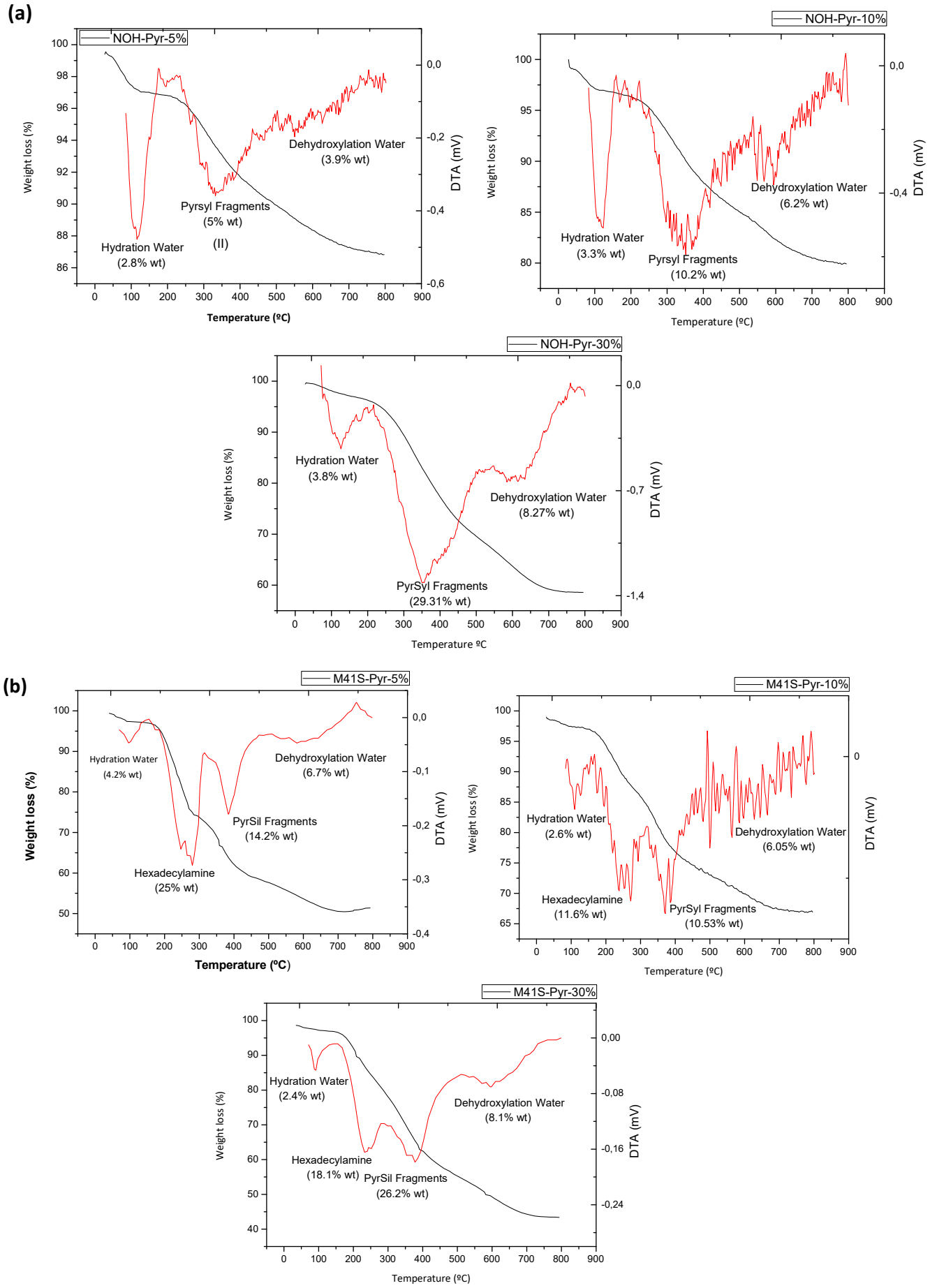
catalysts

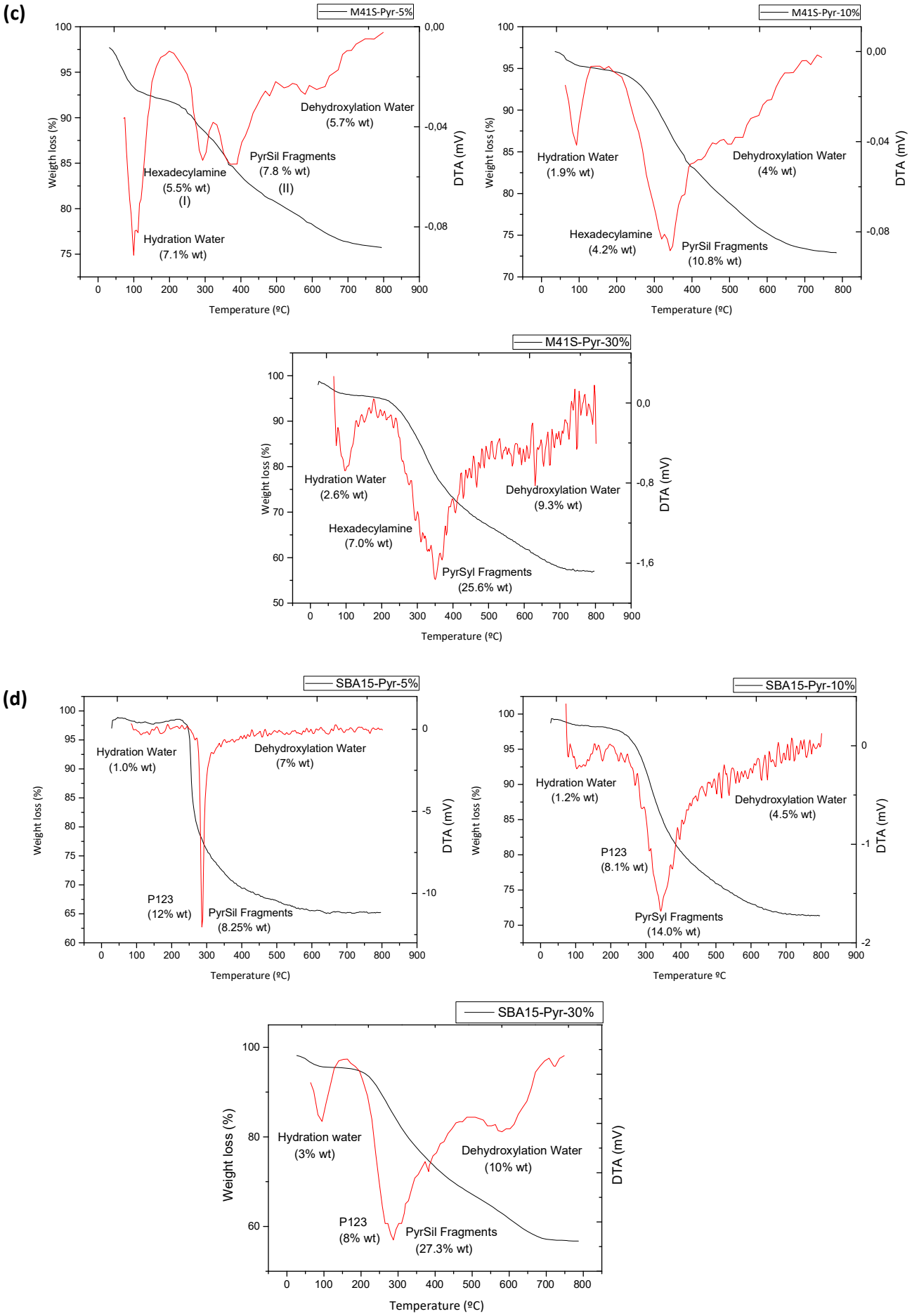
Influence of the Framework Topology on the Reactivity of Chiral Pyrrolidine Units Inserted in Different Porous Organosilicas

Sebastián Llopis, Alexandra Velty and Urbano Díaz *

[1] Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, E-46022 Valencia, Spain

