Electronic Supplementary Information

Zr-MOF-808@MCM-41 catalyzed phosgene-free synthesis of polyurethane precursors

Sergio Rojas-Buzo, Pilar García-García,* Avelino Corma*

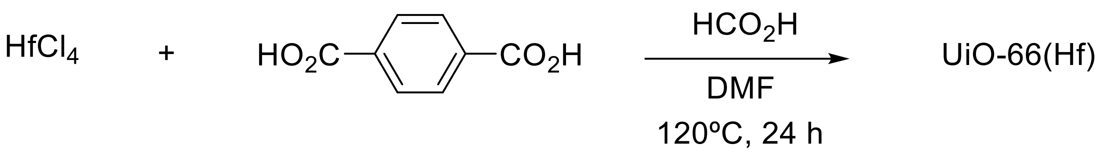
Instituto de Tecnología Química, UPV-CSIC, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas. Avenida de los Naranjos s/n 46022 Valencia, Spain.
Email: pgargar@itq.upv.es; acorma@itq.upv.es

Experimental section. General Information.

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents employed in the reactions were purified using a solvent purification system (SPS) MBraun 800. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by thin layer chromatography on silica gel pre-coated aluminium plates using fluorescence quenching with UV light at 254 nm or $KMnO_4$. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.040-0.063 mm). Chemical yields refer to pure isolated substances unless stated otherwise. All the products obtained were characterised by GC-MS, ^{1}H- and ^{13}C-NMR, and DEPT. When available, characterisation given in the literature was used for comparison. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone using dodecane as an external standard otherwise indicated. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. ^{1}H and ^{13}C NMR were recorded on a Bruker 300 spectrometer and the chemical shifts are reported in ppm relative to residual proton solvents signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublets), coupling constant and integration. Data for ^{13}C NMR spectra are reported in chemical shift (δ, ppm). C, N, and H contents were determined with a Carlo Erba 1106 elemental analyzer. Thermogravimetric and differential thermal analysis (TGA-DTA) were conducted in an air stream with a Metler Toledo TGA/SDTA 851E analyzer. Solid state MAS-NMR spectra were recorded at room temperature under magic angle spinning (MAS) in a Brucker AV-400 spectrometer. The ^{13}C cross-polarization (CP) spectrum was acquired by using a 7 mm Bruker BL-7 probe and at a sample spinning rate of 5kHz. ^{13}C was referred to adamantane. FTIR spectra were recorded with a Nicolet 710 spectrometer (4 cm^{-1} resolution) using conventional greaseless cell. IR spectra of the organic precursors were recorded on KBr disks at room temperature or by impregnating the windows with a dichloromethane solution of the compound and leaving to evaporate before analysis. Photoelectron spectra were recorded using a SPECS spectrometer equipped with a 150MCD-9 Phoibos detector and using a non monochromatic Al Kα (1486.6eV) X-ray source. Spectra were recorded at 25 ºC using an analyzer pass energy of 30 eV, an X-ray power of 100W and under operating pressure of 10^{-9} mbar. Samples were fixed on a Mo sample holder. Spectra treatment has been performed using the CASA software.

1. Synthesis of Zr- and Hf-based MOFs and characterization

1.1. UiO-66(Hf): It was prepared according to the reported method in the literature.[1]



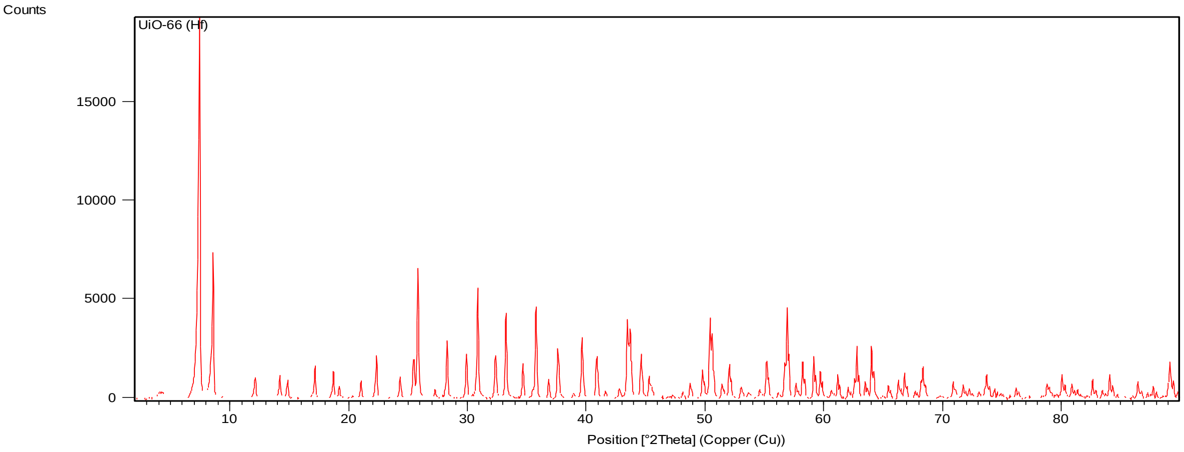


Figure S1. XRD pattern of UiO-66 (Hf)

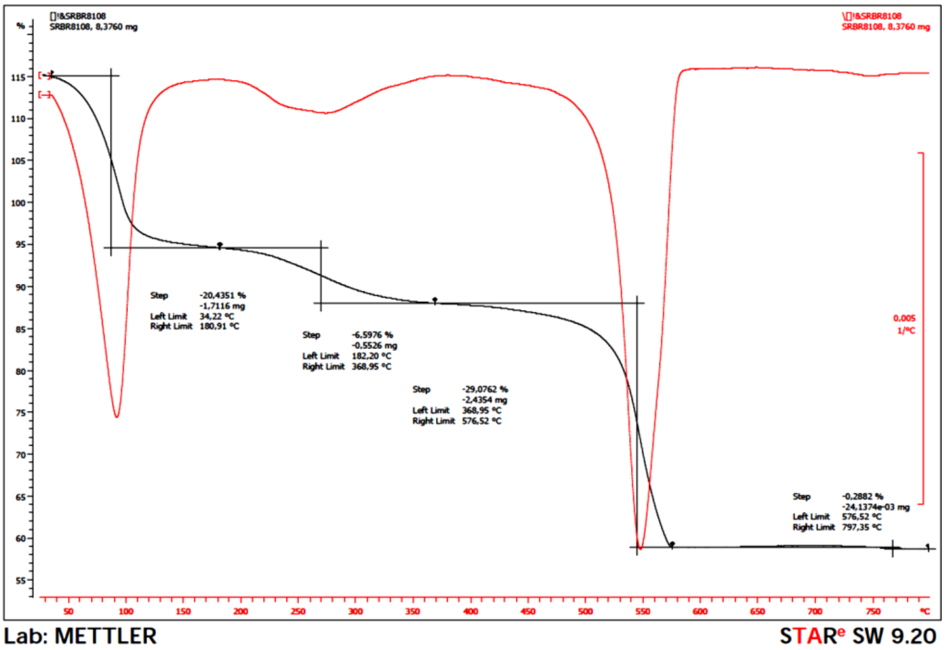


Figure S2. TGA and DTA curves of UiO-66 (Hf) sample.

Table S1. Chemical analysis of UiO-66 (Hf) sample.

					Org.Cont.[a]	
Sample	**C**[a]	**H**[a]	**N**[a]	**Metal**[b]	**CHN**[c]	**TGA**[d]
UiO-66 (Hf)	20.2	1.6	0.2	44	22	35.7

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis, [d]Organic content from thermogravimetrical analysis without taking into account hydration water.

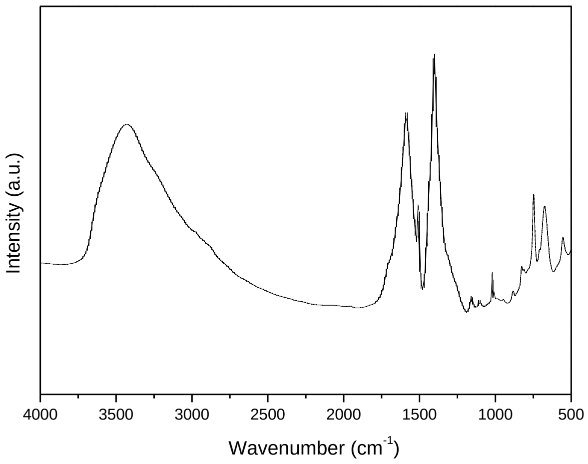


Figure S3. FTIR spectrum of UiO-66(Hf) sample

Table S2. Textural Characteristic of UiO-66(Hf).

Sample	BET Surface Area/m^2g^{-1}	Total Pore Volume/cm^3g^{-1}
UiO-66(Hf).	584	0.45

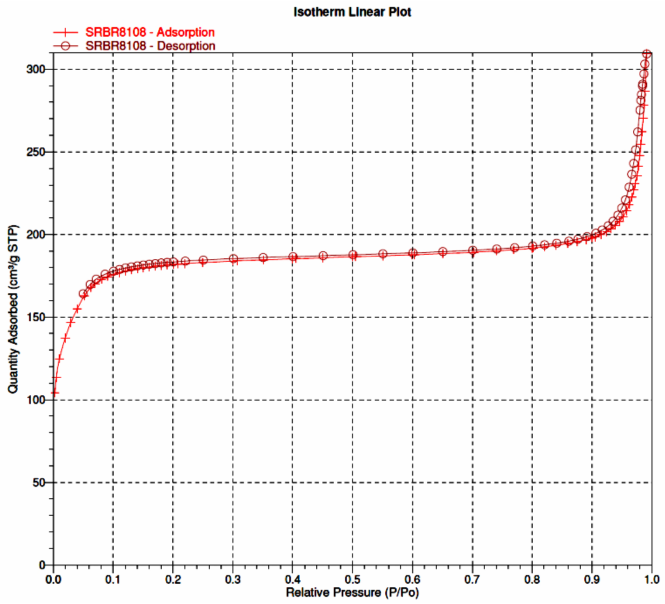
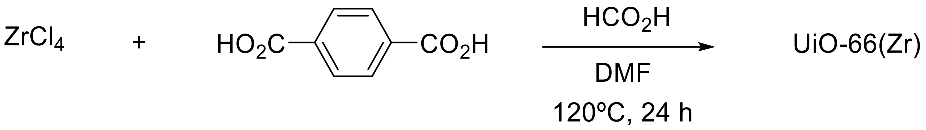


Figure S4. N_2 adsorption and desorption isotherm of UiO-66(Hf) sample

1.2. UiO-66 (Zr): UiO-66-Zr was obtained by the same procedure[1] as for UiO-66(Hf) except $ZrCl_4$ was used instead of $HfCl_4$.



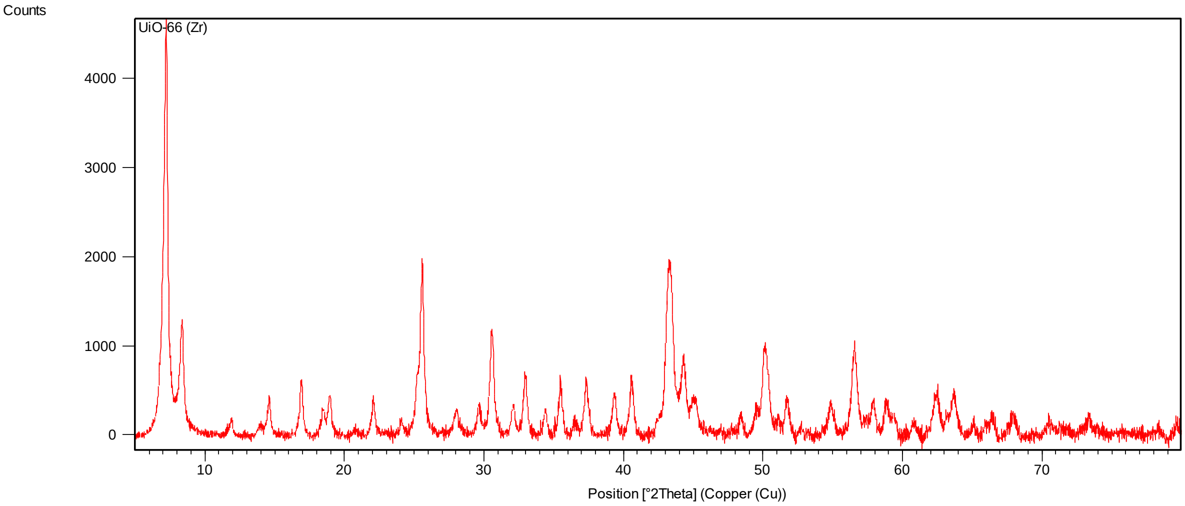


Figure S5. XRD pattern of UiO-66(Zr)

Table S3. Chemical analysis of UiO-66(Zr) sample.

					Org.Cont.[a]	
Sample	**C**[a]	**H**[a]	**N**[a]	**Metal**[b]	**CHN**[c]	**TGA**[d]
UiO-66 (Zr)	26.8	1.9	0.5	28	29.2	47.5

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis, [d]Organic content from thermogravimetrical analysis without taking into account hydration water.

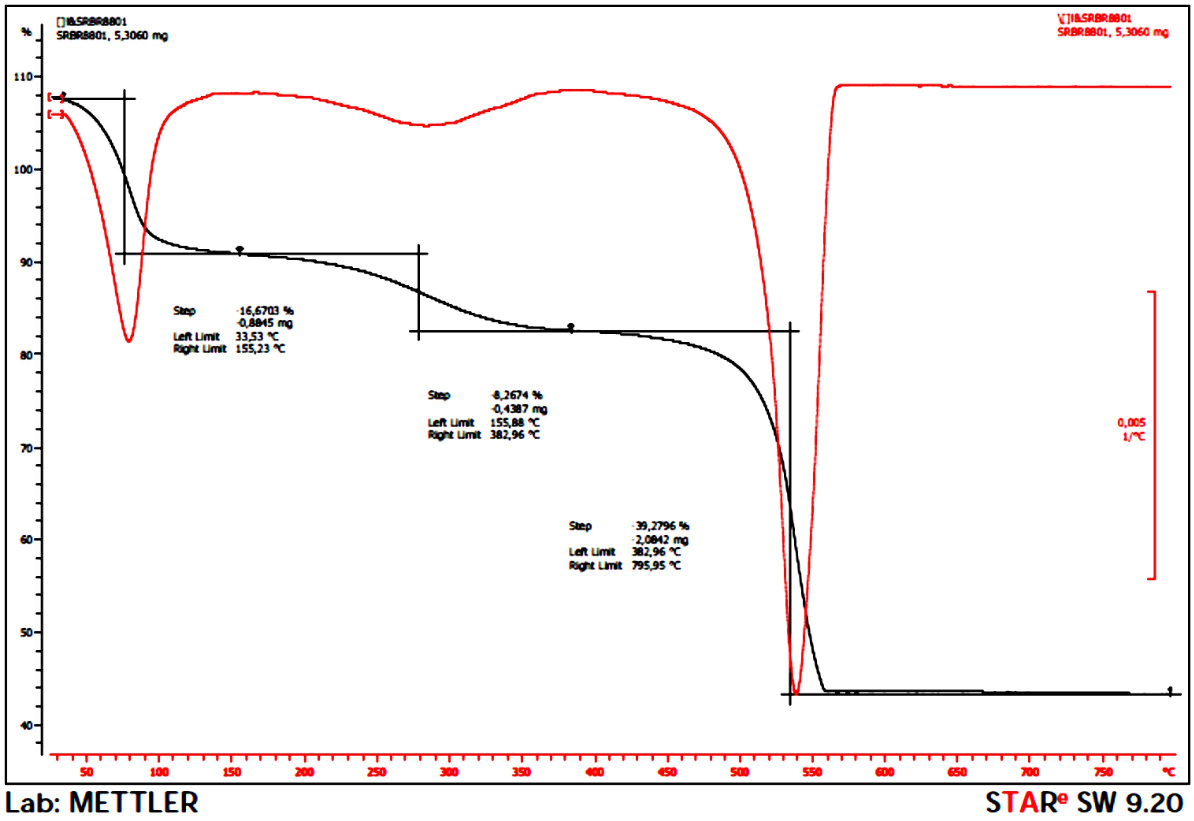


Figure S6. TGA and DTA curves of UiO-66(Zr) sample.

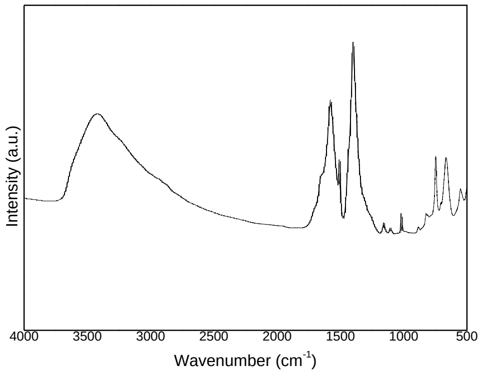


Figure S7. FTIR spectrum of UiO-66(Zr) sample

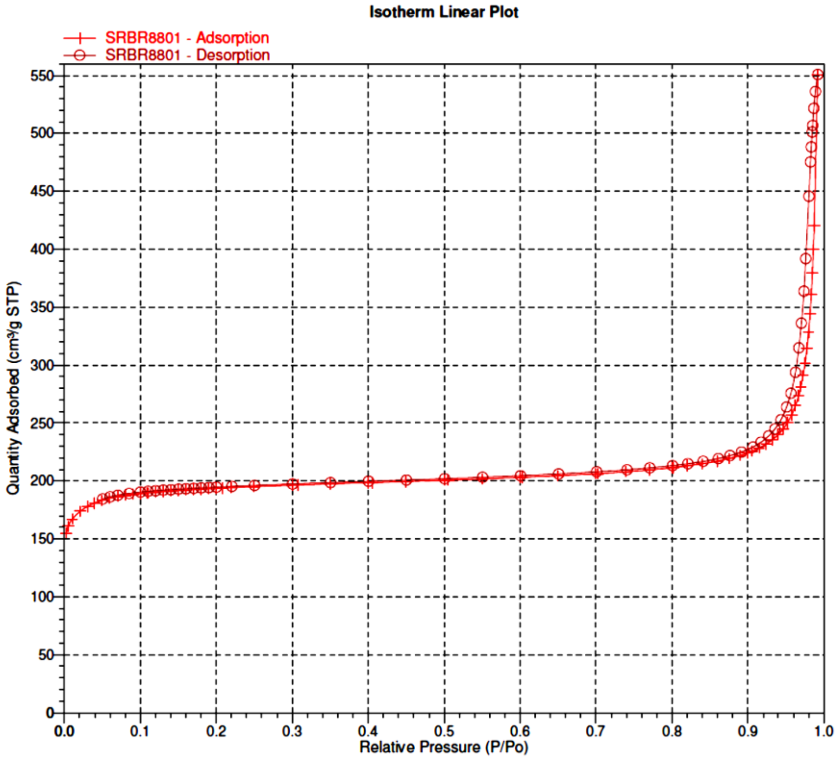
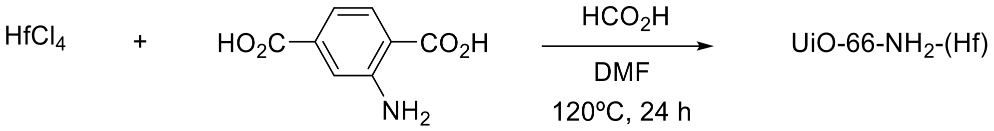


Figure S8. N_2 adsorption and desorption isotherm of UiO-66(Zr) sample

Table S4. Textural Characteristic of UiO-66(Zr).

