6 Fractions of weak, medium and strong Brønsted acid sites in the obtained samples accessible for 2,4,6-tri-*tert*-butylpyridine calculated using the integral intensities of the absorption band at 1612 cm^{-1}.

Sample	Fractions of Brønsted acid sites accessible for TTBPy (%)		
	Weak[a]	Medium	Strong
MB-1	19	35	46
MB-2	21	40	39
MB-3	18	37	45
MB-4	33	34	33
MB-5	37	26	37
MB-6	17	34	48
MB-7	39	48	12
MB-8	38	52	10
CB-1	41	37	22

[a] Weak acid sites – TTBPy is desorbed in the range of 150 – 250 °C, medium acid sites – TTBPy is desorbed in the range of 250 – 350 °C, strong acid sites – TTBPy remains after desorption at 350 °C.

Table S7 Recyclability test of MB-4 in the Prins–Friedel–Crafts reaction between butyraldehyde, 3-buten-1-ol and anisole.

Cycle	Butyraldehyde conversion (%)	4-Aryltetrahydropyrans selectivity (%)	4-Aryltetrahydropyrans yield (%)
1[a]	57	44	25
2[b]	51	38	19
3[c]	55	34	19
4[c]	50	30	15

[a] Reaction conditions: 2.5 mmol of butyraldehyde, 5 mmol of 3-buten-1-ol, 10 ml of anisole (also as a solvent), 0.2 g of *n*-dodecane (internal standard), 50 mg of catalyst, 60 °C, 6 h. [b] For the 2nd cycle, the used catalyst was washed with anisole and acetone, dried and activated at 450 °C for 5 h. [c] The 3rd and 4th cycles were carried out with the catalyst washed with anisole and acetone, dried and calcined at 550 °C for 6 h after using in the previous reaction.

Table S8 Recyclability test of CB-2 in the Prins–Friedel–Crafts reaction between butyraldehyde, 3-buten-1-ol and anisole.

Cycle	Butyraldehyde conversion (%)	4-Aryltetrahydropyrans selectivity (%)	4-Aryltetrahydropyrans yield (%)
1[a]	53	39	21
2[b]	56	38	21
3[c]	46	23	11
4[c]	46	22	10

[a] Reaction conditions: 2.5 mmol of butyraldehyde, 5 mmol of 3-buten-1-ol, 10 ml of anisole (also as a solvent), 0.2 g of *n*-dodecane (internal standard), 50 mg of catalyst, 60 °C, 6 h. [b] For the 2nd cycle, the used catalyst was washed with anisole and acetone, dried and activated at 450 °C for 5 h. [c] The 3rd and 4th cycles were carried out with the catalyst washed with anisole and acetone, dried and calcined at 550 °C for 6 h after using in the previous reaction.