* Correspondence: udiaz@itq.upv.es; Tel.: +34963877811


(a)
NOH-Pyr-5%
Weight loss (%)
DTA (mV)
Temperature (ºC)
Dehydroxylation Water
(3.9% wt)
Pyrsyl Fragments
(5% wt)
Hydration Water
(2.8% wt)
(II)
NOH-Pyr-10%
Hydration Water
(3.3% wt)
Pyrsyl Fragments
(10.2% wt)
Dehydroxylation Water
(6.2% wt)
NOH-Pyr-30%
Hydration Water
(3.8% wt)
Dehydroxylation Water
(8.27% wt)
PyrSyl Fragments
(29.31% wt)
Temperature ºC
(b)
M41S-Pyr-5%
Hydration Water
(4.2% wt)
Dehydroxylation Water
(6.7% wt)
PyrSil Fragments
(14.2% wt)
Hexadecylamine
(25% wt)
M41S-Pyr-10%
Hydration Water
(2.6% wt)
Dehydroxylation Water
(6.05% wt)
Hexadecylamine
(11.6% wt)
PyrSyl Fragments
(10.53% wt)
M41S-Pyr-30%
Hydration Water
(2.4% wt)
Dehydroxylation Water
(8.1% wt)
Hexadecylamine
(18.1% wt)
PyrSil Fragments
(26.2% wt)


(c)
M41S-Pyr-5%
Weigth loss (%)
DTA (mV)
Temperature (ºC)
Hydration Water
(7.1% wt)
Hexadecylamine
(5.5% wt)
(I)
PyrSil Fragments
(7.8 % wt)
(II)
Dehydroxylation Water
(5.7% wt)
M41S-Pyr-10%
Weight loss (%)
DTA (mV)
Temperature (ºC)
Hydration Water
(1.9% wt)
Hexadecylamine
(4.2% wt)
PyrSil Fragments
(10.8% wt)
Dehydroxylation Water
(4% wt)
M41S-Pyr-30%
Weight loss (%)
DTA (mV)
Temperature (ºC)
Hydration Water
(2.6% wt)
Hexadecylamine
(7.0% wt)
PyrSyl Fragments
(25.6% wt)
Dehydroxylation Water
(9.3% wt)
(d)
SBA15-Pyr-5%
Weight loss (%)
DTA (mV)
Temperature (ºC)
Hydration Water
(1.0% wt)
P123
(12% wt)
PyrSil Fragments
(8.25% wt)
Dehydroxylation Water
(7% wt)
SBA15-Pyr-10%
Weight loss (%)
DTA (mV)
Temperature ºC
Hydration Water
(1.2% wt)
P123
(8.1% wt)
PyrSyl Fragments
(14.0% wt)
Dehydroxylation Water
(4.5% wt)
SBA15-Pyr-30%
Weight loss (%)
DTA (mV)
Temperature (ºC)
Hydration water
(3% wt)
P123
(8% wt)
PyrSil Fragments
(27.3% wt)
Dehydroxylation Water
(10% wt)

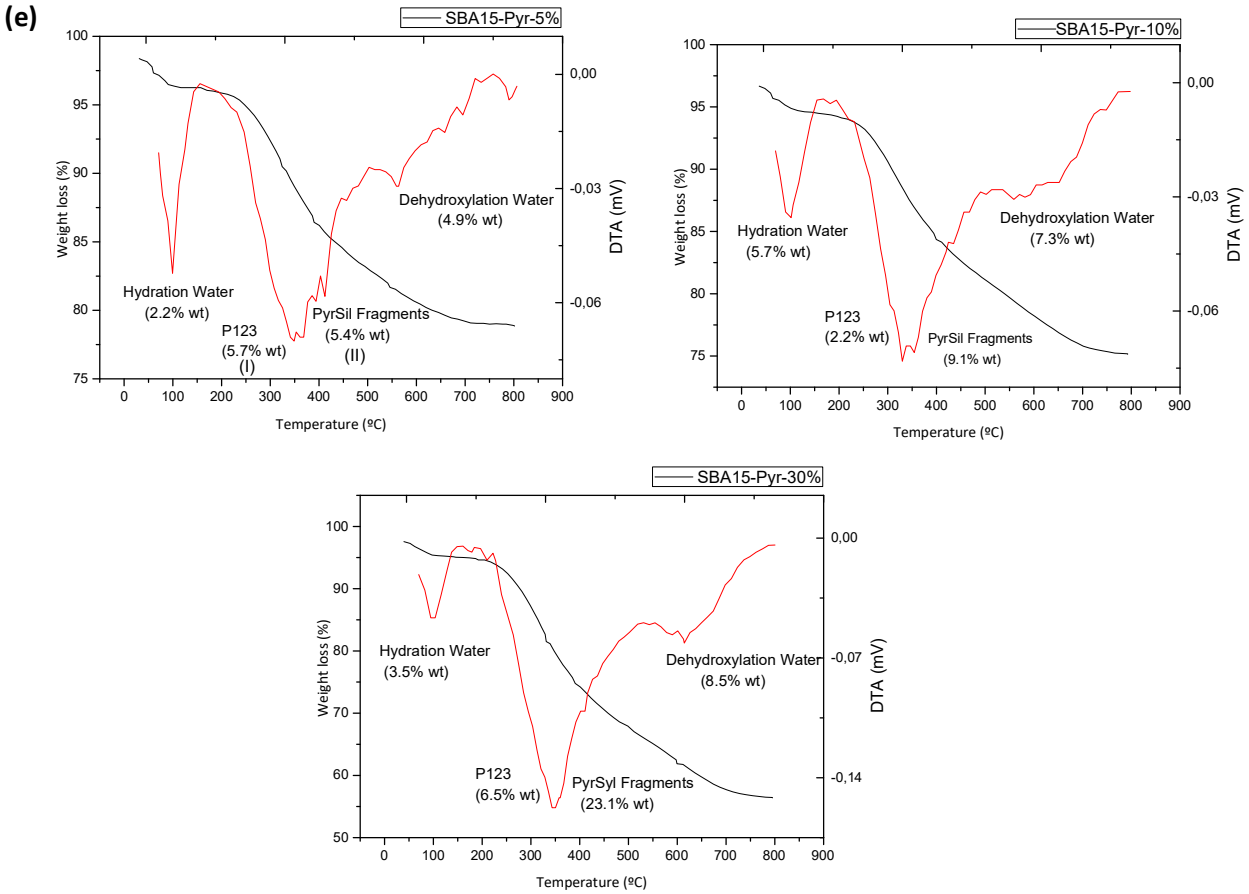
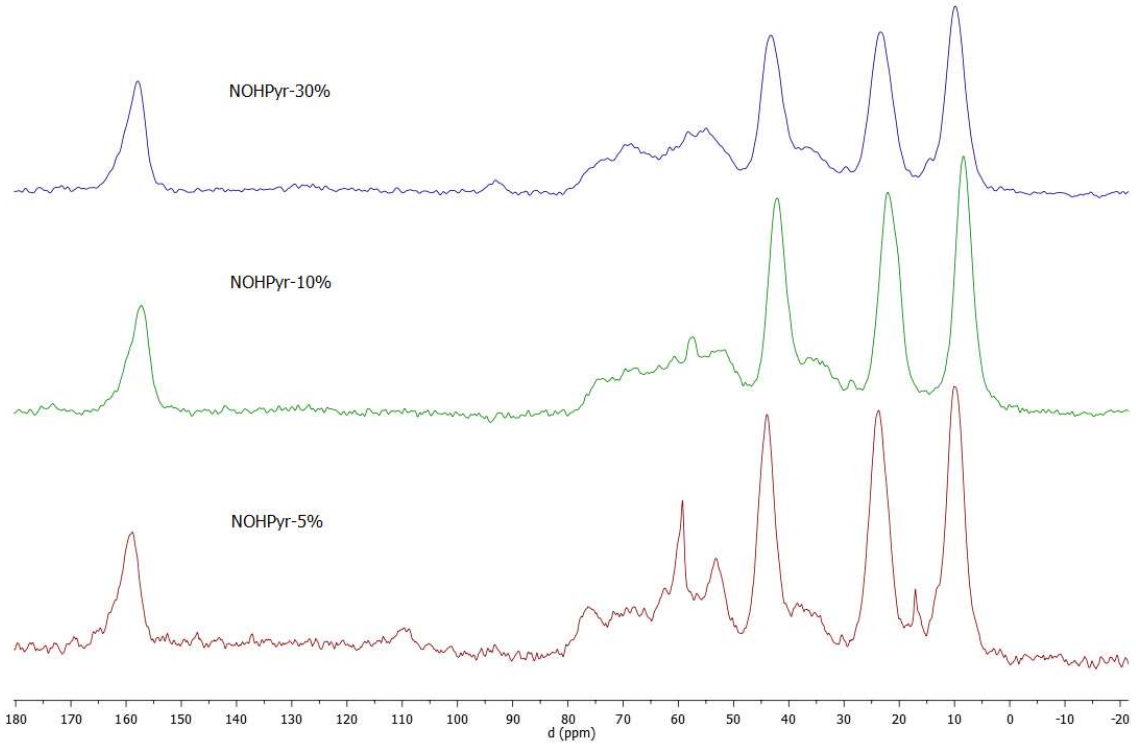
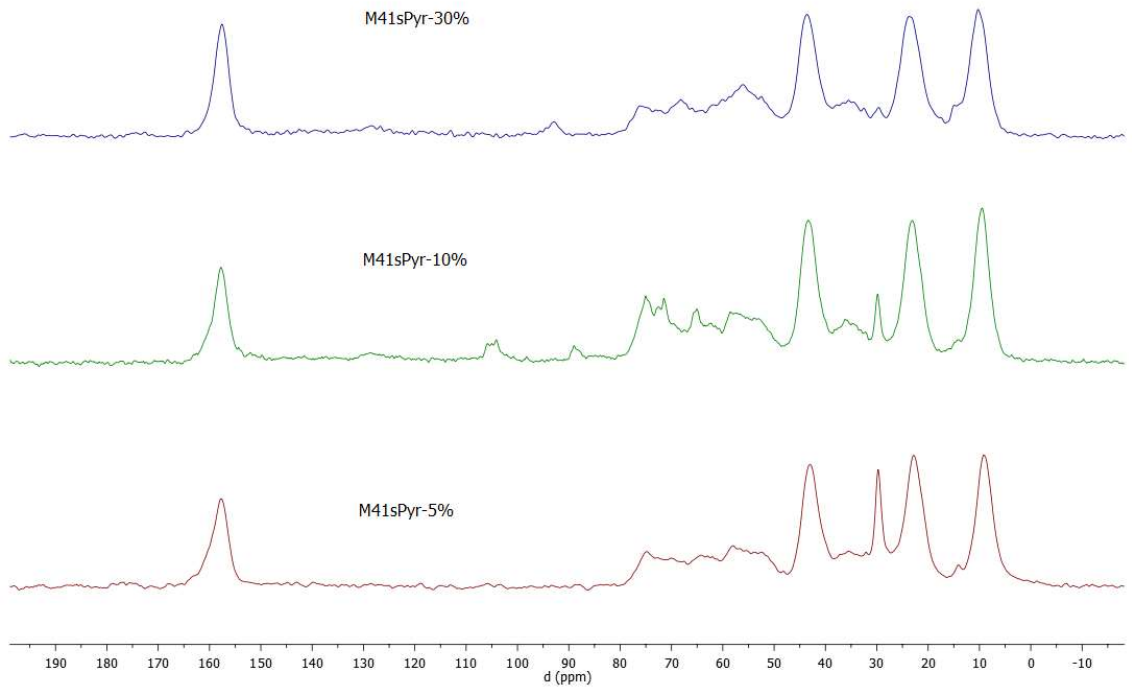