Sample	BET Surface Area/m^2g^{-1}	Total Pore Volume/cm^3g^{-1}
UiO-66 (Zr).	619	0.78

1.3. UiO-66-NH$_2$(Hf): UiO-66-NH$_2$(Hf) was obtained by the same procedure[1] as for UiO-66 (Hf) except 2-aminoterephthalic acid was used instead of terephthalic acid.



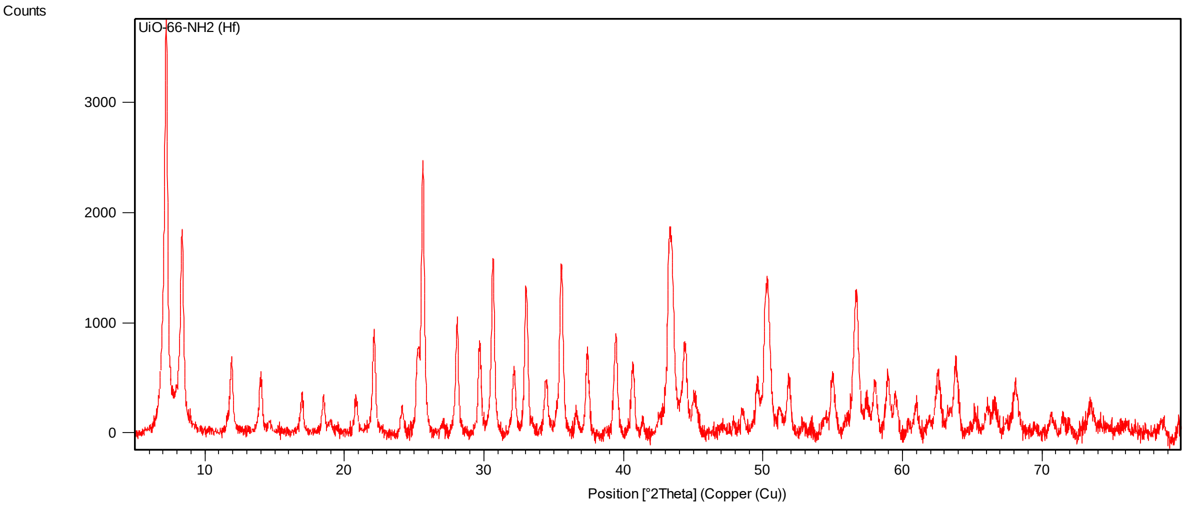


Figure S9. XRD pattern of UiO-66-NH$_2$(Hf)

Table S5. Chemical analysis of UiO-66-NH$_2$(Hf) sample.

					Org.Cont.[a]	
Sample	**C[a]**	**H[a]**	**N[a]**	**Metal[b]**	**CHN[c]**	**TGA[d]**
UiO-66-NH$_2$(Hf)	20.1	2.1	2.8	38	25	40

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis, [d]Organic content from thermogravimetrical analysis without taking into account hydration water.

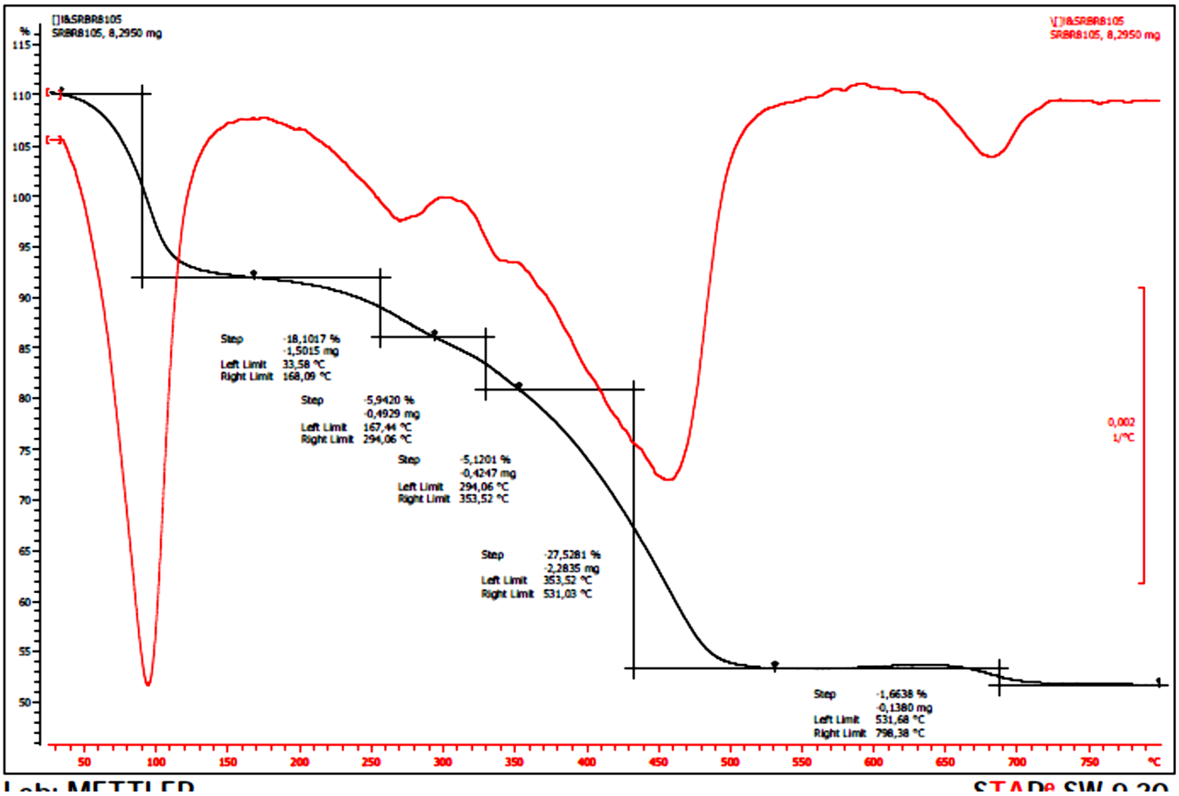


Figure S10. TGA and DTA curves of UiO-66-NH_2(Hf) sample.

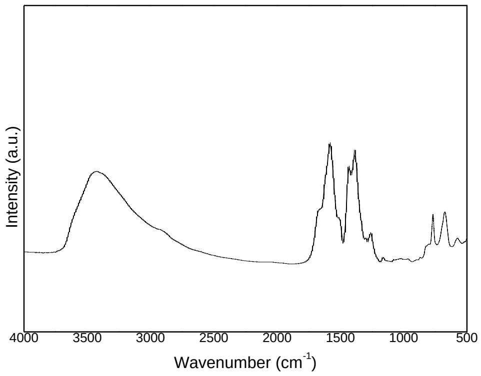


Figure S11. FTIR spectrum of UiO-66-NH_2(Hf) sample

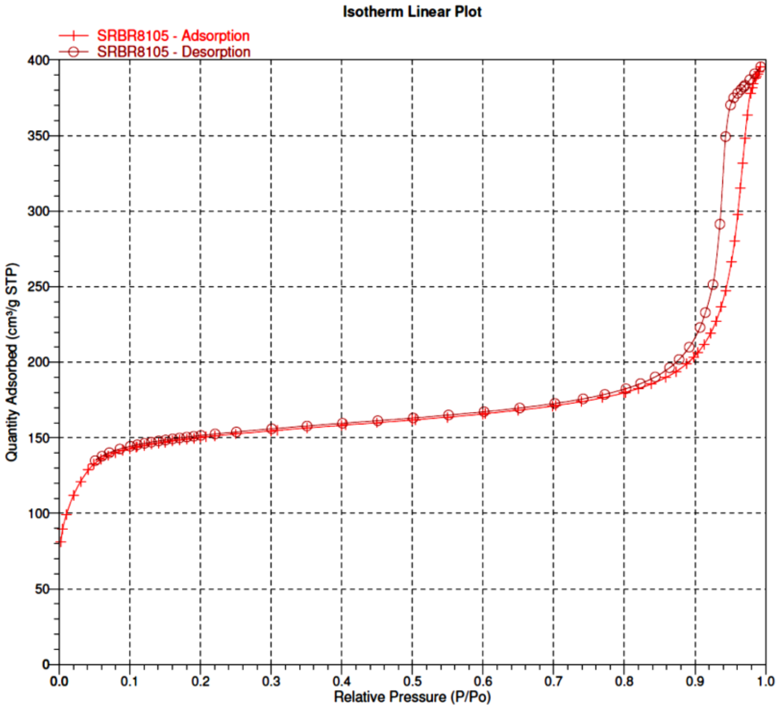
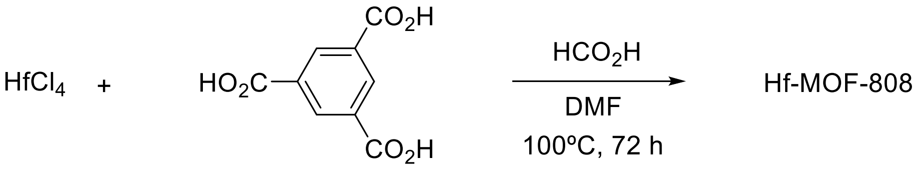


Figure S12. N_2 adsorption and desorption isotherm of UiO-66-NH_2(Hf) sample

Table S6. Textural Characteristic of UiO-66-NH_2(Hf)

Sample	BET Surface Area/m^2g^{-1}	Total Pore Volume/cm^3g^{-1}
UiO-66-NH_2(Hf)	490	0.60

1.4. Hf-MOF-808: It was prepared according to the reported method in the literature[2]



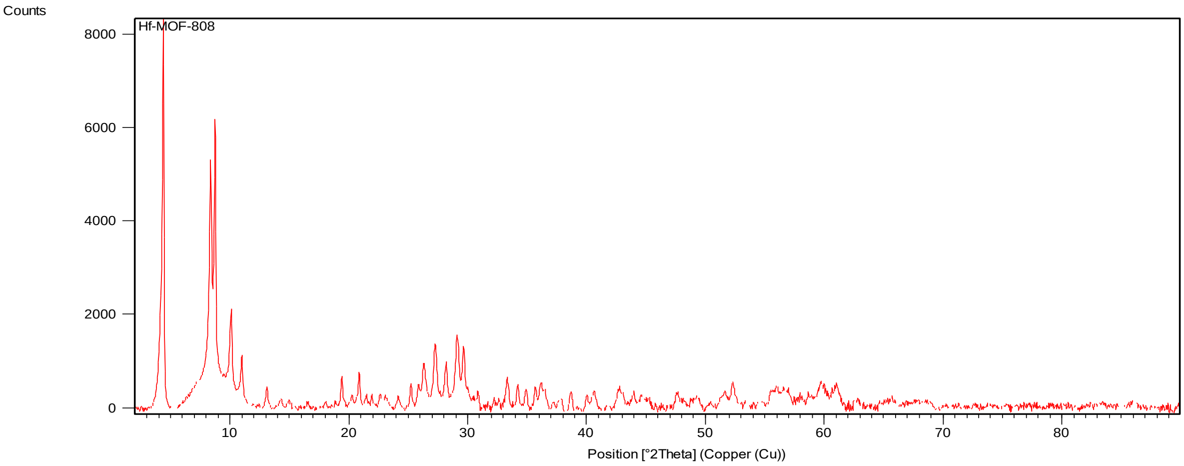


Figure S13. XRD pattern of Hf-MOF-808

Table S8. Chemical analysis of Hf-MOF-808 sample.

Sample	C[a]	H[a]	N[a]	Metal[b]	Org.Cont.[a] CHN[c]	Org.Cont.[a] TGA[d]
Hf-MOF-808	13.9	1.3	0.3	46	15.5	29

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis, [d]Organic content from thermogravimetrical analysis without taking into account hydration water.

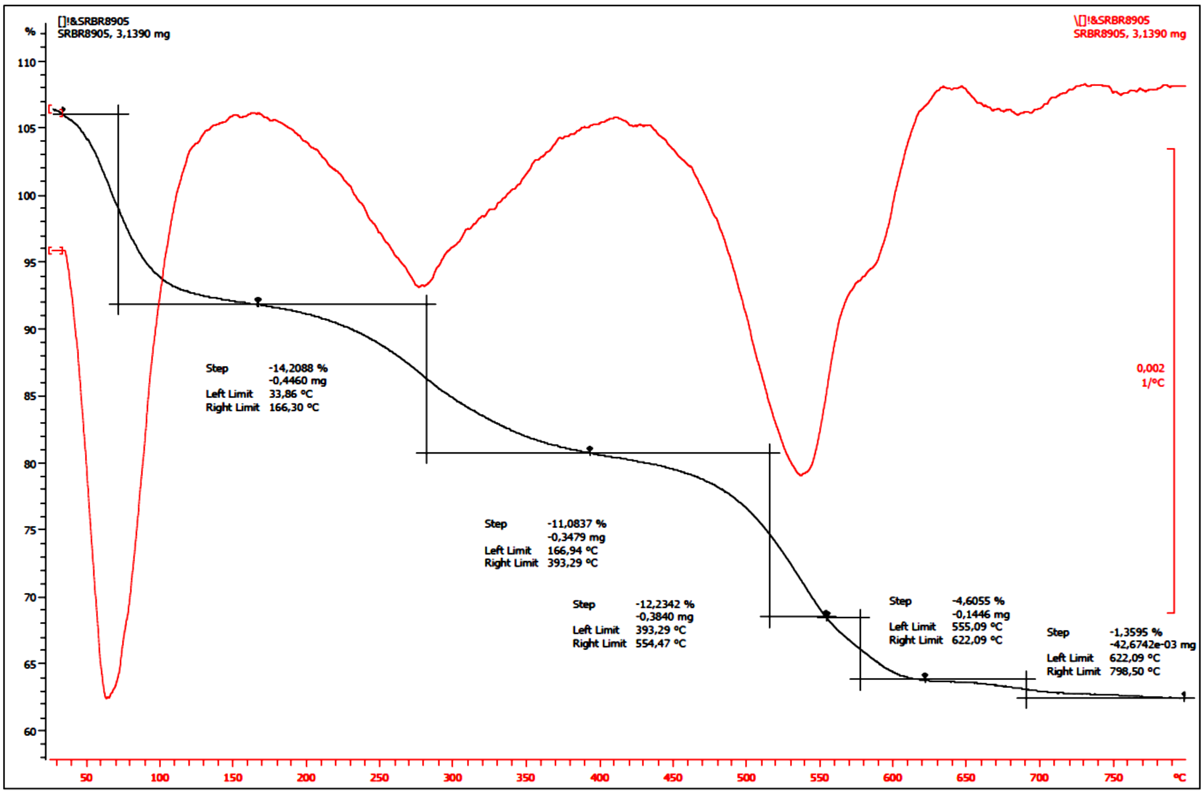


Figure S14. TGA and DTA curves of Hf-MOF-808 sample.

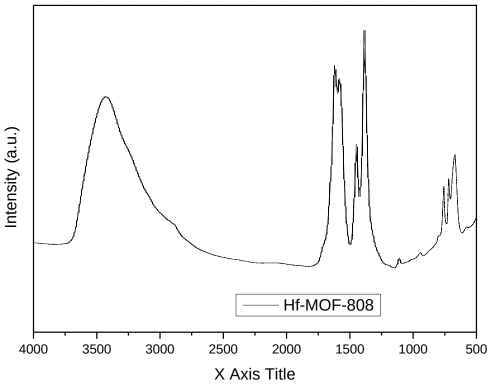


Figure S15. FTIR spectrum of Hf-MOF-808 sample

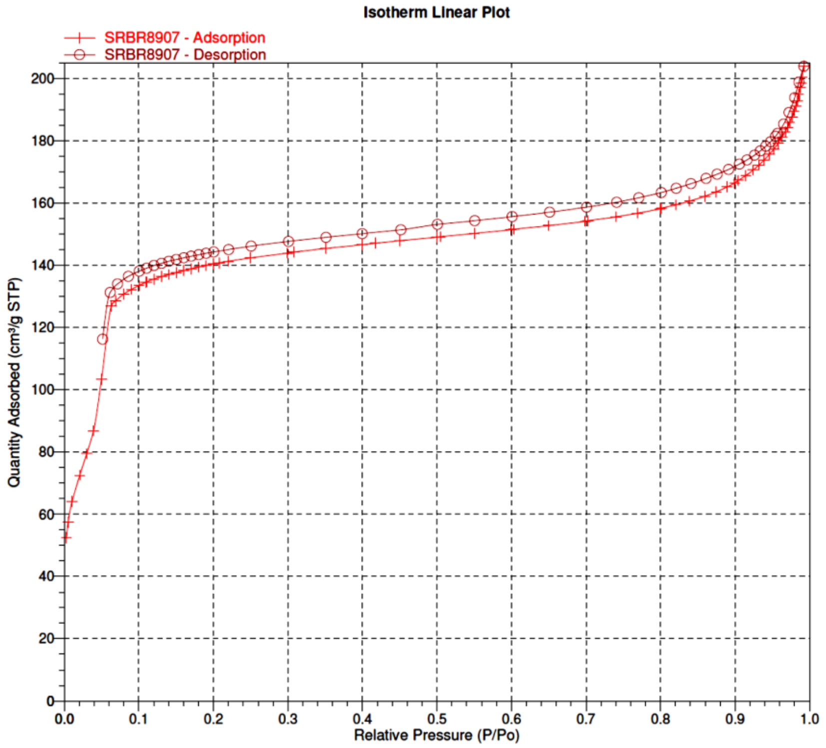


Figure S16. N_2 adsorption and desorption isotherm of Hf-MOF-808 sample

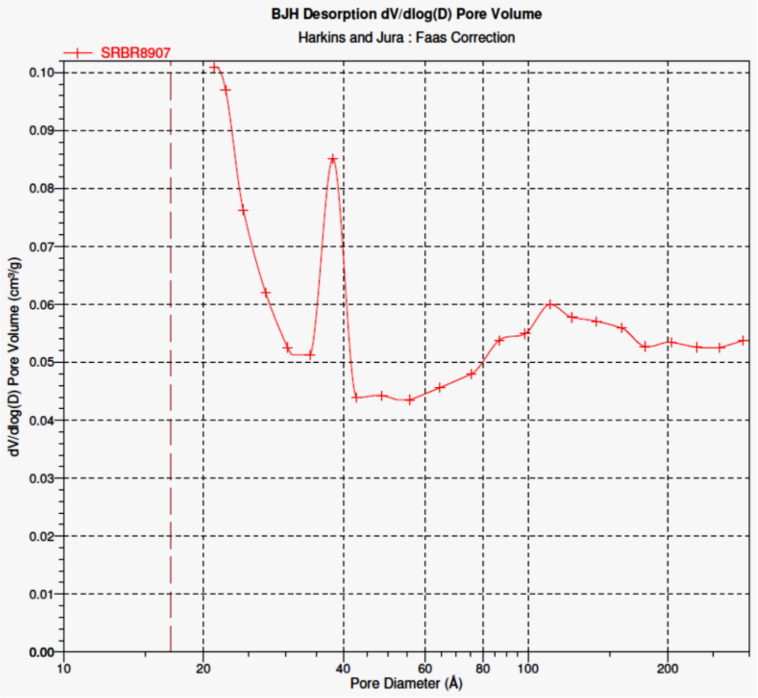
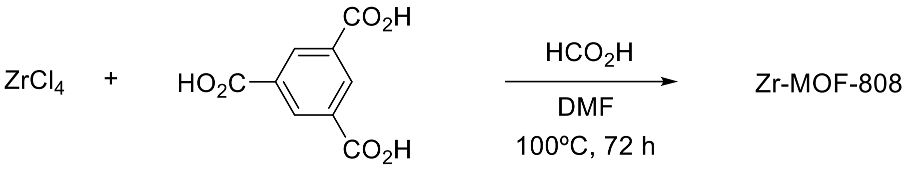


Figure S17. Pore size distribution of Hf-MOF-808 sample calculated by BJH model.

Table S9. Textural Characteristic of Hf-MOF-808.

Sample	BET Surface Area/m^2g^{-1}	Total Pore Volume/cm^3g^{-1}
Hf-MOF-808	458	0.30

1.5. Zr-MOF-808: Zr-MOF-808 was obtained by the same procedure[2] as for Hf-MOF-808 except $ZrCl_4$ was used instead of $HfCl_4$.



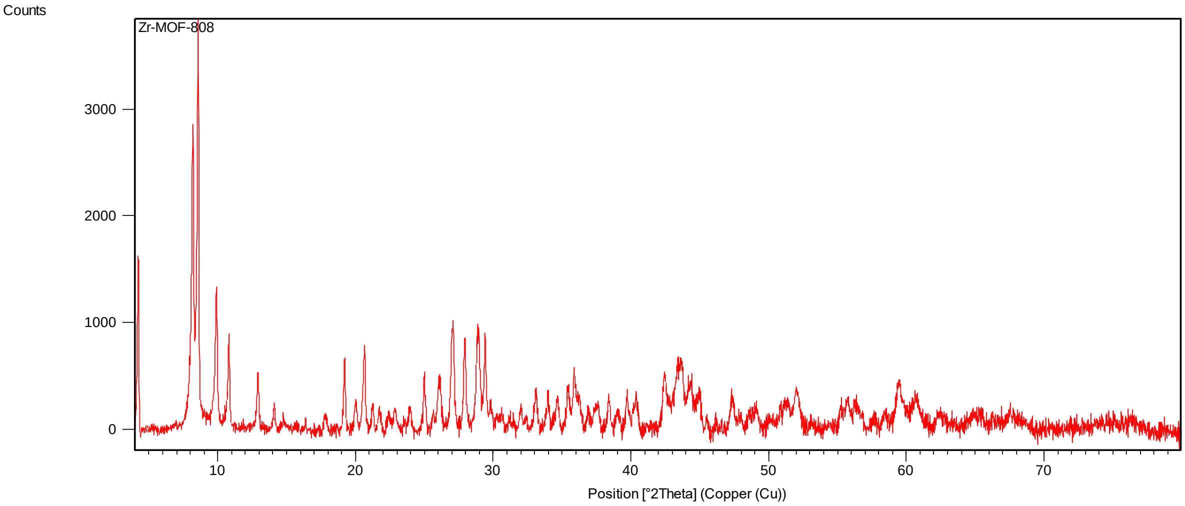


Figure S18. XRD pattern of Zr-MOF-808

Table S10. Chemical analysis of Zr-MOF-808 sample.

					Org.Cont.[a]	
Sample	**C[a]**	**H[a]**	**N[a]**	**Metal[b]**	**CHN[c]**	**TGA[d]**
Zr-MOF-808	19.6	2.7	1.1	31	23.4	42

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis, [d]Organic content from thermogravimetrical analysis without taking into account hydration water.

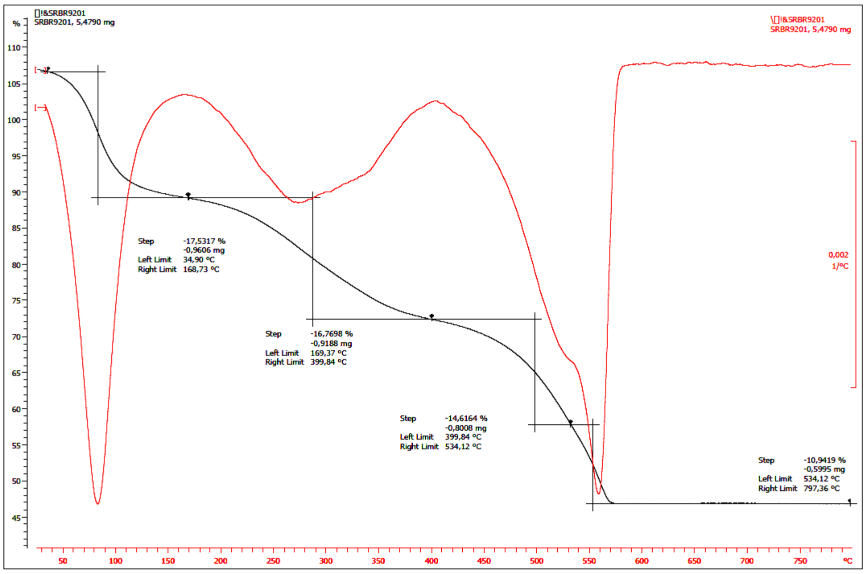


Figure S19. TGA and DTA curves of Zr-MOF-808 sample.

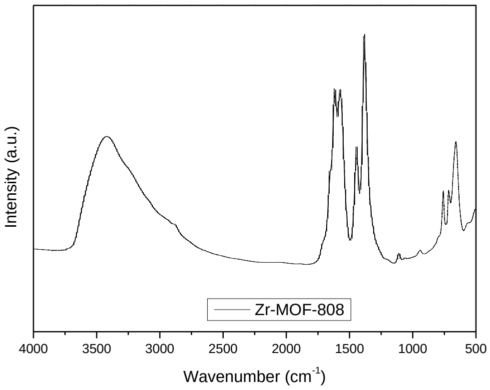


Figure S20. FTIR spectrum of Zr-MOF-808 sample

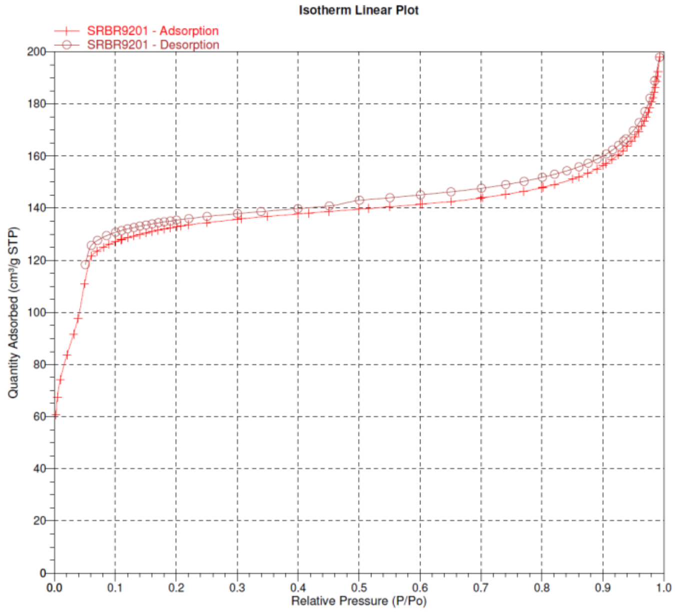


Figure S21. N_2 adsorption and desorption isotherm of Zr-MOF-808 sample

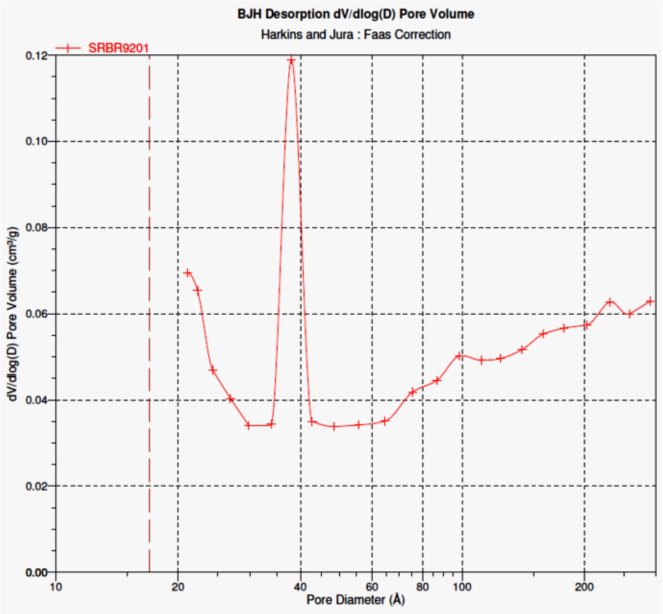


Figure S22. Pore size distribution of Zr-MOF-808 sample calculated by BJH model.

Table S11. Textural characteristics of Zr-MOF-808.

Sample	BET Surface Area/m^2g^{-1}	Total Pore Volume/cm^3g^{-1}
Zr-MOF-808	431	0.28

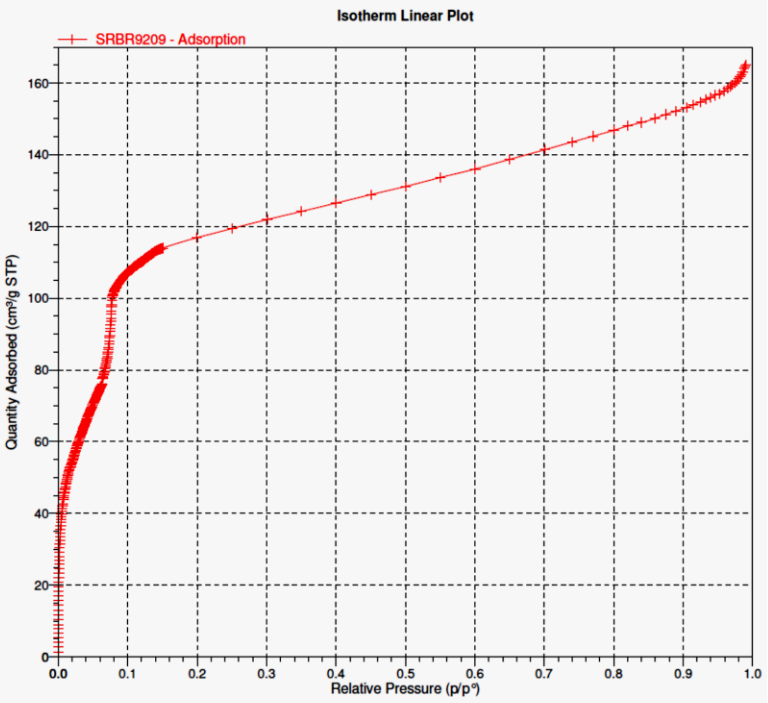


Figure S23. Ar adsorption isotherm of Zr-MOF-808 sample

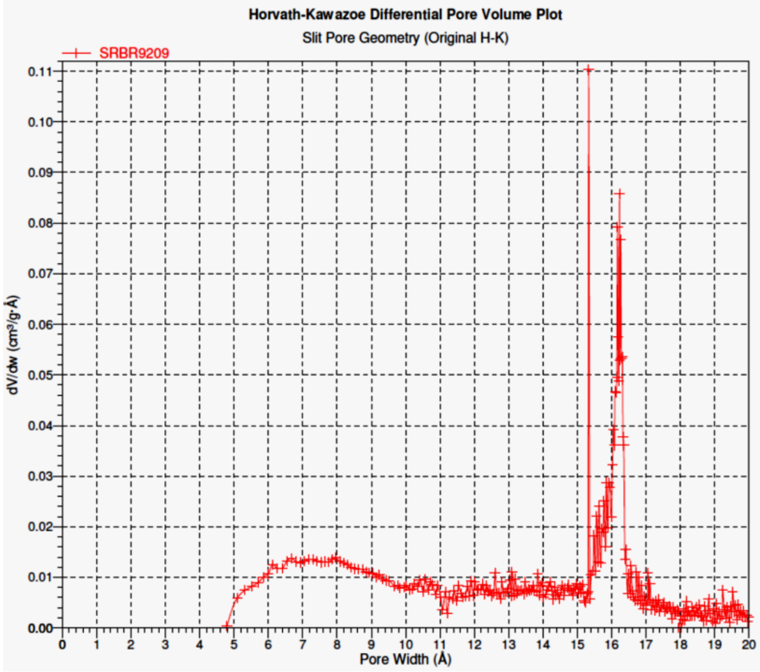


Figure S24. Pore size distribution of Zr-MOF-808 calculated by the Hörvath-Kawazoe model.

2. Synthesis of Zr-MOF-808@MCM-41:

First, 1,3,5-benzenetricarboxylic acid (44.3 mg, 0.2 mmol) was deprotonated using a solution of triethylamine (62.5 mg, 0.6 mmol) in water (1.7 mL) to give a ligand salt precursor. Secondly, 500 mg of MCM-41 were impregnated with the ligand salt solution and then dried at 50 ºC under vacuum in a rotary evaporator for 2 h. The resulting dry material was treated with a nitrogen flow saturated with HCl for 2 h at room temperature and then purged with a nitrogen flow for 2 h to remove the excess of HCl. The metal salt precursor was prepared dissolving $ZrCl_4$ (90.2 mg, 0.4 mmol) in water (1.2 mL) and the solid obtained previously was impregnated with this solution. The resulting solid was then dried at 50 ºC under vacuum in a rotary evaporator for 2 h. The obtained solid was divided in three parts (150 mg each), which were added in three autoclaves (35 mL) along with DMF (7 mL) and HCOOH (7 mL). The solvothermal synthesis was carried out at 100ºC for 72 h. The resulting catalyst was washed with water to remove the unreacted metal or organic salts and with DMF and acetone in order to remove the organic components. When the solid was used in catalytic tests, it was activated and heated at 100 ºC during 12 h to remove water and volatile organic solvent.

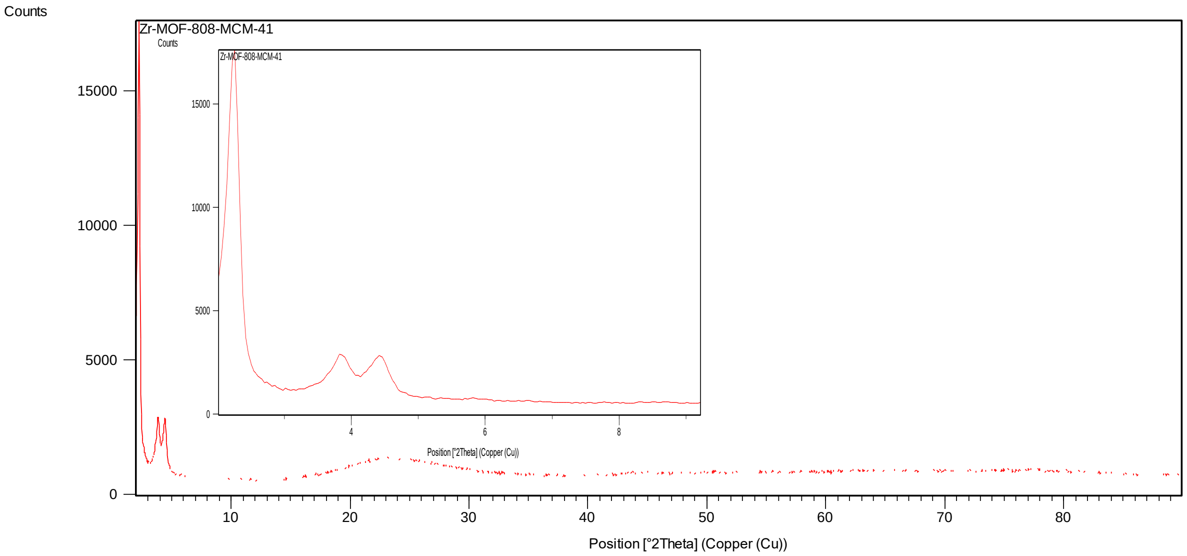


Figure S25. XRD pattern of Zr-MOF-808@MCM-41.

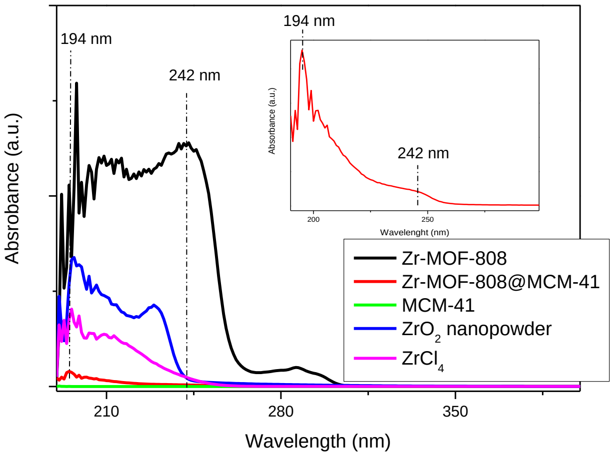


Figure S26. UV-Vis spectra of Zr-MOF-808, Zr-MOF-808@MCM-41 showing the peak around 242 nm which can be attributed to the absorption of Zr-O clusters. Inset: amplified UV-Vis spectra of Zr-MOF-808@MCM-41.The UV-Vis spectra of MCM-41, $ZrCl_4$ and ZrO_2 nanopowder are also shown.