Figure S1. Thermogravimetrical curves (TGA) and corresponding derivatives (DTA) of (**a**) NOH-Pyr, (**b**) as-synthesized M41S-Pyr, (**c**) extracted M41S-Pyr, (**d**) as-synthesized SBA-15-Pyr and (**e**) extracted SBA-15-Pyr materials with different content of bis-silylated pyrrolidine fragments.

a)


NOHPyr-30%
NOHPyr-10%
NOHPyr-5%
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
d (ppm)

b)


M41sPyr-30%
M41sPyr-10%
M41sPyr-5%
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
d (ppm)

c)

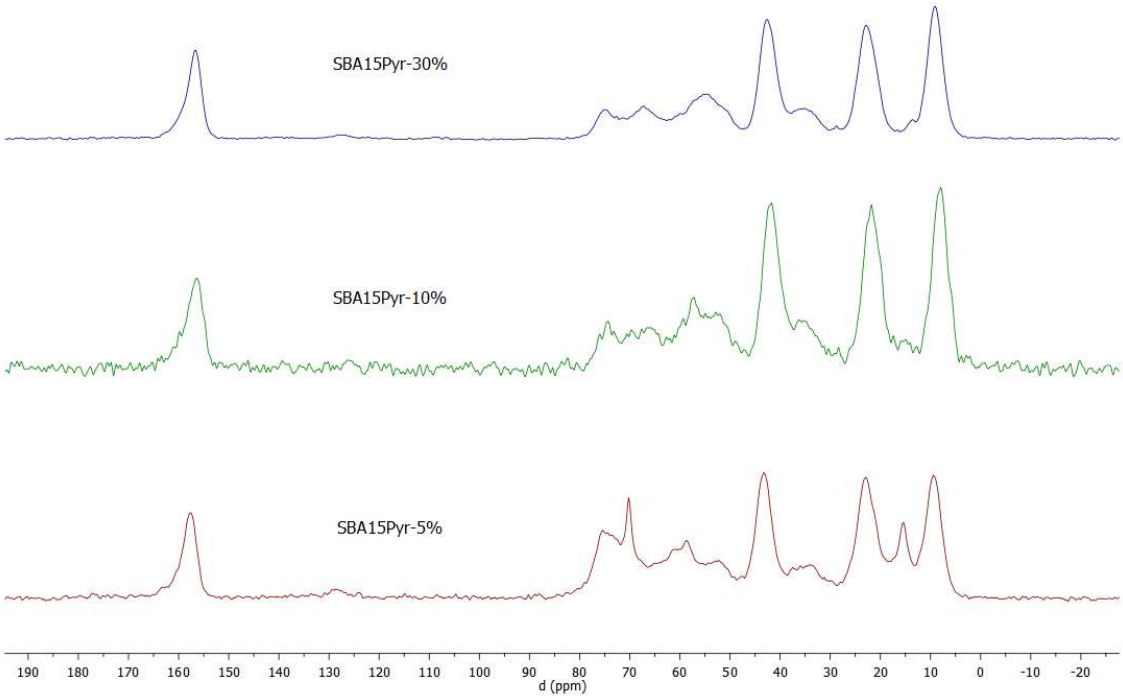


Figure S2. ^{13}C MAS NMR spectra of (a) NOH-Pyr, (b) M41S-Pyr and (c) SBA-15-Pyr materials containing different content of bis-silylated pyrrolidine fragments, obtained after extraction processes.