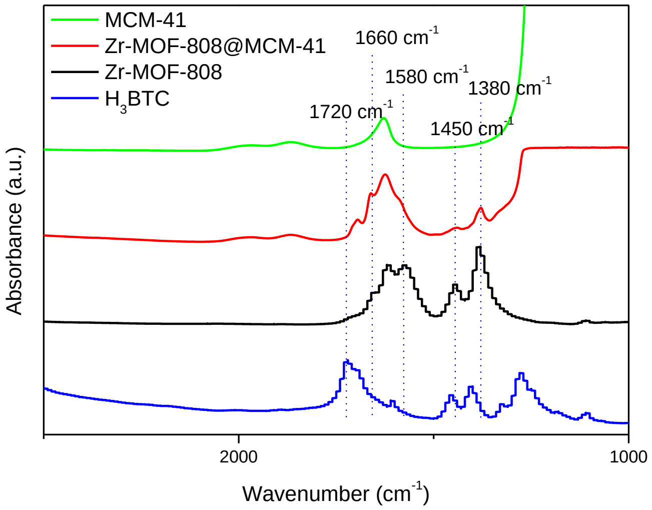


Figure S27. FTIR spectra

Table S12. Textural characteristic of pure silica MCM-41 and Zr-MOF-808@MCM-41

Sample	**BET Surface Area/m^{2}g^{-1}**	**Total Pore Volume/cm^{3}g^{-1}**
Pure silica MCM-41	955	0.68
Zr-MOF-808@MCM-41	777	0.45

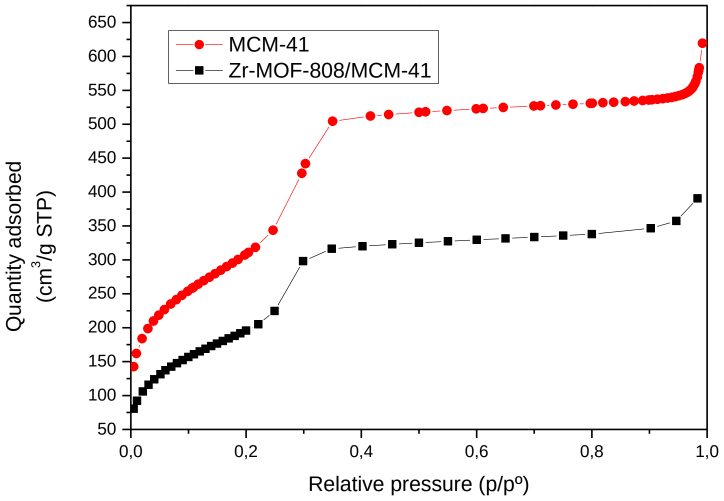


Figure S28. N_2 physisorption isotherm of MCM-41 and Zr-MOF-808@MCM-41 samples

Table S13. Chemical analysis of Zr-MOF-808@MCM-41 sample

Sample	**C^a**	**H^a**	**N^a**	**Zr^b**	**CHN^c**
Zr-MOF-808@MCM-41	4.5	1.3	0.17	3.2	6

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis

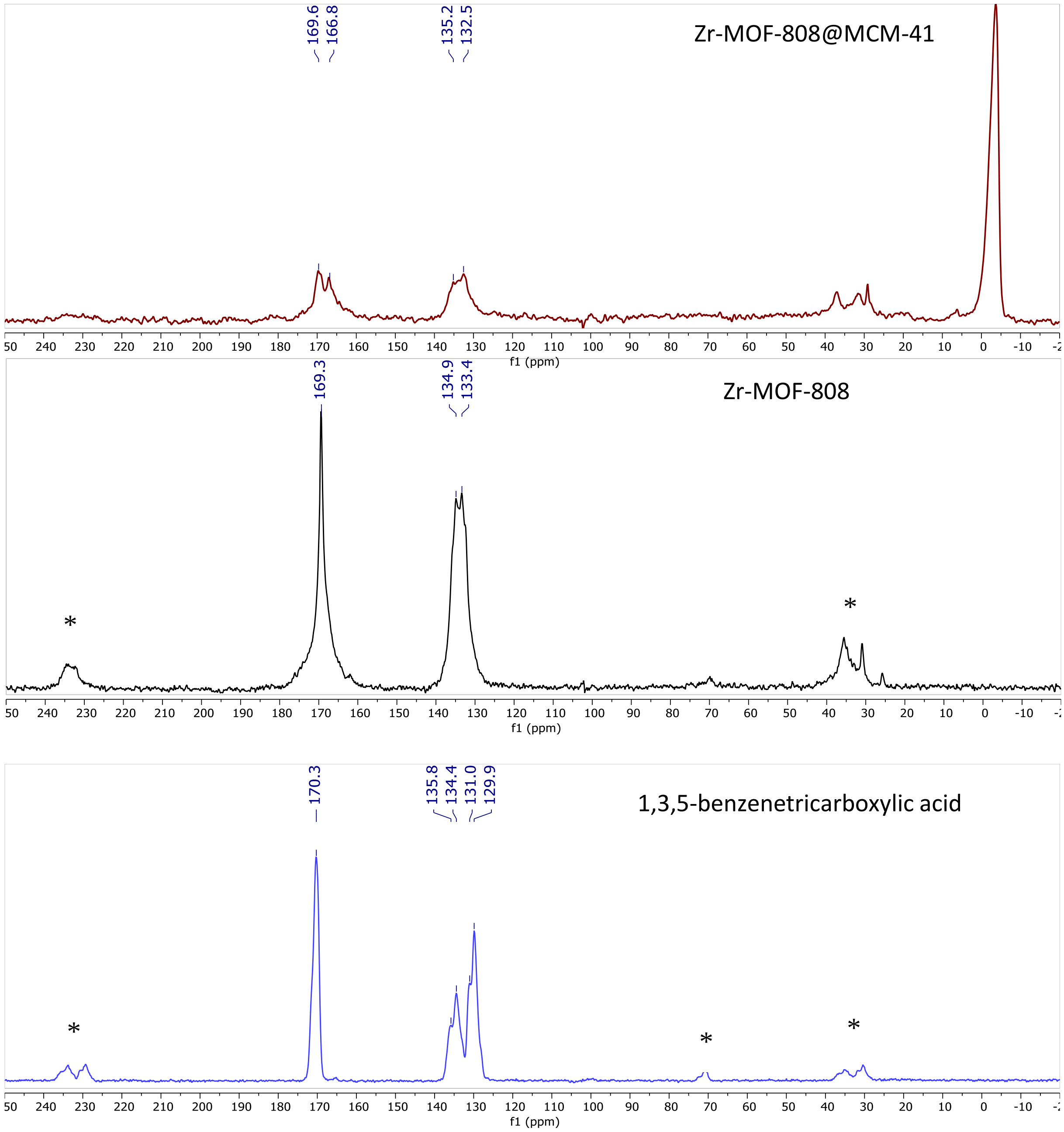


Figure S29. ^{13}C CP/MAS NMR spectra. Asterisks represent spinning bands.

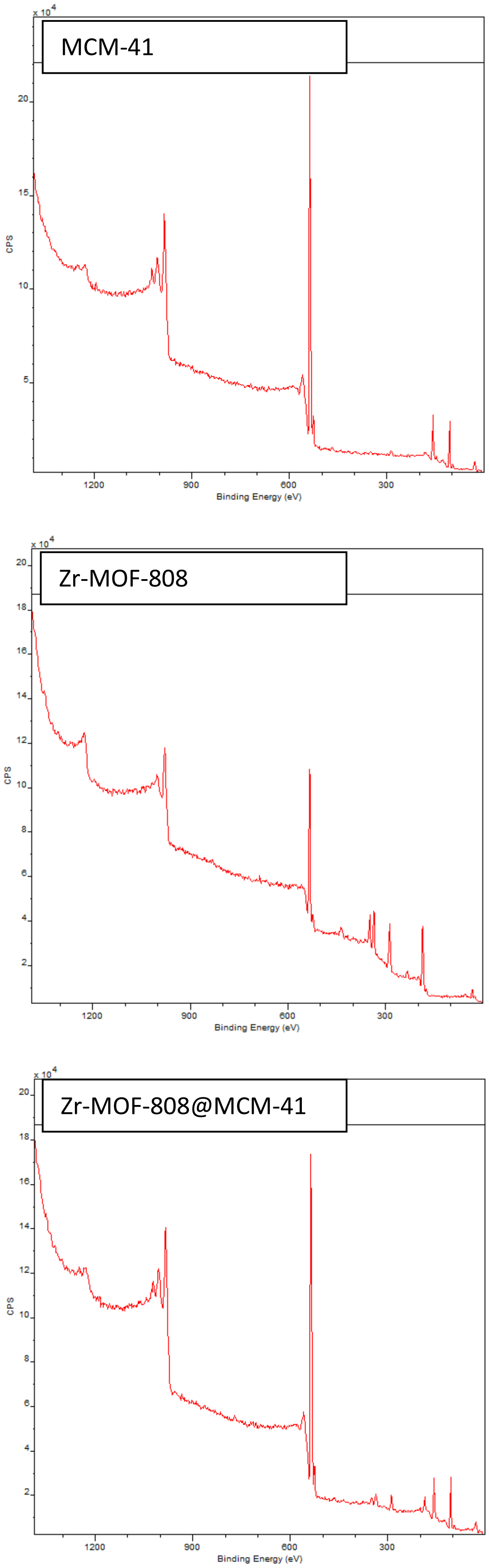


Figure S30. XPS spectra of MCM-41, Zr-MOF-808 and Zr-MOF-808@MCM-41 samples.

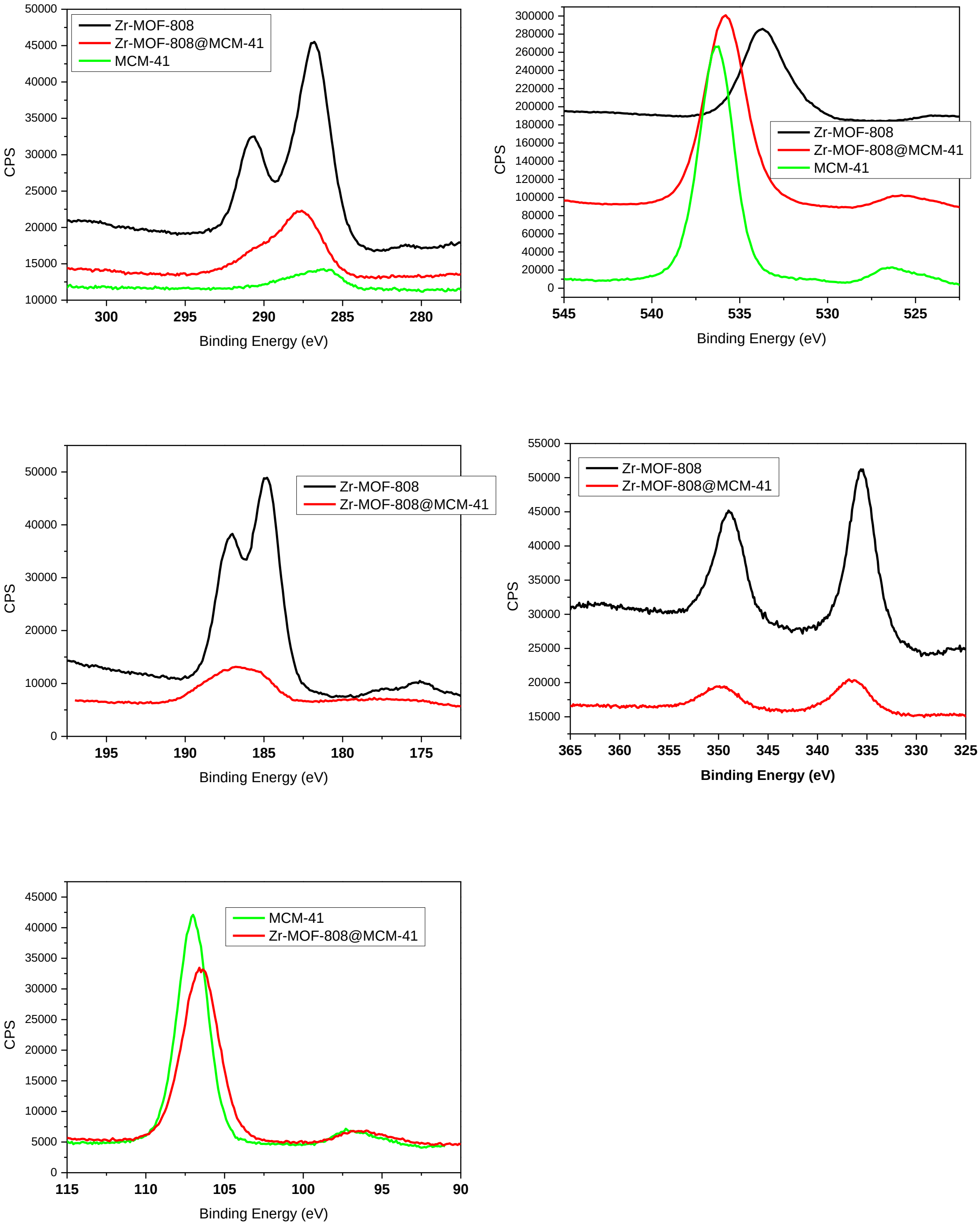
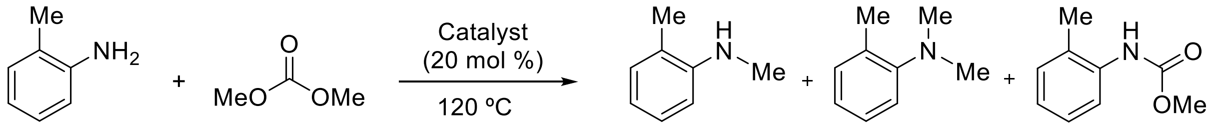


Figure S31. XPS spectra of MCM-41, Zr-MOF-808 and Zr-MOF-808@MCM-41 samples.

3. Hafnium and zirconium-based MOF catalysts for the carbamoylation reaction of aromatic amines with dimethyl carbonate.

3.1 Initial experiments: Hf-based MOFs catalysts were used initially to narrow down experimental reaction conditions.

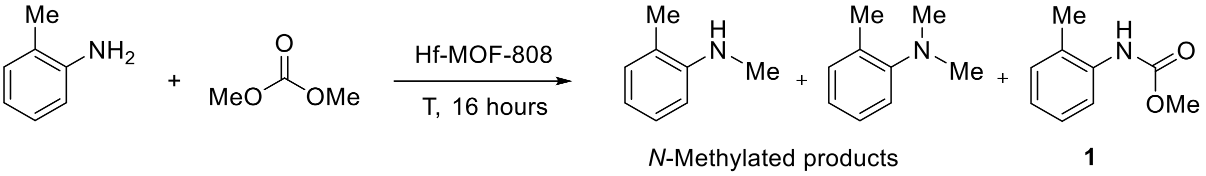
Catalyst screening: o-toluidine (0.1 mmol), catalyst (20 mol % in metal), dodecane (10 µL) as internal standard and dimethyl carbonate (0.25 mL) were added to a 1.5 mL glass vessel. The reaction mixture was left to stir at 120 ºC. The yield was determined by analysis by gas chromatography of aliquots taken from the reaction mixture at different times. Higher activity and selectivity was observed for Hf-MOF-808 compared with UiO-66(Hf) (see table below).



N-Methylated products **1**

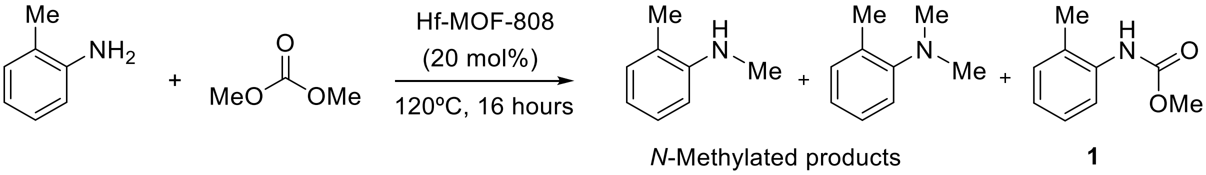
Catalyst	Time (h)	Conv. (%)	N-Methylated products (%)	Yield **1** (%)	Select. (%)
UiO-66(Hf)	16	38	10	28	74
	36	60	16	44	73
Hf-MOF-808	16	53	8	45	85
	36	79	8	71	90

Temperature and catalyst loading: o-toluidine (0.1 mmol), Hf-MOF-808 catalyst (20 or 30 mol% in metal), dodecane (10 µL) as internal standard and dimethyl carbonate (0.25 mL) were added to a 1.5 mL glass vessel. The reaction mixture was left to stir at the indicated temperature for 16 hours. The yield was determined by analysis by gas chromatography. 30 mol% loading and 120ºC results in higher conversion and high selectivity of the carbamate product **1** (see table below).



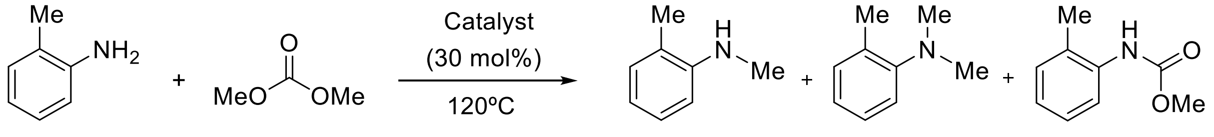
Load (mol %)	T (ºC)	Conv. (%)	*N*-Methylated products (%)	Yield **1** (%)	Select. (%)
20	120	53	8	45	85
30	120	84	7	77	92
20	140	76	3	73	97

Dimethyl carbonate concentration: o-toluidine (0.1 mmol), catalyst (20 mol% in metal), dodecane (10 µL) as internal standard and dimethyl carbonate (see table below) were added to a 1.5 mL glass vessel. The reaction mixture was left to stir at 120ºC for 16 hours. The yield was determined by analysis by gas chromatography. Higher concentration resulted beneficial achieving higher yield of the carbamate product **1** with a DMC:*o*-toluidine ratio of 12:1.



Conc. (M)	Conver. (%)	N-Methylated products (%)	Yield 1 (%)	Select. (%)
0.25	61	4	57	93
0.4	53	8	45	85
1	79	7	72	91

3.2 Catalyst screening (kinetic study): catalyst was placed in a 10 mL glass vessel that can withstand pressure. *O*-toluidine (53.6 mg, 0.5 mmol), DMC (0.5 mL, 6 mmol) and dodecane (37 mg) as internal standard were then added. The reaction was left to stir at 120 ºC. The yield was determined by analysis by gas chromatography of aliquots taken from the reaction mixture at different times.



N-Methylated products **1**

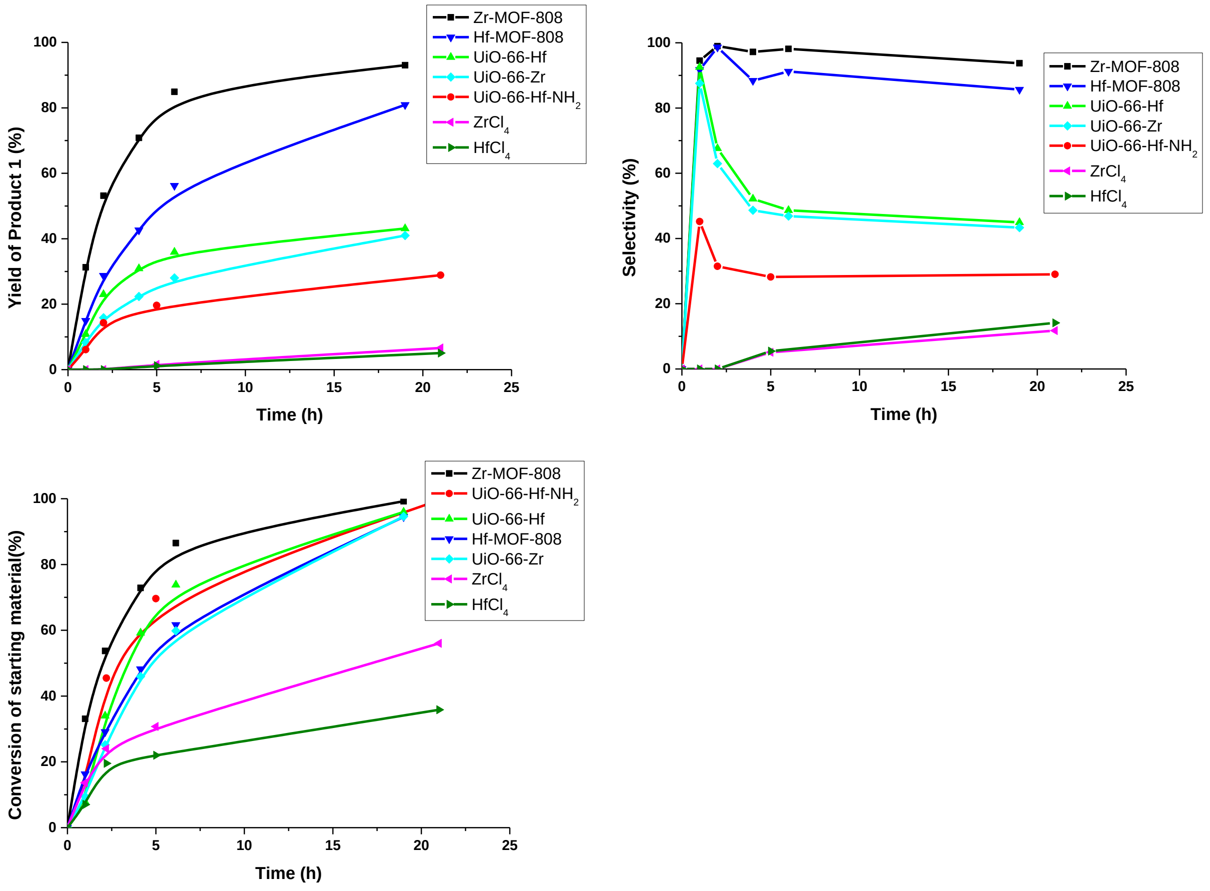
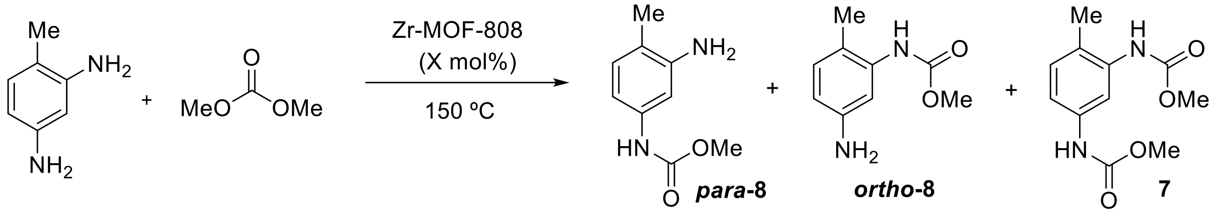


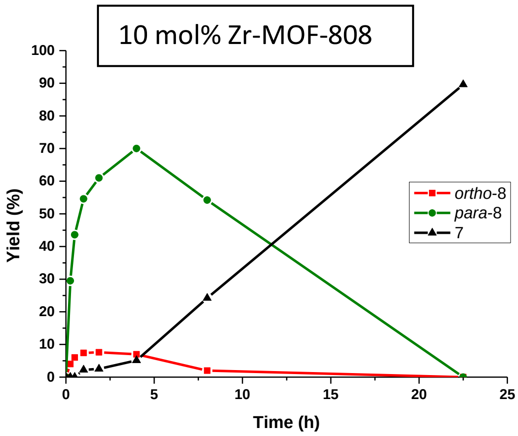
Figure S32. Hafnium and zirconium catalysts for the reaction of *o*-toluidine with DMC. Reaction conditions: 0.5 mmol *o*-toluidine, catalyst (30 mol% in metal), dodecane (35 mg) as internal standard, DMC (0.5 mL), Tª = 120 ºC.

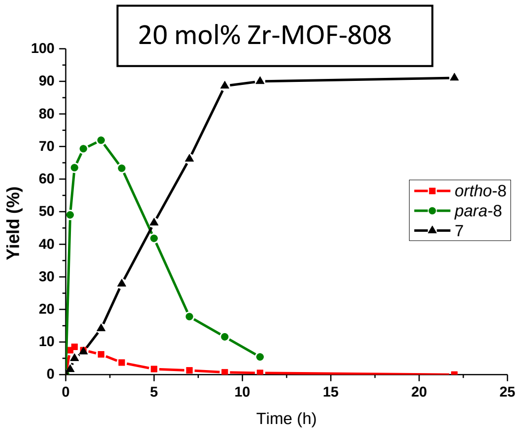
3.3 General procedure for the synthesis of carbamates using Zr-MOF-808 catalyst. Zr-MOF-808 (30 mol%) was placed in a 10 mL pyrex glass vessel. The vessel can withstand pressure. Aromatic amine (0.5 mmol) and dimethylcarbonate (0.5 mL, 6 mmol) were then added and the mixture was left to stir vigorously at 120 ºC for the corresponding time (see

Table 1 in the manuscript). The reaction mixture was then filtered in order to separate the catalyst that was washed with ethyl acetate. Solvent was then removed under reduced pressure and the crude product was purified by column chromatography using hexane/ethyl acetate as eluent. All the products obtained have been described previously and have been here characterized by GC-MS and NMR spectroscopy.

3.4 Kinetic profile for the reaction of 2,4-diaminotoluene with dimethyl carbonate using Zr-MOF-808 catalyst







3.5. Stability and reuses of Zr-MOF-808 in the carbamoylation reaction of *o*-toluidine with DMC.

Filtration test in the carbamoylation reaction of o-toluidine with DMC: *o*-toluidine (0.5 mmol), catalyst (30 mol % in metal), dodecane (35 mg) as internal standard and DMC (0.5 mL) were added to a 10 mL glass vessel. The vessel can withstand pressure. The reaction mixture was left to stir at 120 ºC. The solid was filtered off after 1 hour reaction time and the filtrate was left to stir further at 120ºC. The yield was determined by analysis by gas chromatography of aliquots taken from the reaction mixture at different times.

Reuse study in the carbamoylation reaction of o-toluidine with DMC: *o*-toluidine (0.5 mmol), catalyst (30 mol % in metal), dodecane (35 mg) as internal standard and DMC (0.5 mL) were added to a 10 mL glass vessel. The vessel can withstand pressure. The reaction mixture was left to stir at 120 ºC for 10 hours. The yield was determined by analysis by gas chromatography. The solid catalyst was then separated by centrifugation and then washed with EtOAc and acetone. The catalyst was activated in *vacuo* for 2 h at room temperature and then used for the next run. The yield of the carbamate product in the second run was 14%. The recovered catalyst was analyzed by XRD and the pattern shows that crystallinity of the material is lost (see Figure S28).

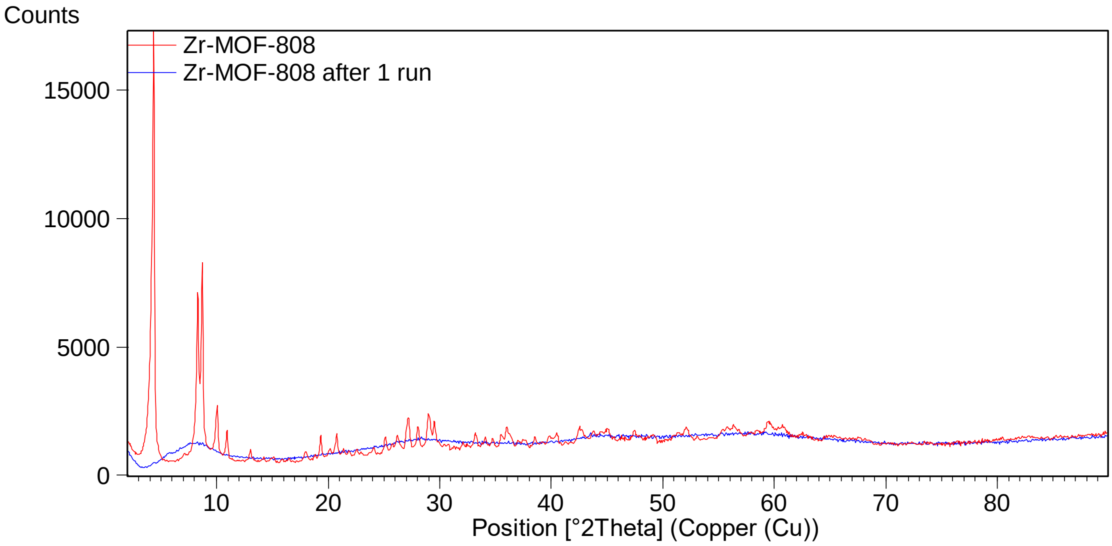
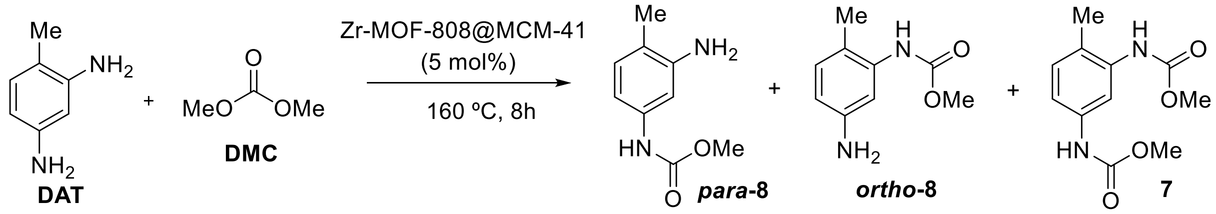


Figure S33. XRD pattern of Zr-MOF-808 as synthesized (red line). XRD pattern of Zr-MOF-808 after being used one time in the carbamoylation reaction of *o*-toluidine with DMC (blue line).

4. Zr-MOF-808@MCM-41 as catalyst for the carbamoylation reaction of aromatic amines with dimethyl carbonate.

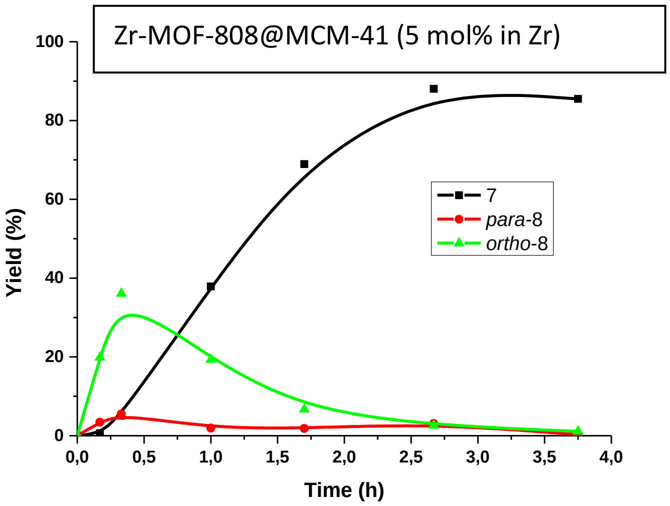
4.1 Zr-MOF-808@MCM-41 and related solids as catalysts for the carbamoylation reaction of 2,4-toluene diamine with dimethyl carbonate.

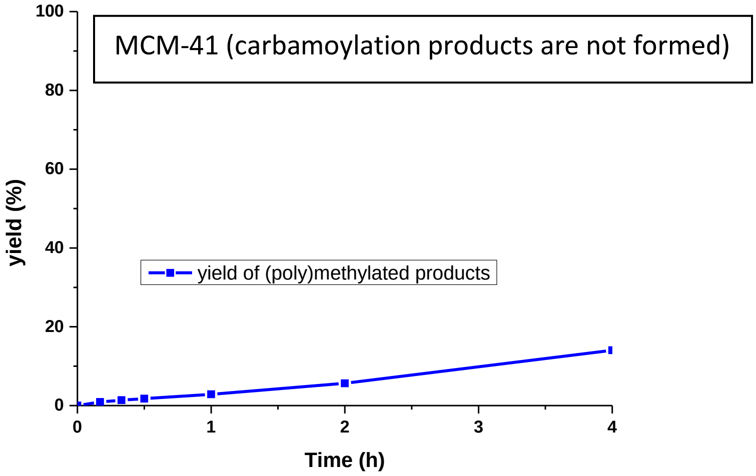
Catalyst was placed in a 10 mL glass vessel that can withstand pressure. 2,4-Diaminetoluene, DAT (62.3 mg, 0.5 mmol), DMC (0.5 mL, 534 mg, 6 mmol) and dodecane (37 mg) as internal standard were then added. The reaction was left to stir at 160 ºC during 8 h. The reaction products were analyzed by GC-chromatography.

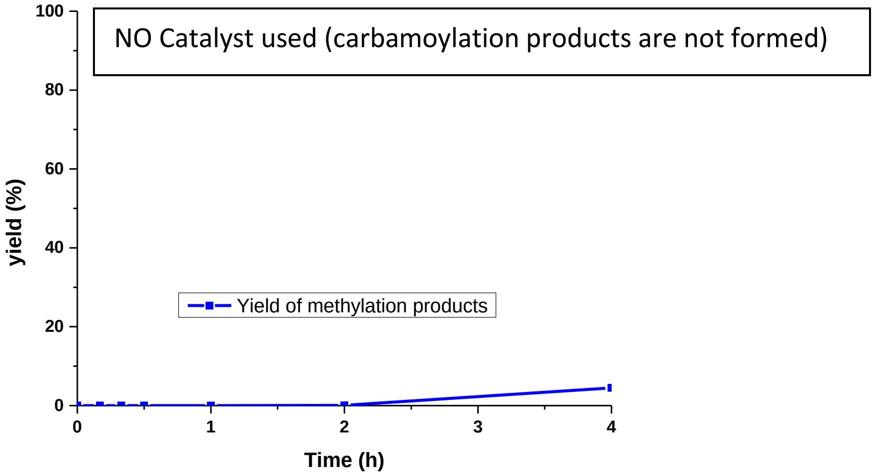


Catalyst	mg, load (mol%)	Conv. (%)	N-methylation Yield (%)	Yield *o*-8 (%)	Yield *p*-8 (%)	Yield 7 (%)
ZrO_2 nanopowder	3.5 mg, 5	1	1	-	-	-
MCM-41	70 mg, --	47	41	1	3	2
ZrO_2@MCM-41	70 mg, 1.5	96	89	1	5	1
Zr-MOF-808@MCM-41	70 mg, 5	100	5	3	3	80

Kinetic profiles for different catalysts used:



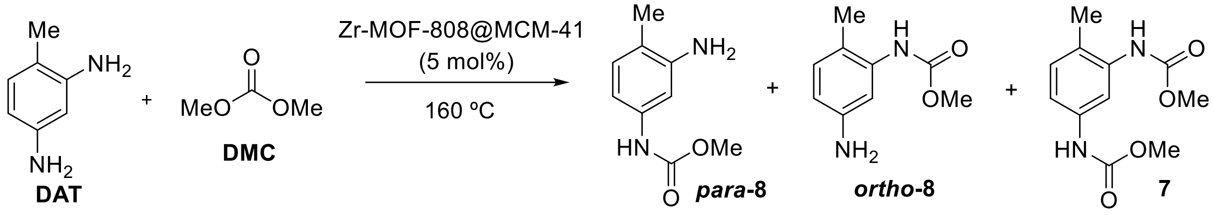


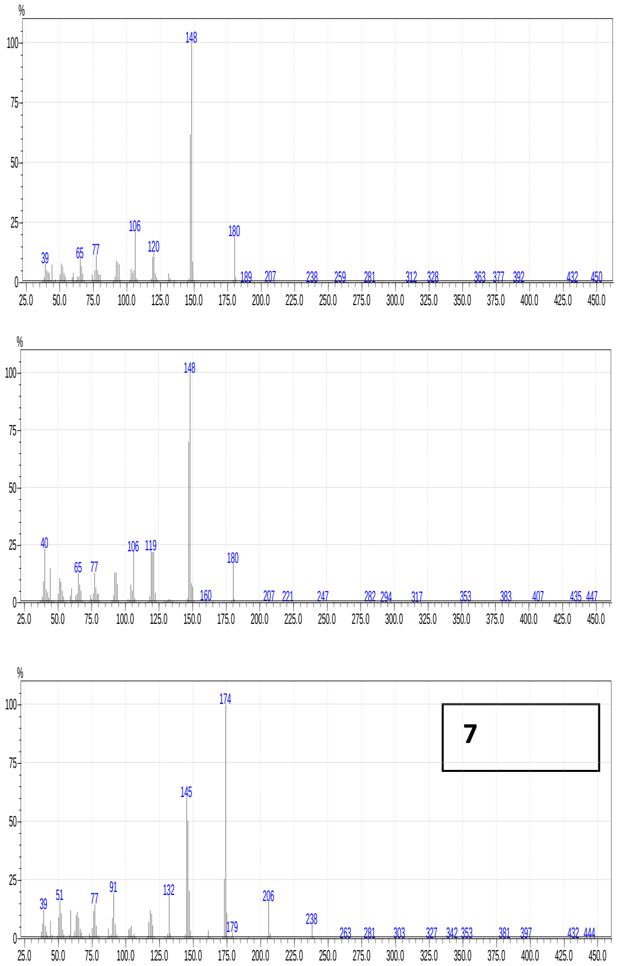


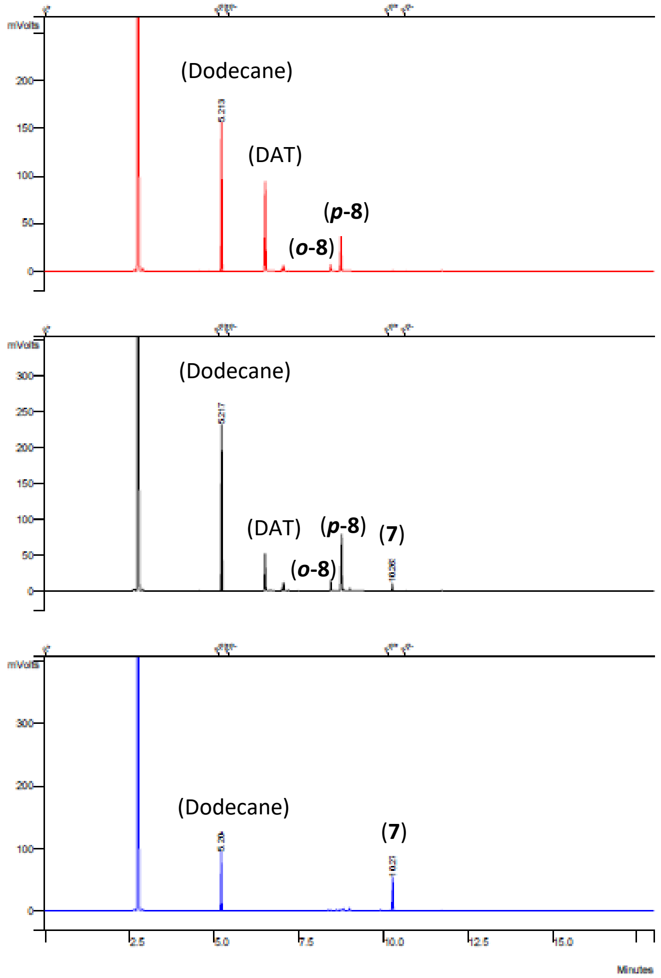
Synthetic preparation of ZrO_2@MCM-41:

The reported procedure was followed.[3] MCM-41 (200 mg), was impregnated with an aqueous solution of $ZrOCl_2.8H_2O$ (7.2 mg, 0.02 mmol) in water (0.32 mL). The resulting mixture was heated at 100 ºC during a night to volatize the solvent. The resulting solid was calcined in air with a ramp of 7ºC/min to a T_{max}=500 ºC during 2 h to obtain ZrO_2@MCM-41. ICP analysis determined 1 wt% of Zr in the sample.