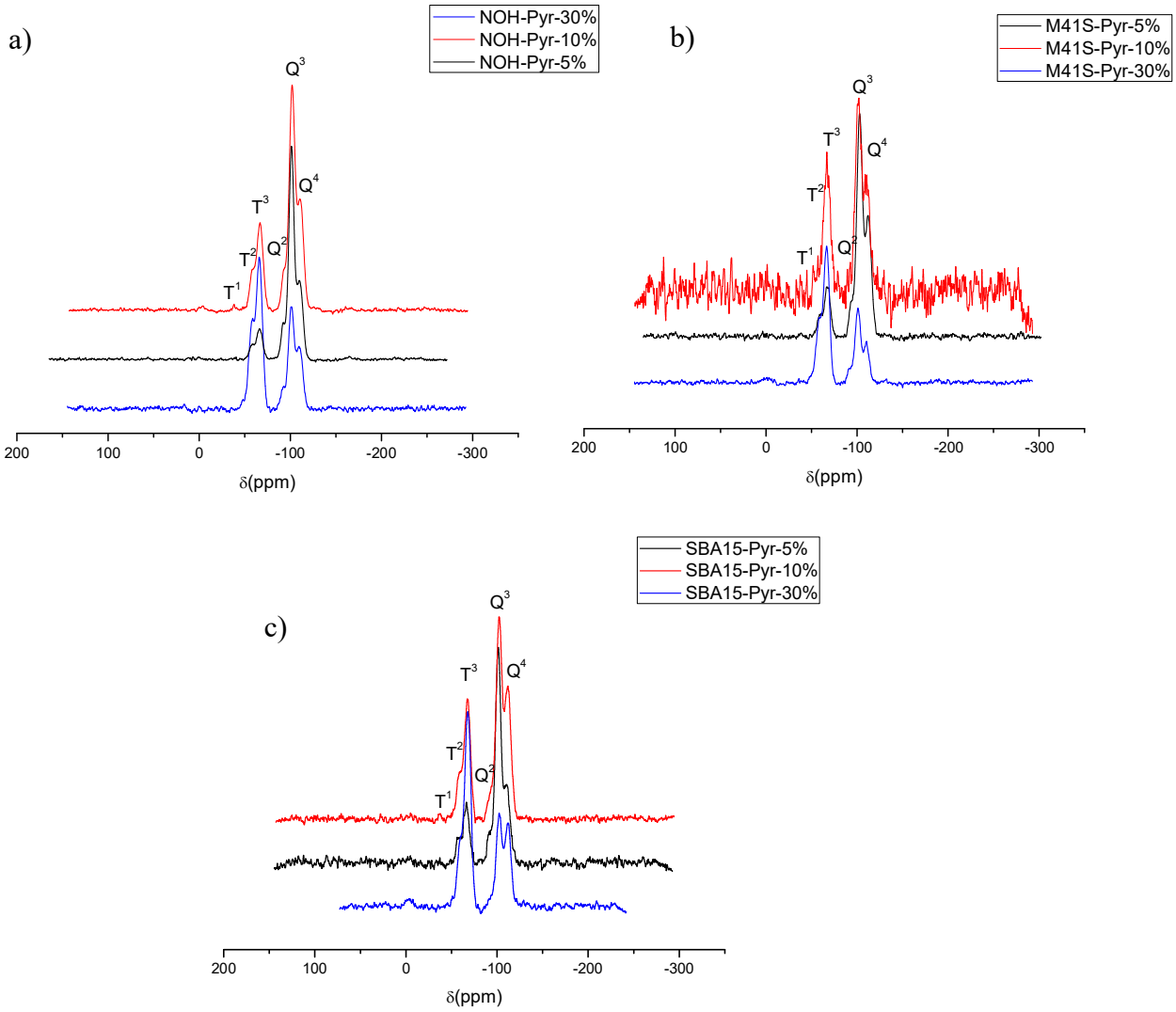


Figure S3. ^{29}Si CP/MAS NMR spectra of (a) NOH-Pyr, (b) M41S-Pyr and (c) SBA-15-Pyr materials, containing different content of bis-silylated pyrrolidine fragments, obtained after extraction processes, with assignment of T- and Q-type silicon atoms.

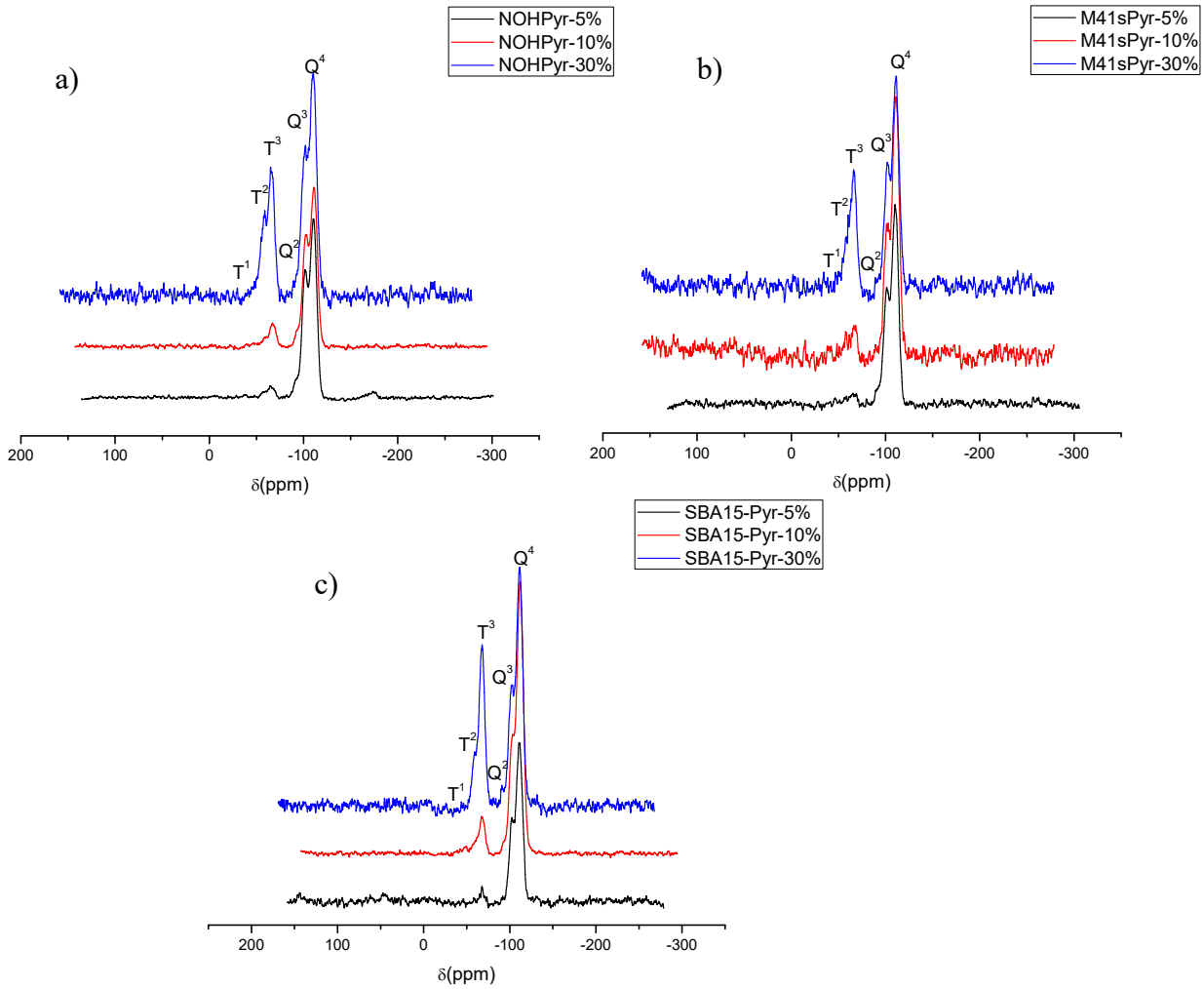


Figure S4. ^{29}Si BD/MAS NMR spectra of (a) NOH-Pyr, (b) M41S-Pyr and (c) SBA-15-Pyr materials, containing different content of bis-silylated pyrrolidine fragments, obtained after extraction processes, with assignment of T- and Q-type silicon atoms.