GC-MS data:


Me
NH2
NH2
DAT
+
O
MeO
OMe
DMC
Zr-MOF-808@MCM-41
(5 mol%)
160 ºC
Me
NH2
HN
OMe
O
para-8
+
Me
H
N
O
OMe
NH2
ortho-8
+
Me
H
N
O
OMe
HN
OMe
O
7


%
100
75
50
25
0
148
106
180
120
39
65
77
40
119
174
145
91
132
206
51
238
7
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0


mVolts
(Dodecane)
(DAT)
(p-8)
(o-8)
(7)
5.213
5.217
10.26
2.5
5.0
7.5
10.0
12.5
15.0
Minutes

4.2 Stability and reuses of Zr-MOF-808@MCM-41 in the carbamoylation reaction of 2,4-toluene diamine with dimethyl carbonate.

Filtration test in the carbamoylation reaction of o-2,4-diaminetoluene with DMC: 2,4-diaminetoluene (0.5 mmol), catalyst (5 mol % in metal), dodecane (35 mg) as internal standard and DMC (0.5 mL) were added to a 10 mL glass vessel. The vessel can withstand pressure. The reaction mixture was left to stir at 160 ºC. The solid was filtered off after 45 min reaction time and the filtrate was left to stir further at 160ºC. The yield was determined by analysis by gas chromatography of aliquots taken from the reaction mixture at different times.

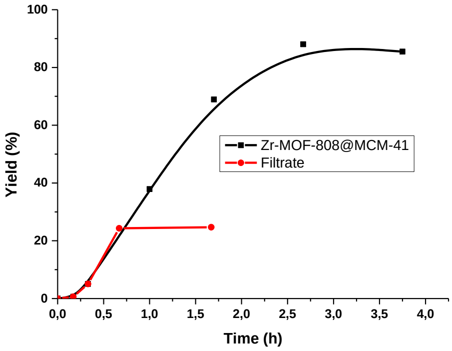


Figure S34. Time-yield plots for the *N*-carbamoylation of 2,4-diaminetoluene with Zr-MOF-808@MCM-41 (black line) and removing the catalyst after 45 min (red line)

Reuse study in the carbamoylation reaction of o-2,4-diaminetoluene with DMC: 2,4-diaminetoluene (0.5 mmol), catalyst (5 mol % in metal), dodecane (35 mg) as internal standard and DMC (0.5 mL) were added to a 10 mL glass vessel. The vessel can withstand pressure. The reaction mixture was left to stir at 160 ºC for 3 hours. The yield was determined by analysis by gas chromatography. The solid catalyst was then separated by centrifugation and then washed with EtOAc and acetone. The catalyst was activated in *vacuo* for 2 h at room temperature and then used for the next run.

Characterization of the catalyst Zr-MOF-808@MCM-41 after repeated reutilization:

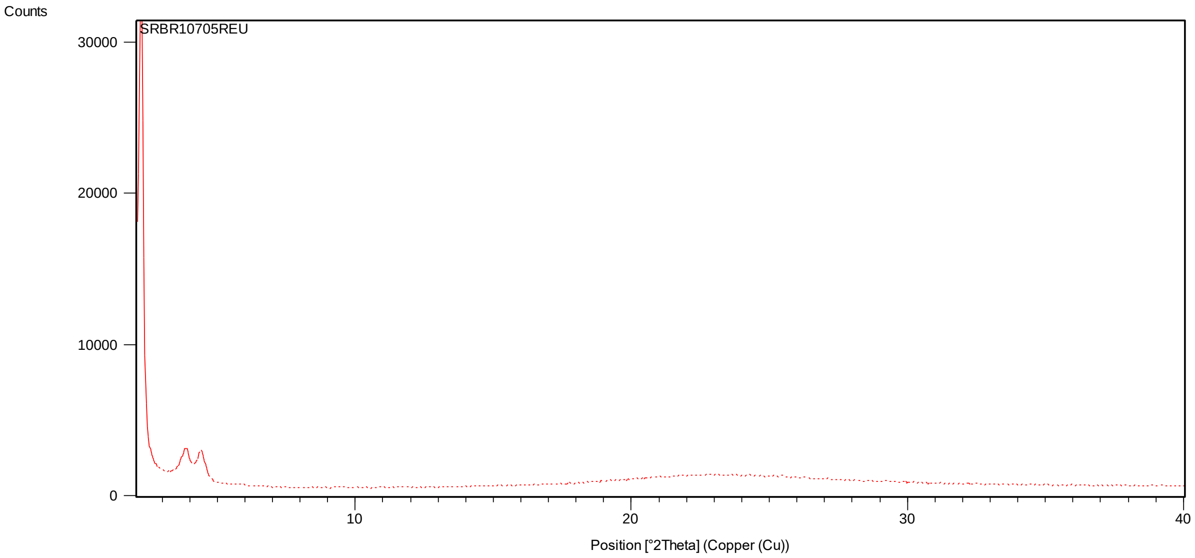


Figure S35. XRD pattern of Zr-MOF-808@MCM-41 after 6 consecutive runs.

Table S14. Textural characteristic of MCM-41 and Zr-MOF-808@MCM-41 as synthesized and after reutilization

Sample	BET Surface Area/m^{2}g^{-1}	Total Pore Volume/cm^{3}g^{-1}
MCM-41	955	0.96
Zr-MOF-808/MCM-41	777	0.60
Zr-MOF-808/MCM-41 after 6 consecutive runs	464	0.38

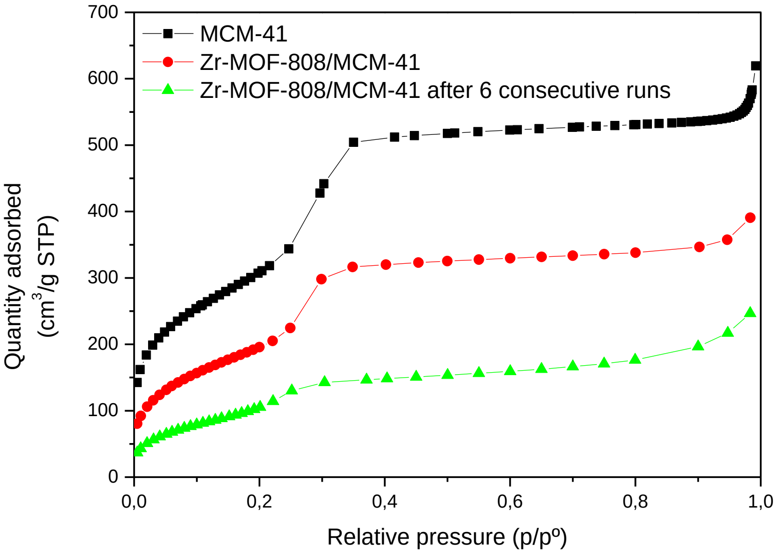


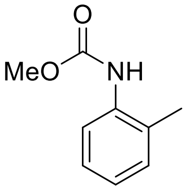
Figure S36. N_2 physisorption isotherms of MCM-41 and Zr-MOF-808@MCM-41 as synthesized and after reutilization.

Table S15. Chemical analysis of Zr-MOF-808@MCM-41 samples

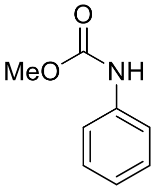
Sample	**C^a**	**H^a**	**N^a**	**Zr^b**	**CHN^c**
Zr-MOF-808/MCM-41	4.5	1.3	0.17	3.2	6
Zr-MOF-808/MCM-41 after 6 consecutive runs	38.0	3.8	10.0	1.3	51.8

[a] Percentage in weight (%wt); [b]Determined by ICP analysis [c]Organic content from CHNS elemental analysis

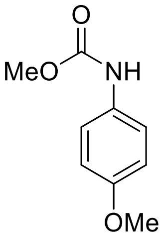
4.3. General procedure for the synthesis of carbamates using Zr-MOF-808@MCM-41 catalyst. Zr-MOF-808@MCM-41 (35 mg, 2.5 mol%, for monoamines and 70 mg, 5 mol% for diamines) was placed in a 10 mL pyrex glass vessel. The vessel can withstand pressure. Aromatic amine or diamine (0.5 mmol) and dimethylcarbonate (0.5 mL, 6 mmol) were then added and the mixture was left to stir vigorously at 160 ºC for the corresponding time. The reaction mixture was then filtered in order to separate the catalyst that was washed with ethyl acetate. Solvent was then removed under reduced pressure and the crude product was purified by column chromatography using hexane/ethyl acetate as eluent. All the products obtained have been described previously (references given below for each of them) and were characterized by GC-MS and NMR spectroscopy.



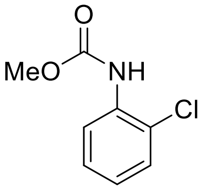
methyl o-tolylcarbamate: The reaction mixture was left for 3 h to give a white solid in 85% yield (70 mg, 0.43 mmol). **^{1}H-NMR (300 MHz, CDCl$_3$):**[4] δ 7.65 (s, 1H), 7.17-7.06 (m, 2H), 6.94 (t, J=6.93 Hz, 1H), 6.38 (s, 1H), 3.69 (s, 3H), 2.15 (s, 3H) . **^{13}C-NMR (75 MHz, CDCl$_3$):** δ 154.46, 135.83, 130.40, 126.85, 124.31, 52.36, 17.60.



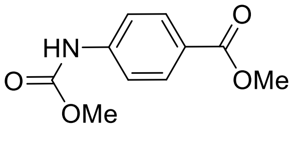
methyl phenylcarbamate: The reaction mixture was left for 2 h to give a white solid in 89% yield (68 mg, 0.45 mmol). **^{1}H-NMR (300 MHz, CDCl$_3$):**[4] δ 7.30 (d, J=7.29, 2H), 7.21 (t, J=7.20, 2H), 6.97 (t, J=6.95 Hz, 1H), 6.77 (s, 1H), 3.68 (s, 3H). **^{13}C-NMR (75 MHz, CDCl$_3$):** δ 154.19, 137.92, 129.01, 123.45, 118.82, 52.3.



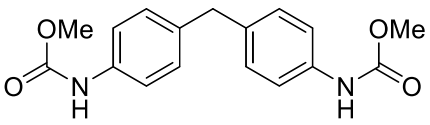
methyl 4-methoxyphenylcarbamate: The reaction mixture was left for 2.5 h to give a white solid in 90% yield (81.5 mg, 0.45 mmol). **^{1}H-NMR (300 MHz, CDCl$_3$):**[4] δ 7.19 (d, J=7.18, 2H), 6.76 (d, J=6.74, 2H), 6.67 (s, 1H), 3.69 (s, 3H), 3.67 (s, 3H). **^{13}C-NMR (75 MHz, CDCl$_3$):** δ 156.00, 154.60, 130.98, 120.82, 114.22, 55.48, 52.25.



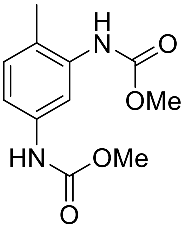
methyl 2-chlorophenylcarbamate: The reaction mixture was left for 5.25 h to give a white solid in 84% yield (78 mg, 0.42 mmol). **^{1}H-NMR (300 MHz, CDCl$_3$):**[4] δ 8.07 (d, J=8.06 Hz , 1H), 7.26 (d, J=7.26 Hz, 1H), 7.18 (t, J=7.17 Hz, 1H), 7.07 (s, 1H), 6.91 (t, J=6.90 Hz, 1H), 3.72 (s, 3H). **^{13}C-NMR (75 MHz, CDCl$_3$):** δ 153.64, 134.72, 129.04, 127.74, 123.73, 122.09, 119.94, 52.53.



methyl 4-(methoxycarbonylamino)benzoate: The reaction mixture was left for 5 h to give a white solid in 89% yield (93 mg, 0.45 mmol). **^{1}H-NMR (300 MHz, CDCl$_3$):**[4] δ 7.92 (d, J=7.90 Hz , 2H), 7.39 (d, J=7.38 Hz , 2H), 6.84 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H). **^{13}C-NMR (75 MHz, CDCl$_3$):** δ 166.65, 153.56, 142.16, 130.93, 124.87, 117.56, 52.56, 51.95.



dimethyl 4,4´-methylenebis(4,1-phenylene)dicarbamate: The reaction mixture was left for 3 h to give a white solid in 95% yield (149.3 mg, 0.48 mmol). **^{1}H-NMR (300 MHz, DMSO-d$_6$):**[4] δ 9.53 (s, 2H), 7.34 (d, J=7.30 Hz , 4H), 7.10 (d, J=7.10 Hz , 4H), 3.78 (s, 2H), 3.64 (s, 6H). **^{13}C-NMR (75 MHz, DMSO-d$_6$):** δ 153.97, 137.01, 135.45, 128.80, 118.35, 51.47.

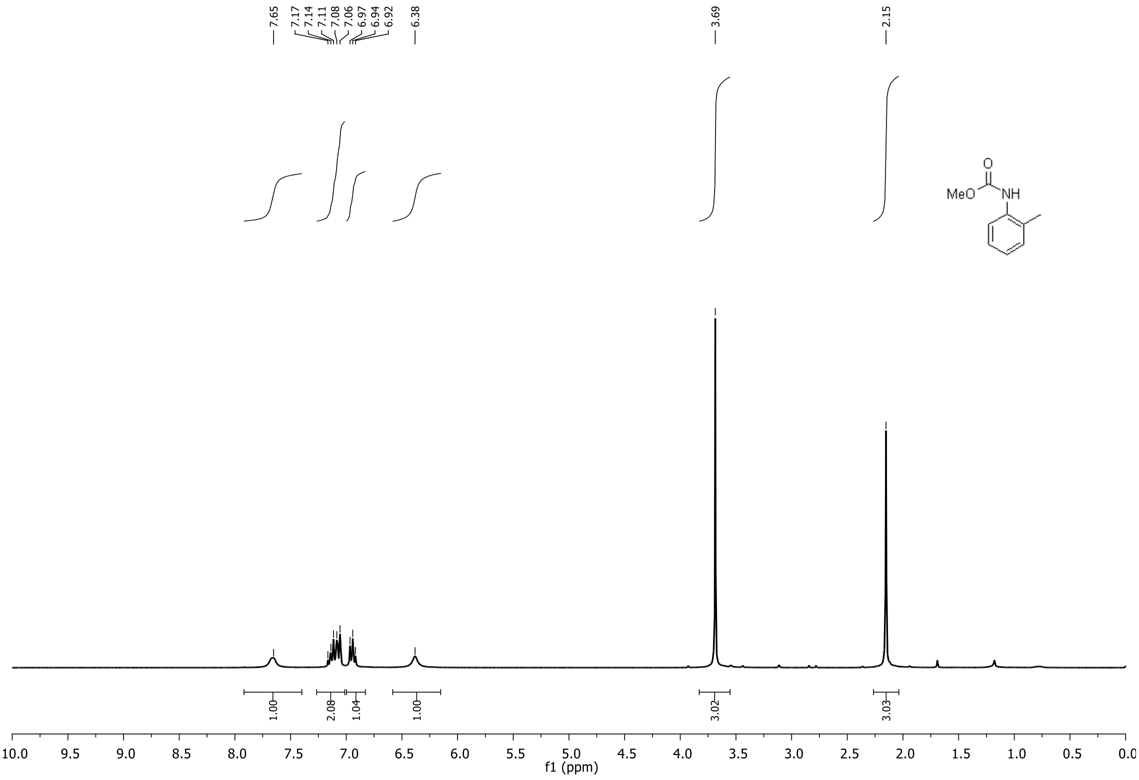


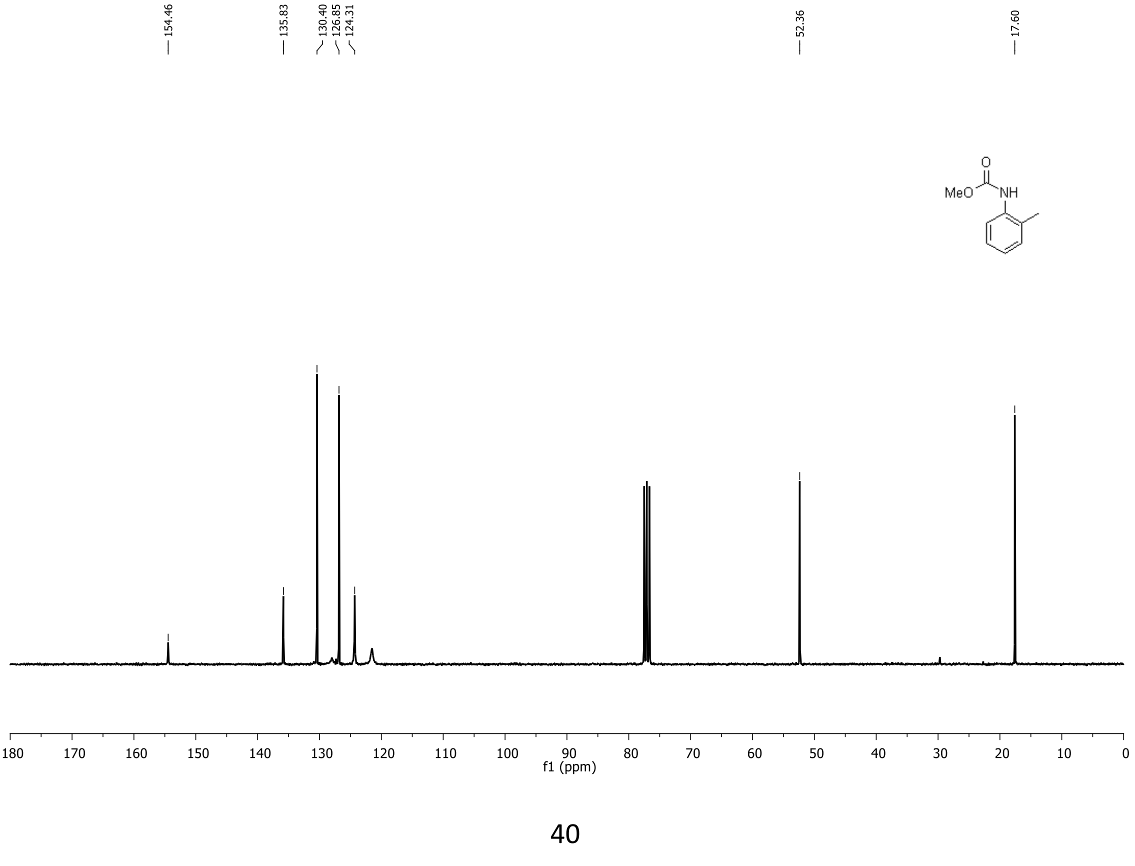
dimethyl 4-methyl-1,3-phenylenedicarbamate: The reaction mixture was left for 2.75 h to give a white solid in 93% yield (110.8 mg, 0.47 mmol). **^{1}H-NMR (300 MHz, DMSO-d$_6$):**[4] δ 9.54 (s, 1H), 8.81 (s, 1H), 7.48 (s, 1H), 7.16 (d, J=7.15 Hz , 2H), 7.06 (d, J=7.05 Hz , 2H), 3.64 (s, 3H), 3.63 (s, 3H), 2.11 (s, 3H). **^{13}C-NMR (75 MHz, DMSO-d$_6$):** δ 154.68, 153.90, 137.12, 136.39, 130.19, 125.52, 114.93, 114.78, 51.58, 51.48, 17.05.