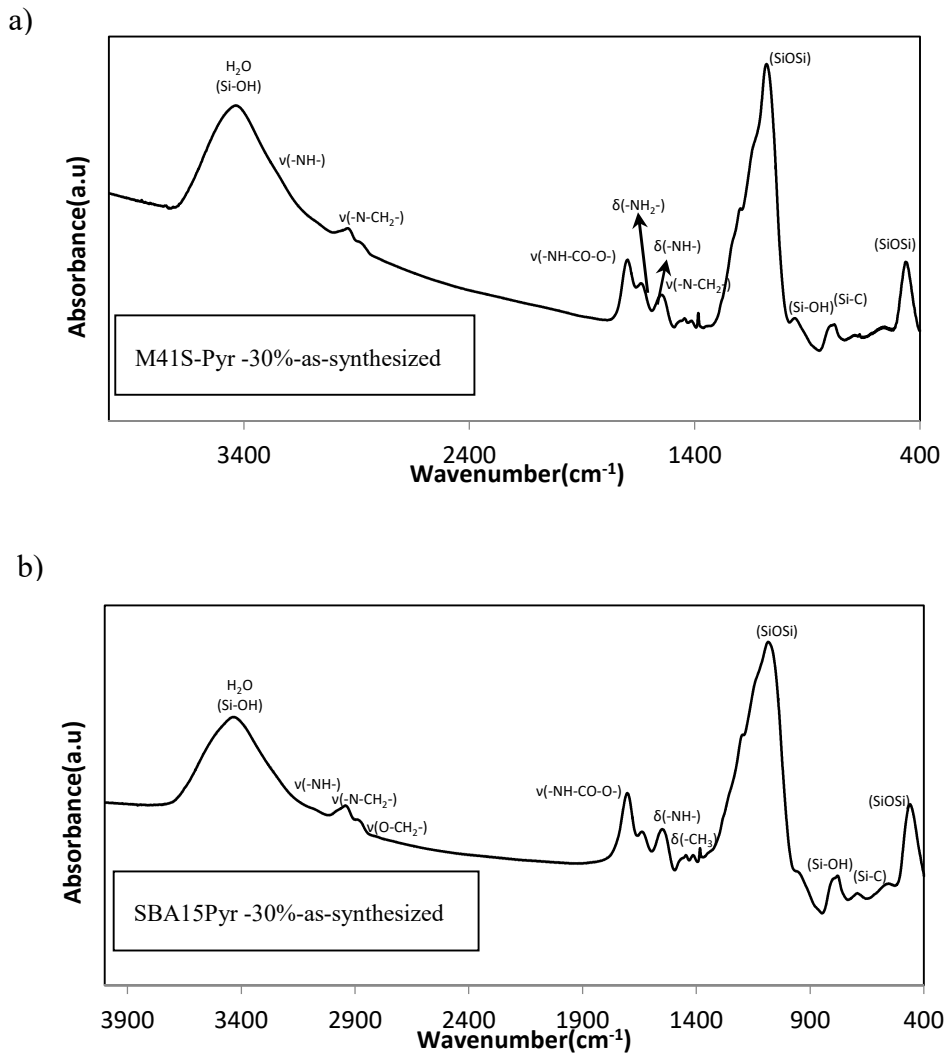
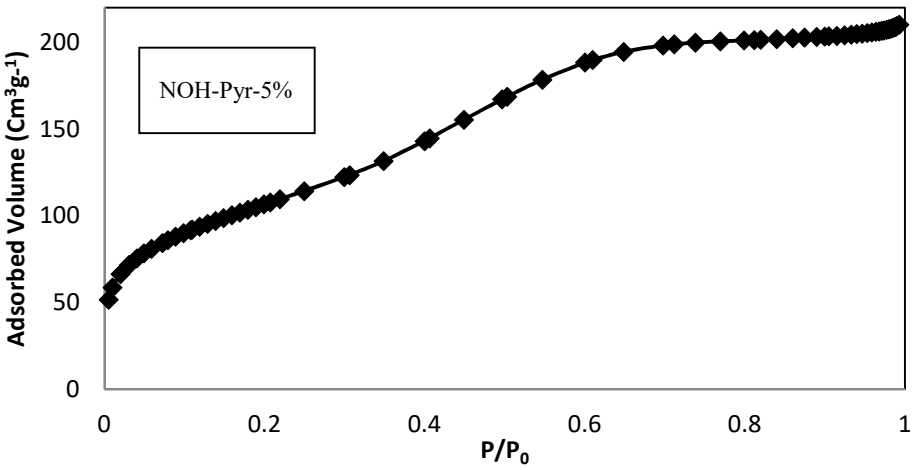
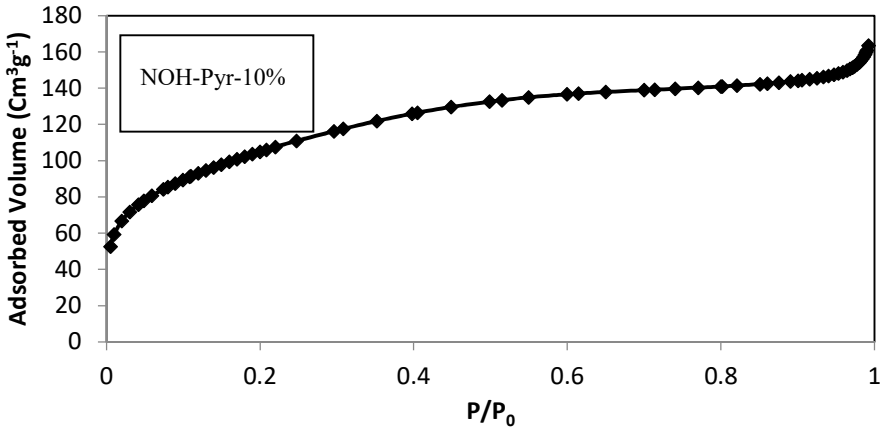
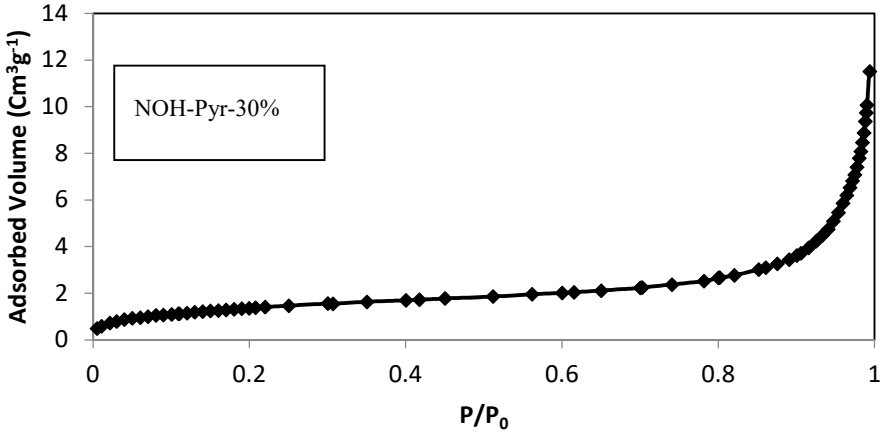


Figure S5. FTIR spectra of as-synthesized (a) M41S-30% and (b) SBA-15-Pyr-30% hybrid materials.

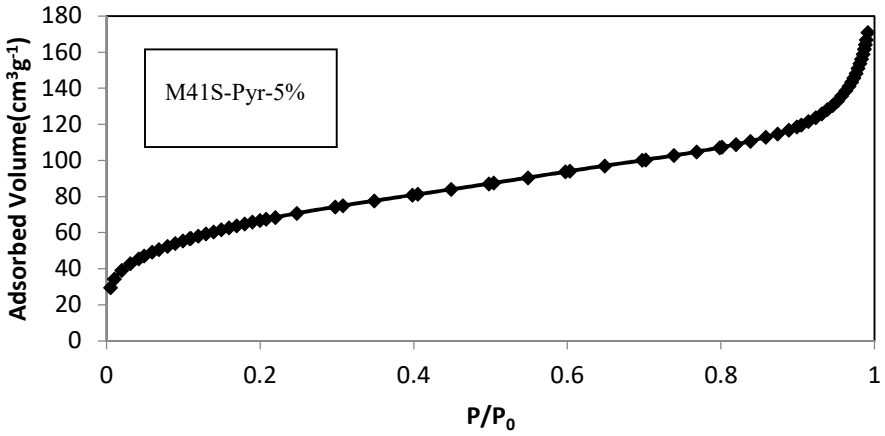
a)