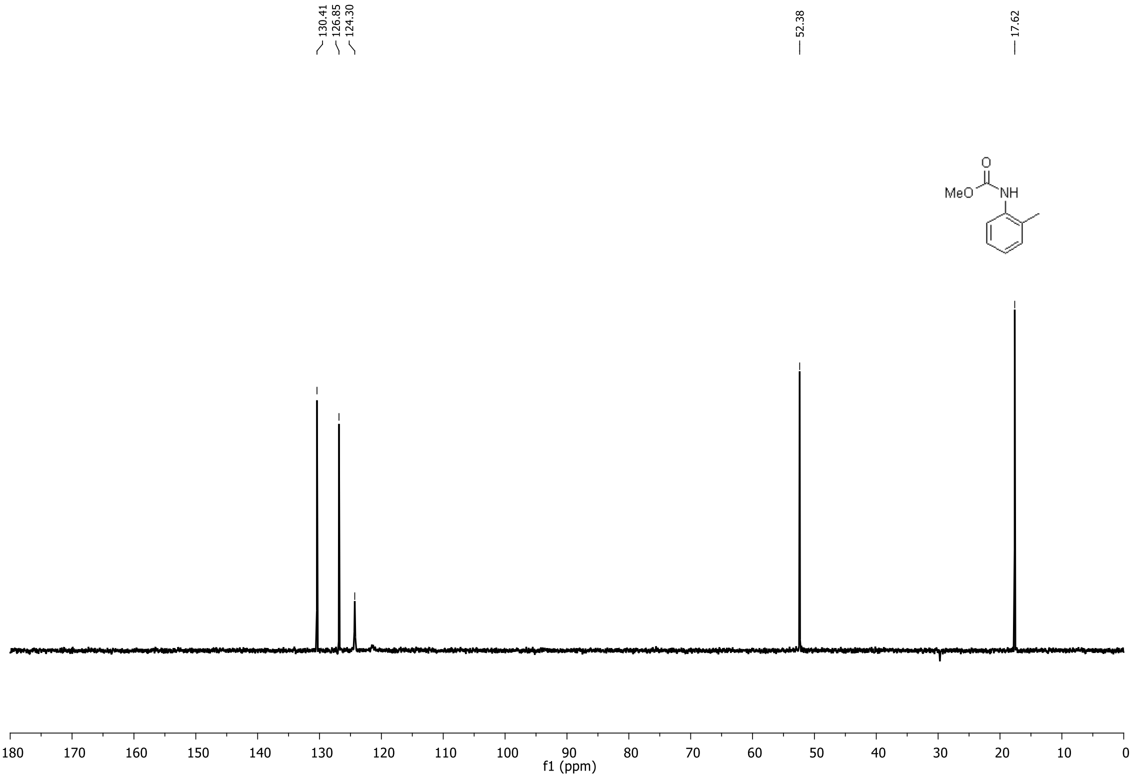
4.4. Experimental procedure for the in situ FTIR experiments: FTIR spectra were collected on a Bruker Vertex70 spectrometer. The infrared cell, connected to a dosing system, was designed to treat the samples in situ under controlled atmospheres and temperatures. The samples were evacuated at 10^{-5} mbar and 393 K for 1.5 h prior to the adsorption experiments. Aniline (1 mbar) and DMC (3.8 mbar) were coadsorbed onto the support surface at room temperature. After reactant adsorption the sample was evacuated to remove the excess of both reactants at room temperature. Spectra were collected at different temperatures.

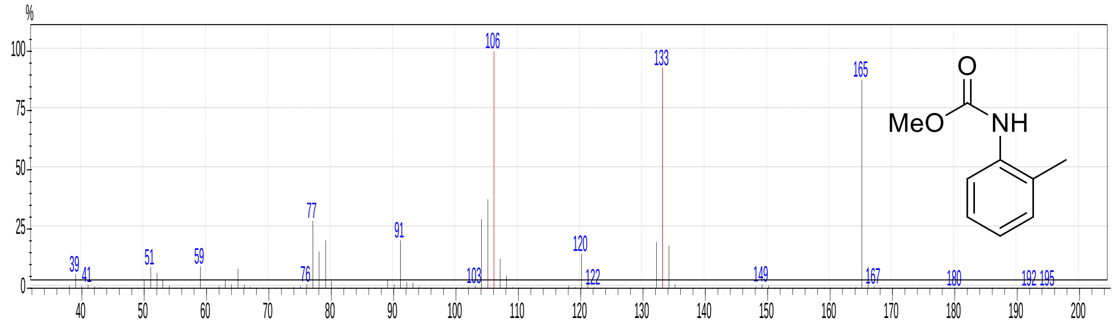
4.5. Synthesis and application of Zr-MOF-808@SiO_2: It was followed the same procedure reported above for MCM-41 (see Section 2), but 500 mg of SiO_2 were used instead of pure silica MCM-41. ICP analysis revealed Zr content of 1.9 wt%. The obtained catalyst was tested in the carbamoylation reaction of 2,4-diamine toluene following the general procedure described in section 4.3. The reaction mixture was left for 2.75 h and the carbamoylated product dimethyl 4-methyl-1,3-phenylenedicarbamate **7** was isolated in 90% yield (107.2 mg, 0.45 mmol).

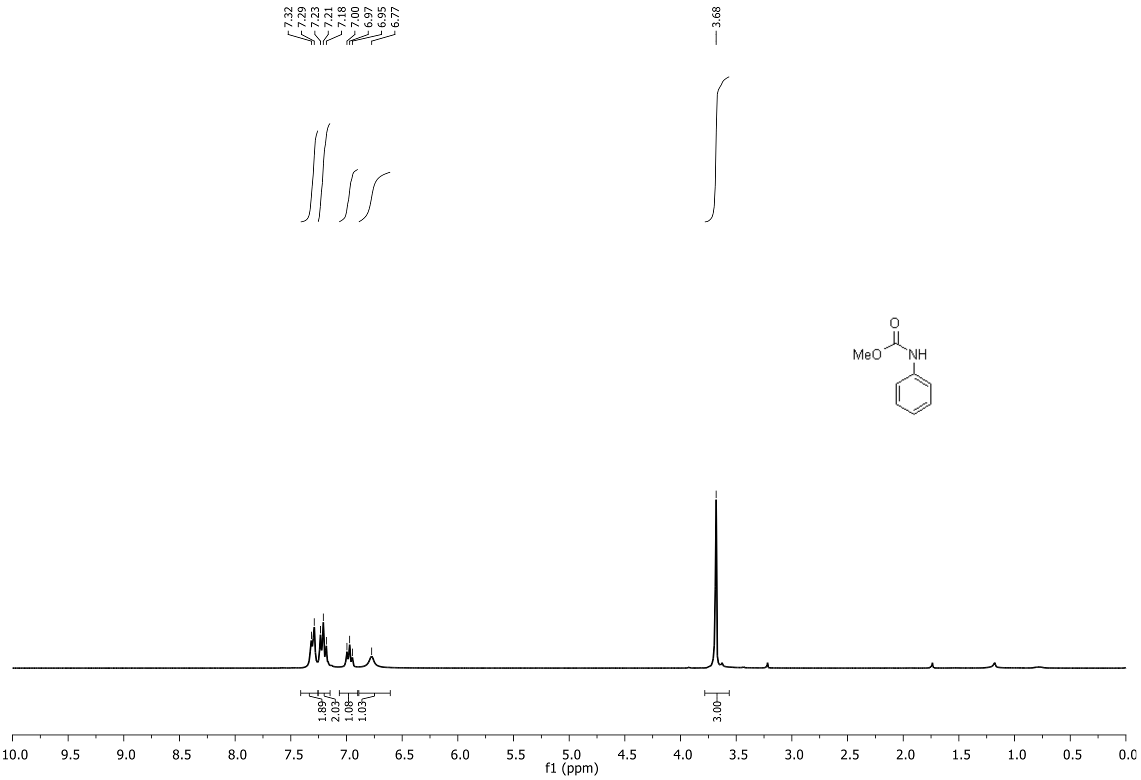
^{1}H and ^{13}C NMR spectra, and MS

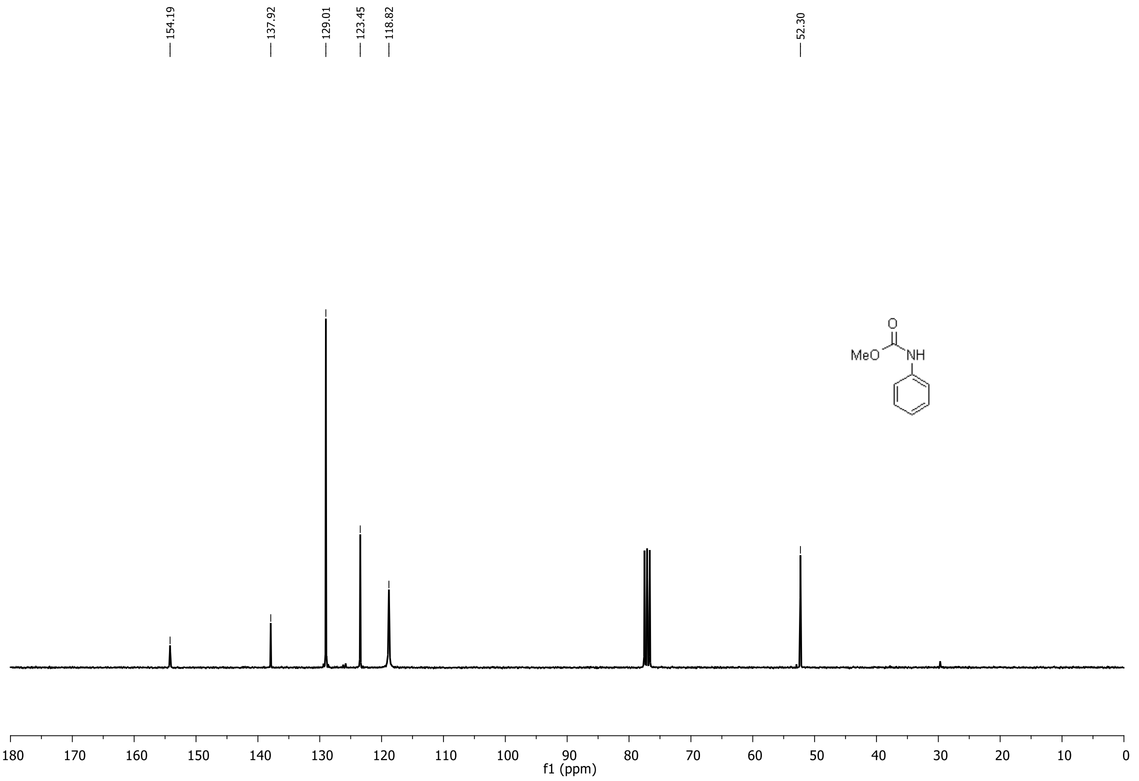


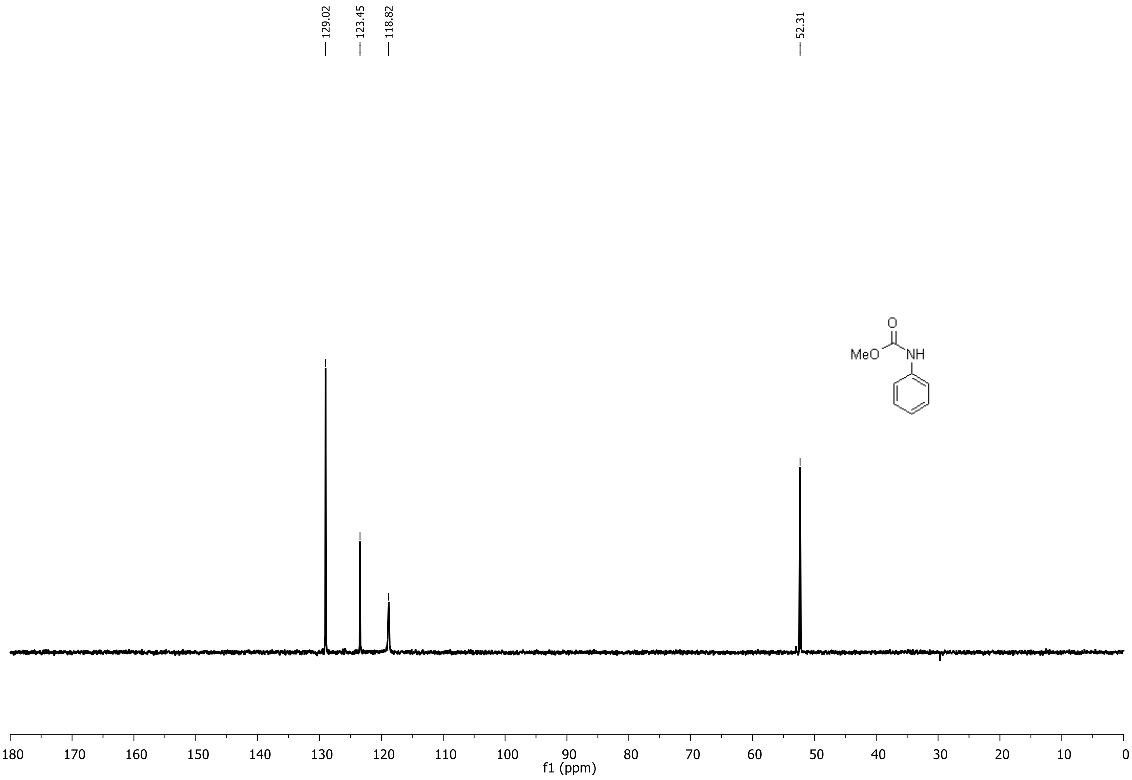


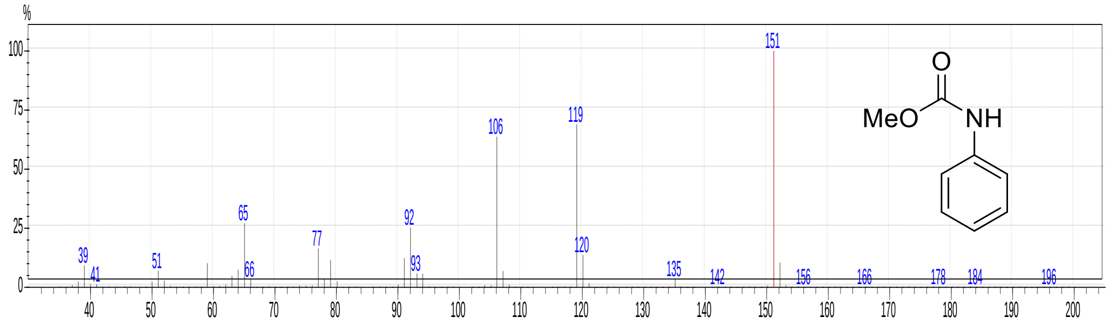

130.41
126.85
124.30
52.38
17.62
O
MeO
NH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