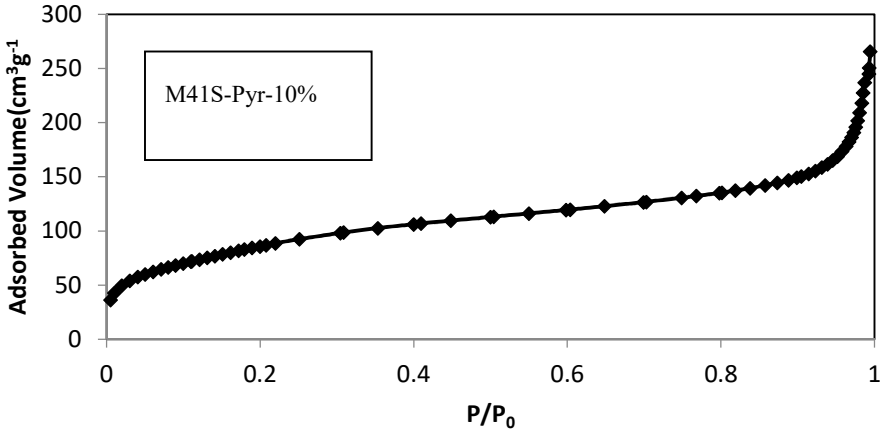

NOH-Pyr-5%
Adsorbed Volume (Cm3g-1)
P/P0
0
50
100
150
200
0
0.2
0.4
0.6
0.8
1

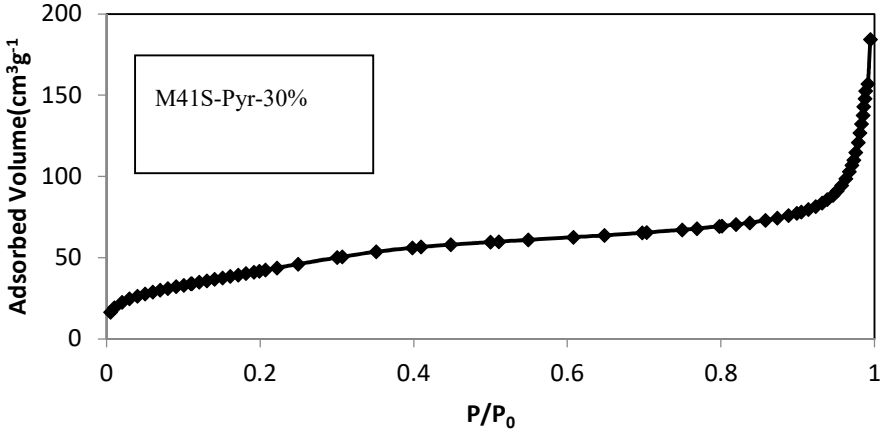

NOH-Pyr-10%
Adsorbed Volume (Cm3g-1)
P/P0
0
20
40
60
80
100
120
140
160
180
0
0.2
0.4
0.6
0.8
1


NOH-Pyr-30%
Adsorbed Volume (Cm3g-1)
P/P0
0
2
4
6
8
10
12
14
0
0.2
0.4
0.6
0.8
1

b)


M41S-Pyr-5%
Adsorbed Volume(cm3g-1)
P/P0
0
20
40
60
80
100
120
140
160
180
0
0.2
0.4
0.6
0.8
1


M41S-Pyr-10%
Adsorbed Volume(cm3g-1
P/P0
0
50
100
150
200
250
300
0
0.2
0.4
0.6
0.8
1


M41S-Pyr-30%
Adsorbed Volume(cm3g-1
P/P0
0
50
100
150
200
0
0.2
0.4
0.6
0.8
1

c)

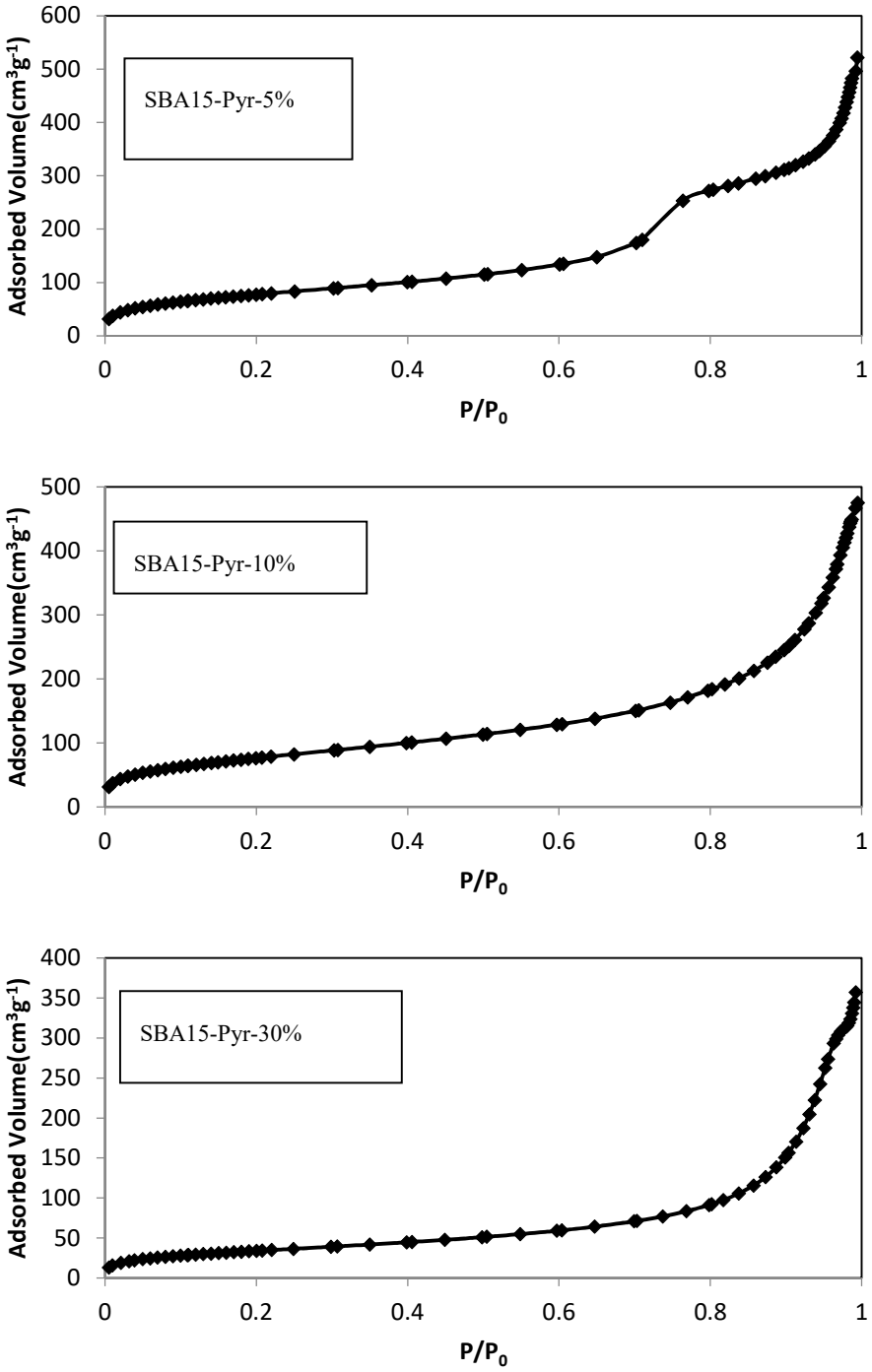


Figure S6. N_2 adsorption isotherms of (a) NOH-Pyr, (b) M41S-Pyr and (c) SBA-15-Pyr materials, containing different content of bis-silylated pyrrolidine fragments, obtained after extraction processes.

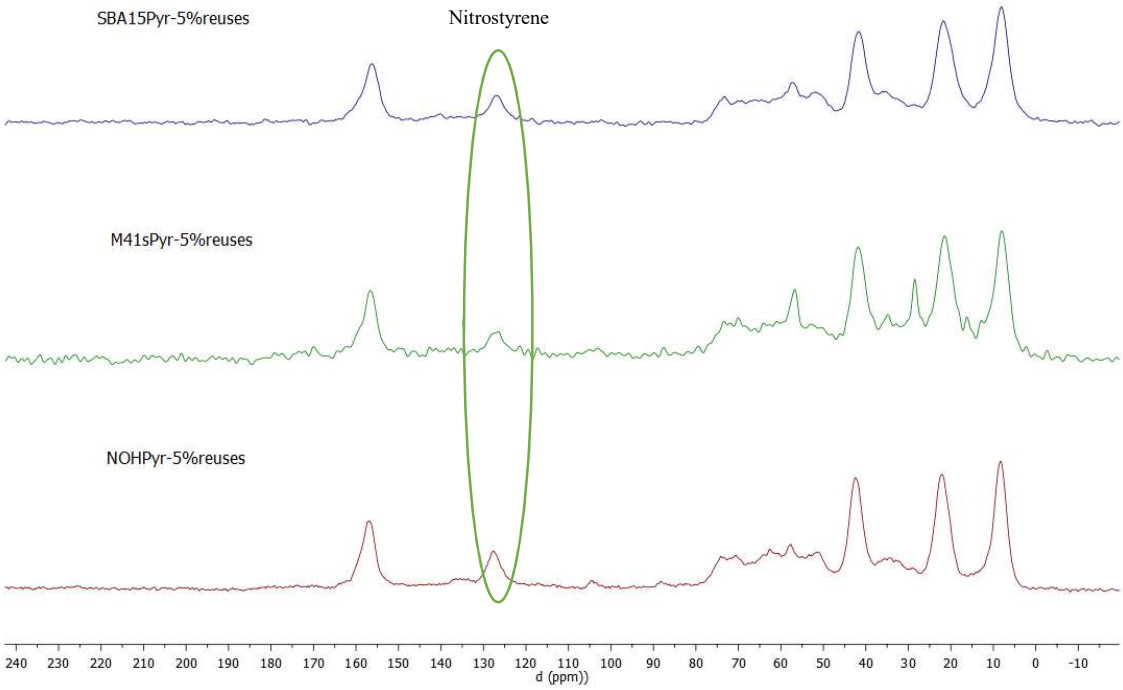


Figure S7. ^{13}C NMR spectra of the different hybrid materials after four/five uses.

Table S1. Integration of T-type and Q-type silicon atoms into the different catalysts obtained after extraction processes.

Catalyst	T^1	T^2	T^3	Q^2	Q^3	Q^4
NOH-Pyr-5%	0.00	0.01	0.03	0.04	0.37	0.56
NOH-Pyr-10%	0.01	0.02	0.07	0.04	0.27	0.54
NOH-Pyr-30%	0.02	0.07	0.22	0.03	0.23	0.45
M41S-Pyr-5%	0.00	0.01	0.03	0.03	0.30	0.54
M41S-Pyr-10%	0.00	0.01	0.03	0.01	0.28	0.79
M41S-Pyr-30%	0.02	0.09	0.20	0.04	0.24	0.41
SBA-15-Pyr-5%	0.00	0.01	0.02	0.01	0.35	1.05
SBA-15-Pyr-10%	0.01	0.02	0.07	0.01	0.21	0.53
SBA-15-Pyr-30%	0.01	0.05	0.28	0.02	0.17	0.47

Table S2. Catalytic results achieved in the presence of the different hybrid materials during several reaction cycles for the enantioselective Michael addition.

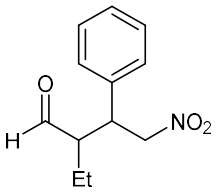
Run	Yield(%)	ee%	dr
NOH-Pyr-5%			
1	96	82%	92:8
2	90	82%	92:8
3	87	82%	90:10
4	89	82%	90:10
5	83	82%	90:10
M41S-Pyr-5%			
1	90	78%	91:9
2	86	78%	91:9
3	82	76%	91:9
SBA-15-Pyr-10%			
1	90	78%	91:9
2	86	78%	91:9
3	82	76%	91:9
4	70	78%	91:9

Table S3. Elemental analysis and C/N molar ratios for NOH-Pyr, M41S-Pyr and SBA-15-Pyr hybrid materials after extraction process and each run.

Run	Catalyst	C%	N%	C/N
0	M41S-Pyr-5%	6.1	1.4	5.0
1	M41S-Pyr-5%	7.1	1.4	5.7
2	M41S-Pyr-5%	7.5	1.4	6.4
3	M41S-Pyr-5%	8.0	1.4	6.7
0	SBA-15-Pyr-10%	10.6	2.6	4.8
1	SBA-15-Pyr-10%	10.7	2.5	5.0
2	SBA-15-Pyr-10%	12.6	2.5	6.0
3	SBA-15-Pyr-10%	13.3	2.4	6.6
0	NOH-Pyr-5%	5.1	1.3	4.6
1	NOH-Pyr-5%	4.9	1.2	4.8
2	NOH-Pyr-5%	6.7	1.5	5.1
3	NOH-Pyr-5%	7.6	1.6	5.5
4	NOH-Pyr-5%	6.8	1.3	6.6

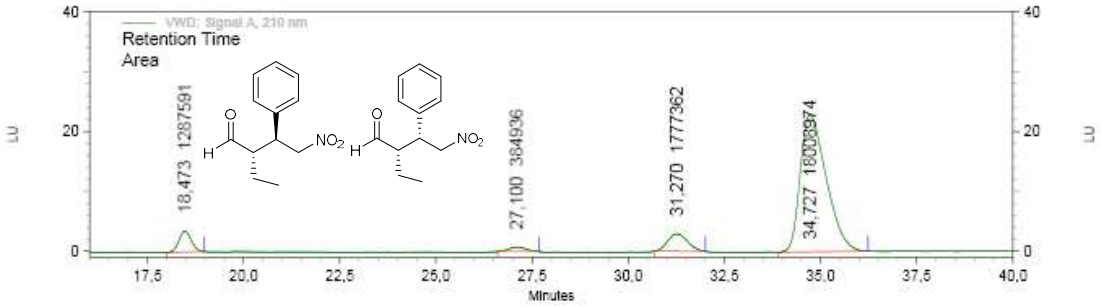
HPLC data

High performance liquid chromatography (HPLC) was performed on an Agilent Technologies chromatograph (1220 Series), using Daicel Chiralpak IC column (4.6 x 250mm).

Product	n-Hexane/*i*-PrOH	Flow rate [mL/min]	λ[nm]	t_R[min]
	90:10	1.0	210	*anti*:18.3,27.0 *syn*: 31.2,35.0

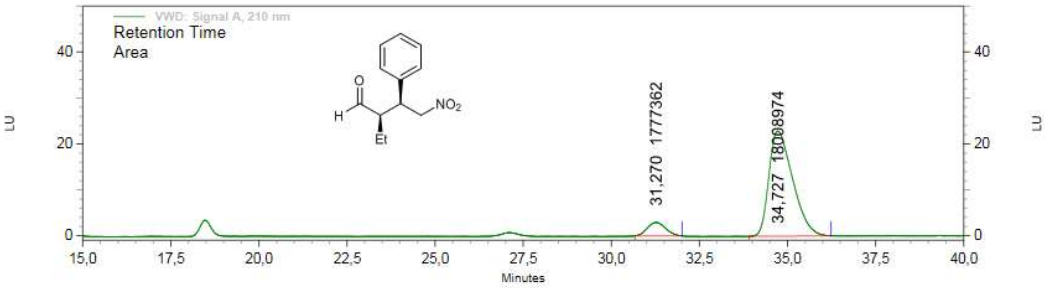
Racemic and chiral HPLC chromatogram for Michael adduct

(2R,3S)-2-ethyl-4-nitro-3-phenylbutanal



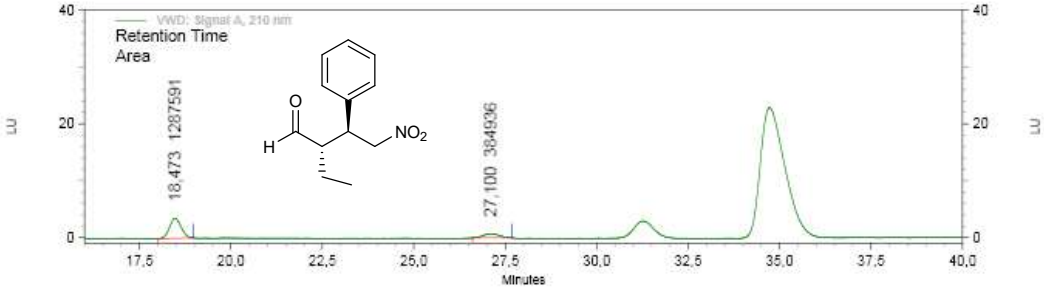
VWD: Signal A, 210 nm
Results

Pk #	*Retention Time*	*Area*	*Area Percent*
1	18,473	1287591	6,000
2	27,100	384936	1,794
3	31,270	1777362	8,283
4	34,727	18008974	83,923
Totals		21458863	100,000



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	49086	31,270	1777362	**8,983**
2	384239	34,727	18008974	**91,017**
Totals	433325		19786336	**100,000**

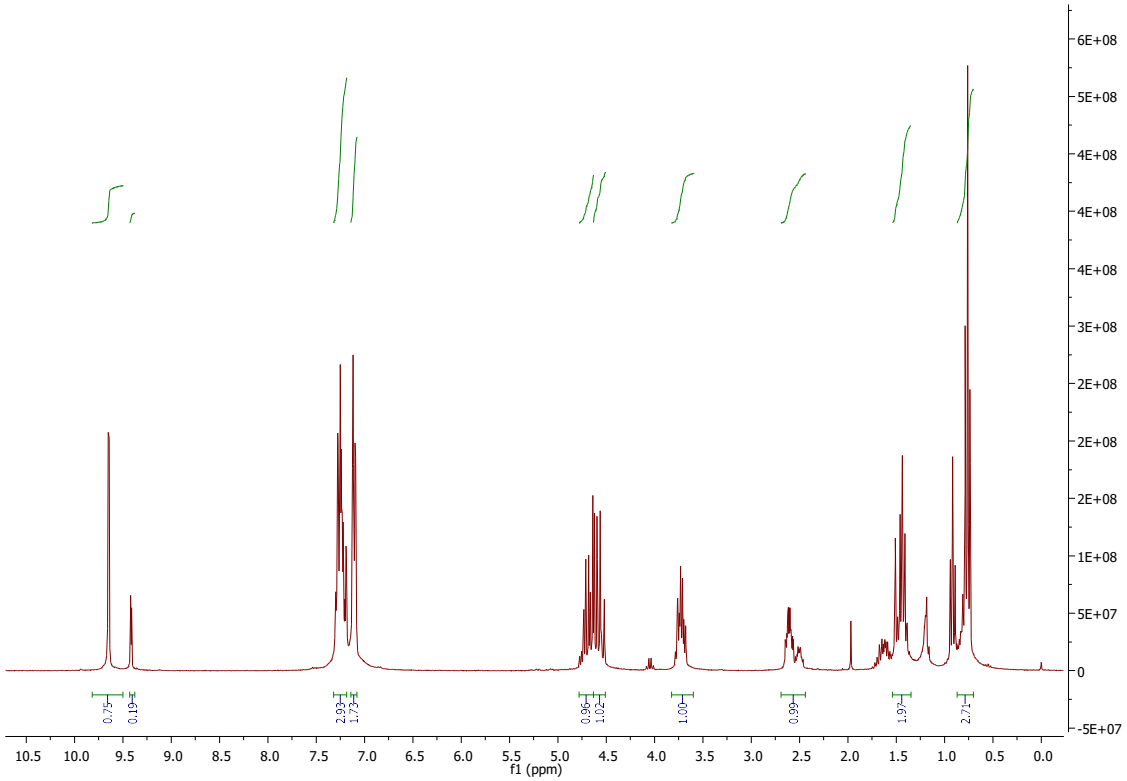


VWD: Signal A, 210 nm Results

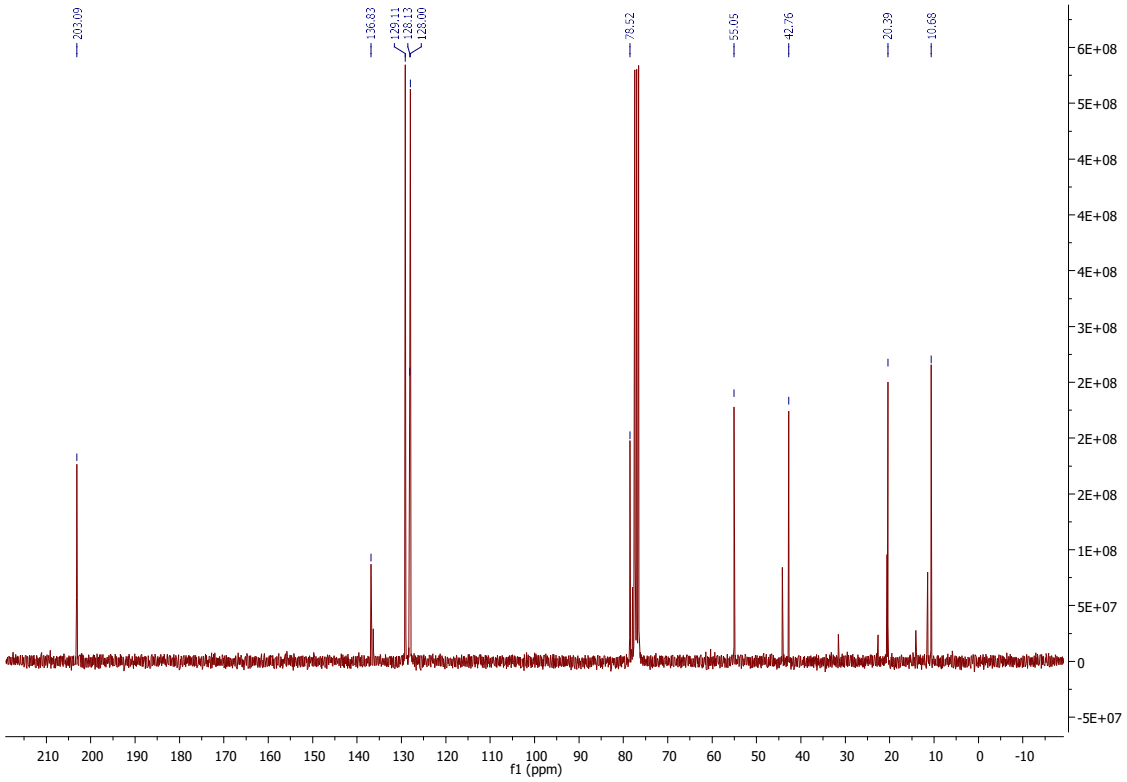
Pk #	*Retention Time*	*Area*	*Area Percent*
1	18,473	1287591	76,985
2	27,100	384936	23,015
Totals		1672527	100,000

and

^{1}H and ^{13}C NMR spectra of Michael adduct



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65 (d, *J* = 2.6 Hz, 1H), 7.31 – 7.18 (m, 3H), 7.11 (m, 2H), 4.70 (dd, *J* = 10.8, 5.4 Hz, 1H), 4.60 (dd, *J* = 12.9, 9.3 Hz, 1H), 3.72 (dt, *J* = 9.6, 5.2 Hz, 1H), 2.61 (dddd, *J* = 9.9, 7.6, 5.3, 2.6 Hz, 1H), 1.54 – 1.37 (m, 3H), 0.76 (t, *J* = 7.5 Hz, 1H).



^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 136.9, 129.1 (x2), 128.1, 128.00 (x2), 78.5, 55.1, 42.8, 20.4, 10.7.