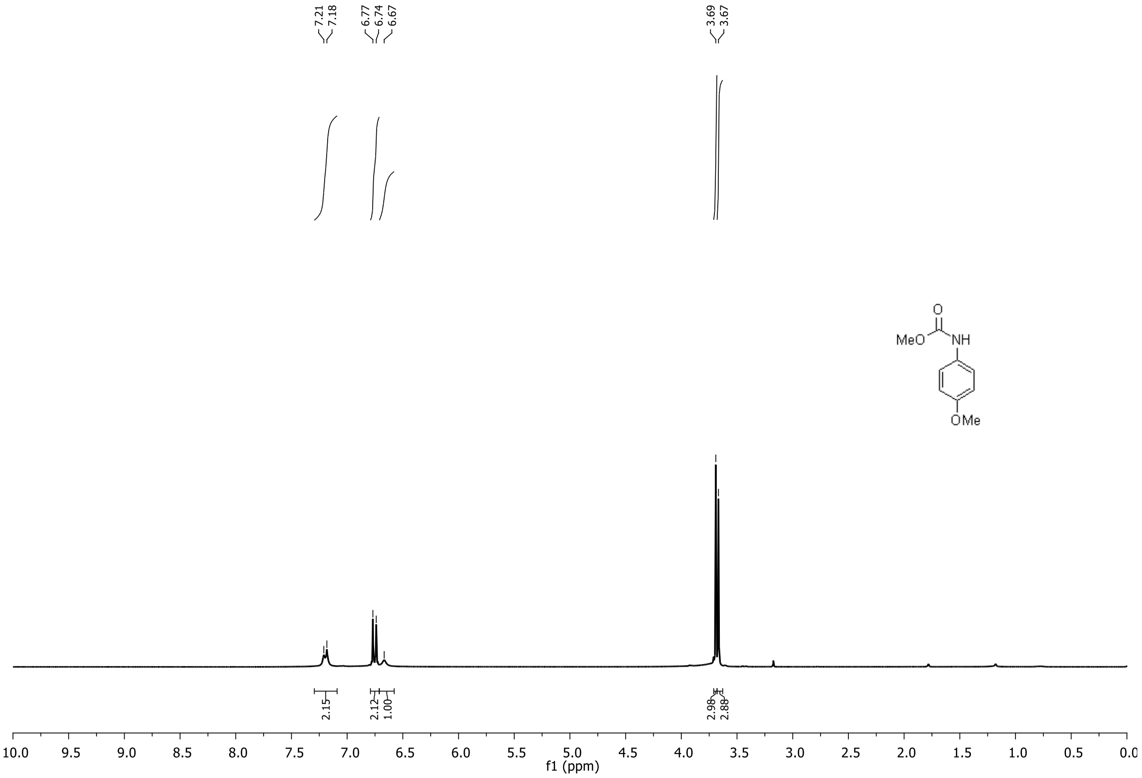

%
100
75
50
25
0
106
133
165
77
91
120
39
41
51
59
76
103
122
149
167
180
192
195
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
O
MeO
NH

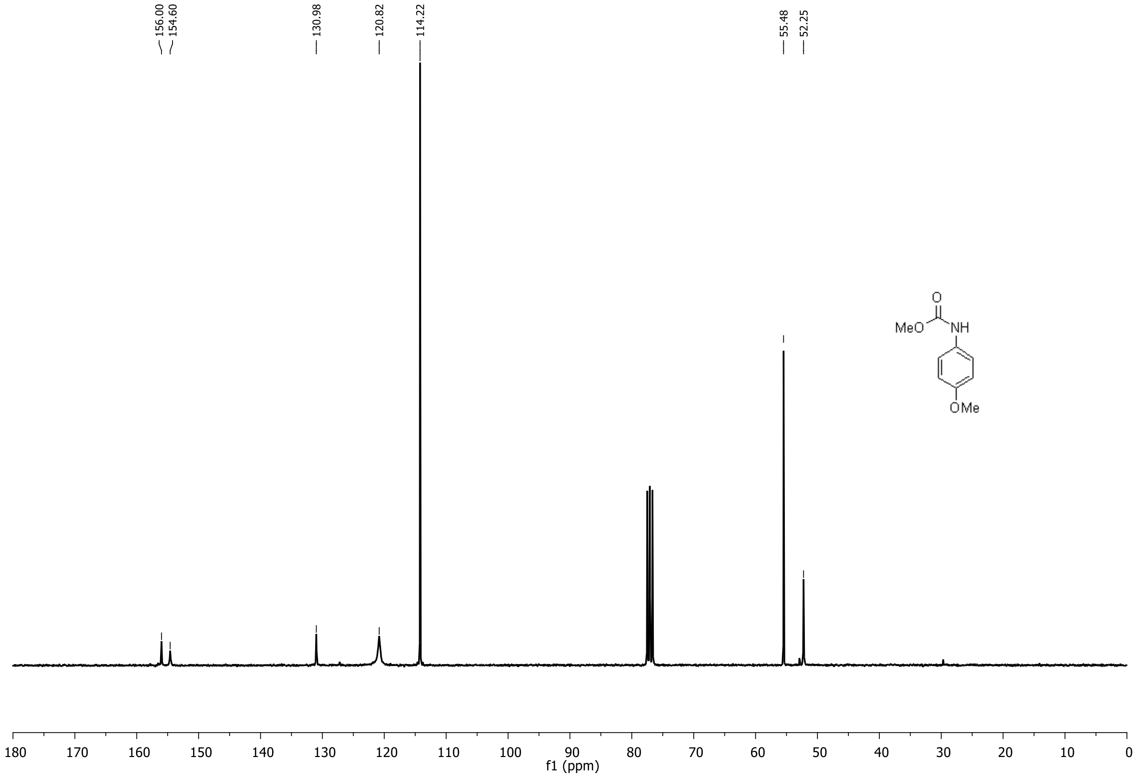

7.32
7.29
7.23
7.21
7.18
7.00
6.97
6.95
6.77
3.68
MeO
O
NH
1.89
2.03
1.08
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

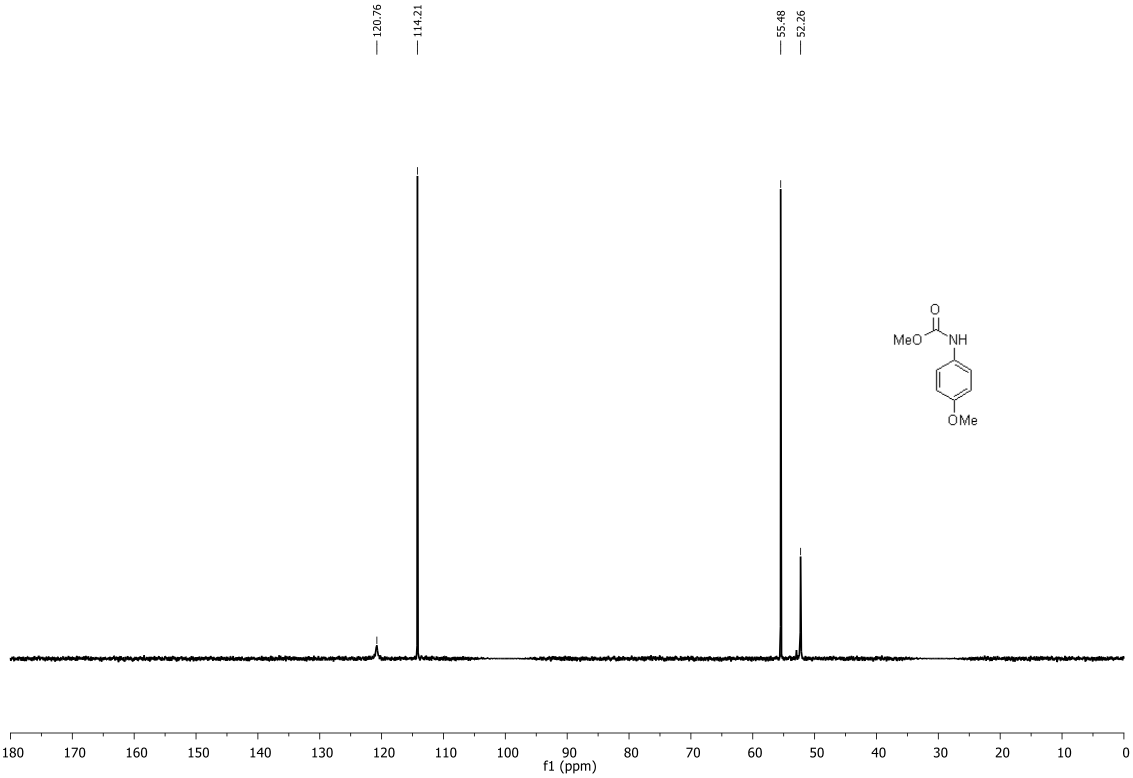

154.19
137.92
129.01
123.45
118.82
52.30
MeO
O
NH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

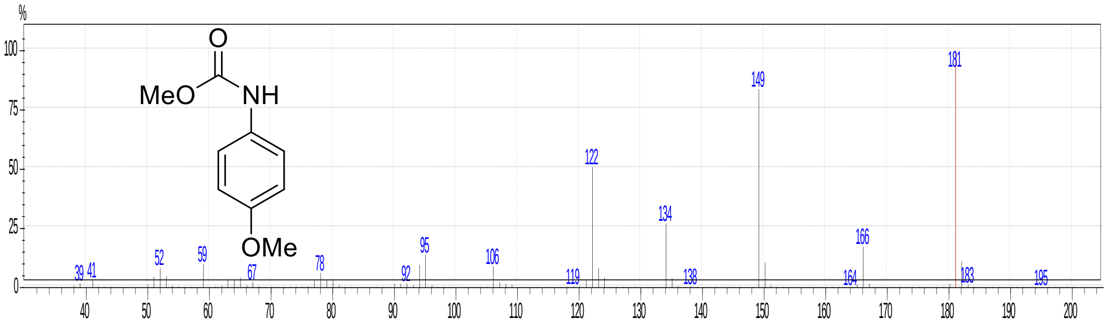

129.02
123.45
118.82
52.31
O
MeO
NH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

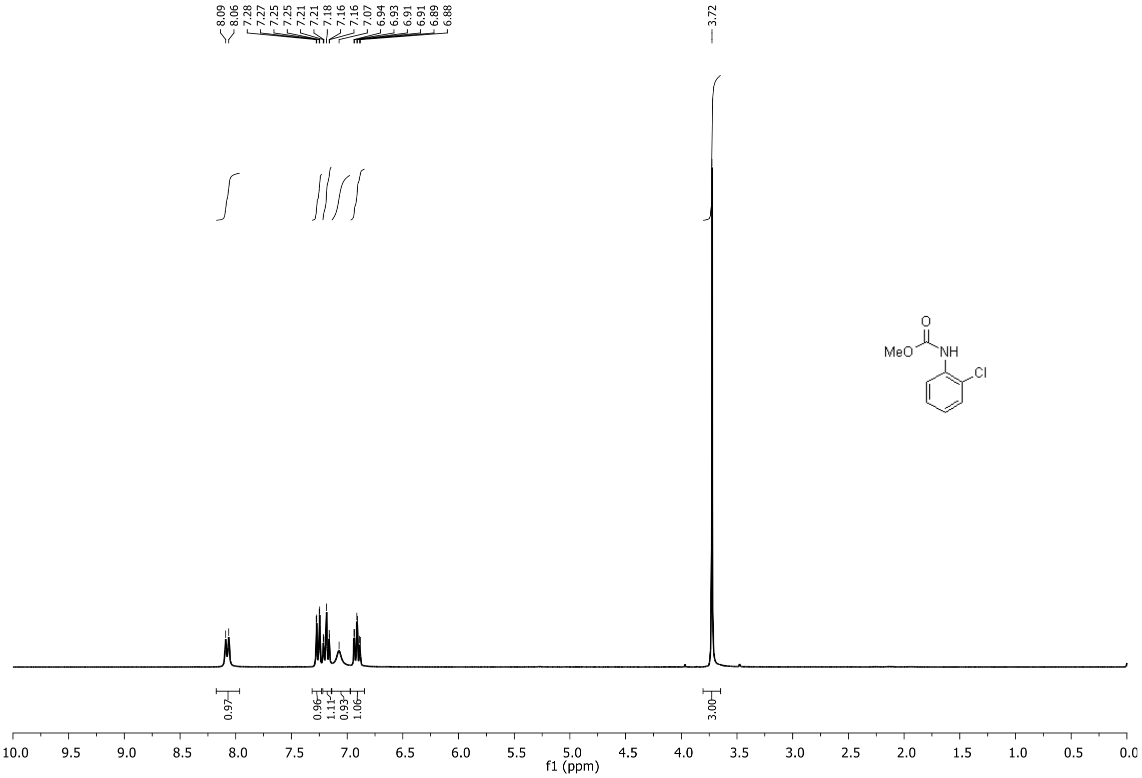

%
100
75
50
25
0
151
119
106
65
92
77
120
39
41
51
66
93
135
142
156
166
178
184
196
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
O
MeO
NH

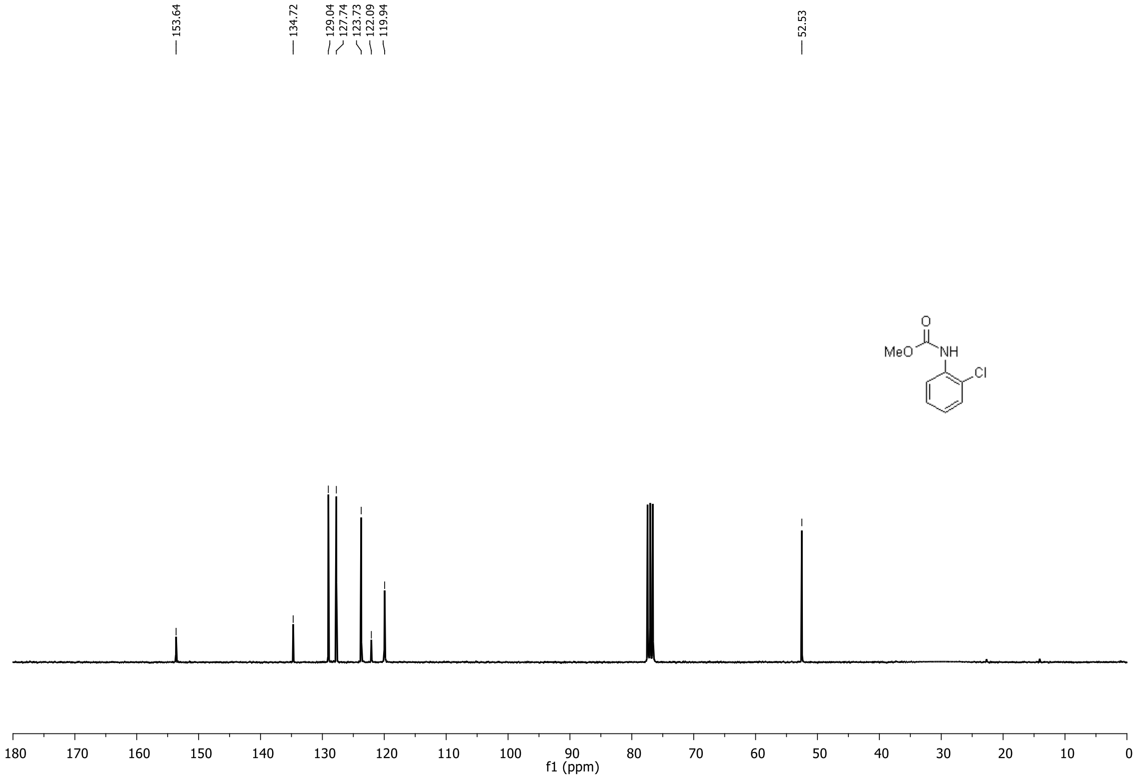

7.21
7.18
6.77
6.74
6.67
3.69
3.67
2.15
2.12
1.00
2.98
2.88
MeO
O
NH
OMe
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

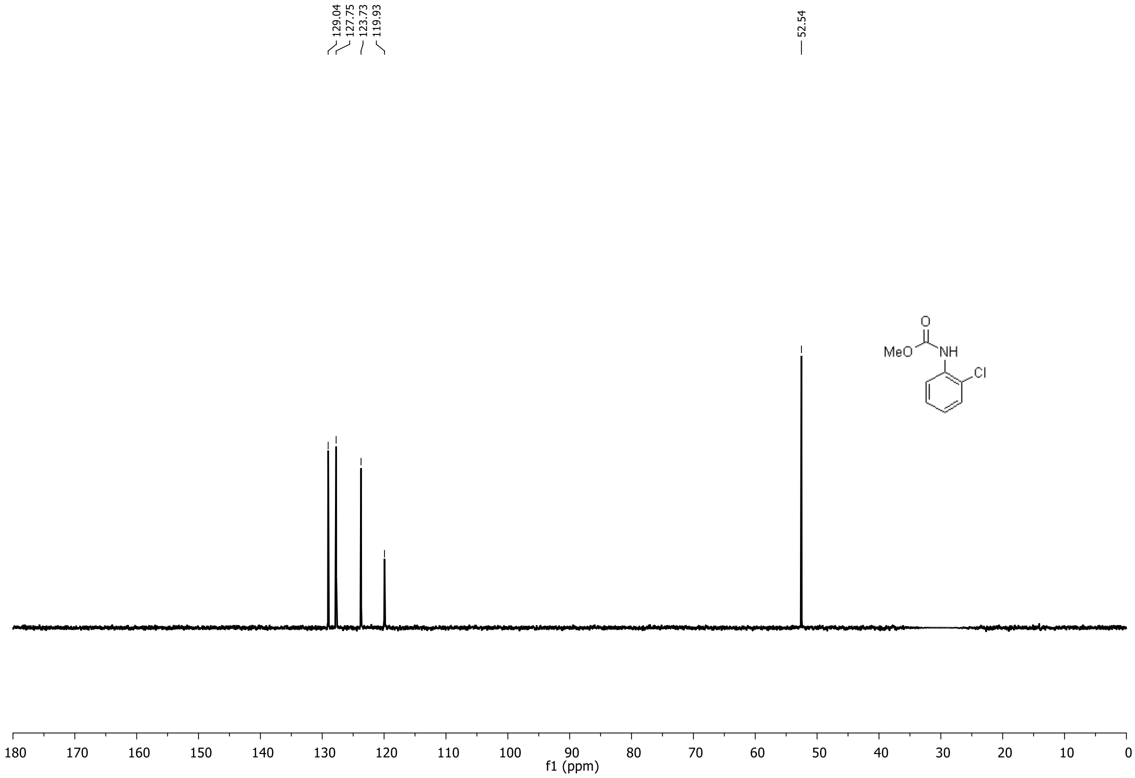

156.00
154.60
130.98
120.82
114.22
55.48
52.25
MeO
O
NH
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

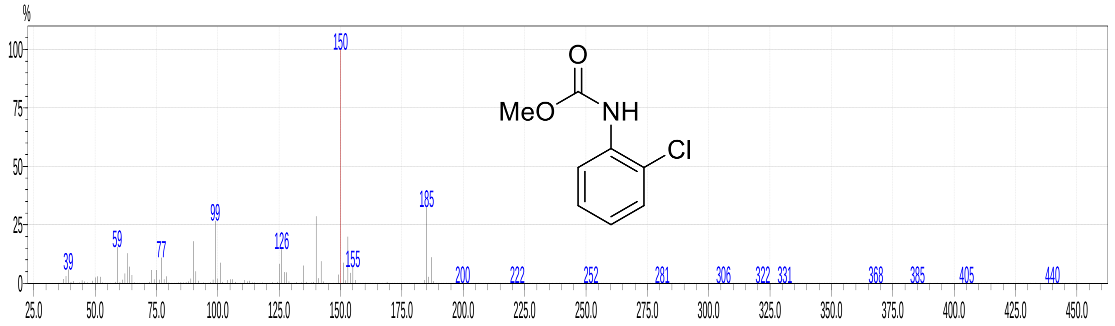

120.76
114.21
55.48
52.26
O
MeO
NH
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

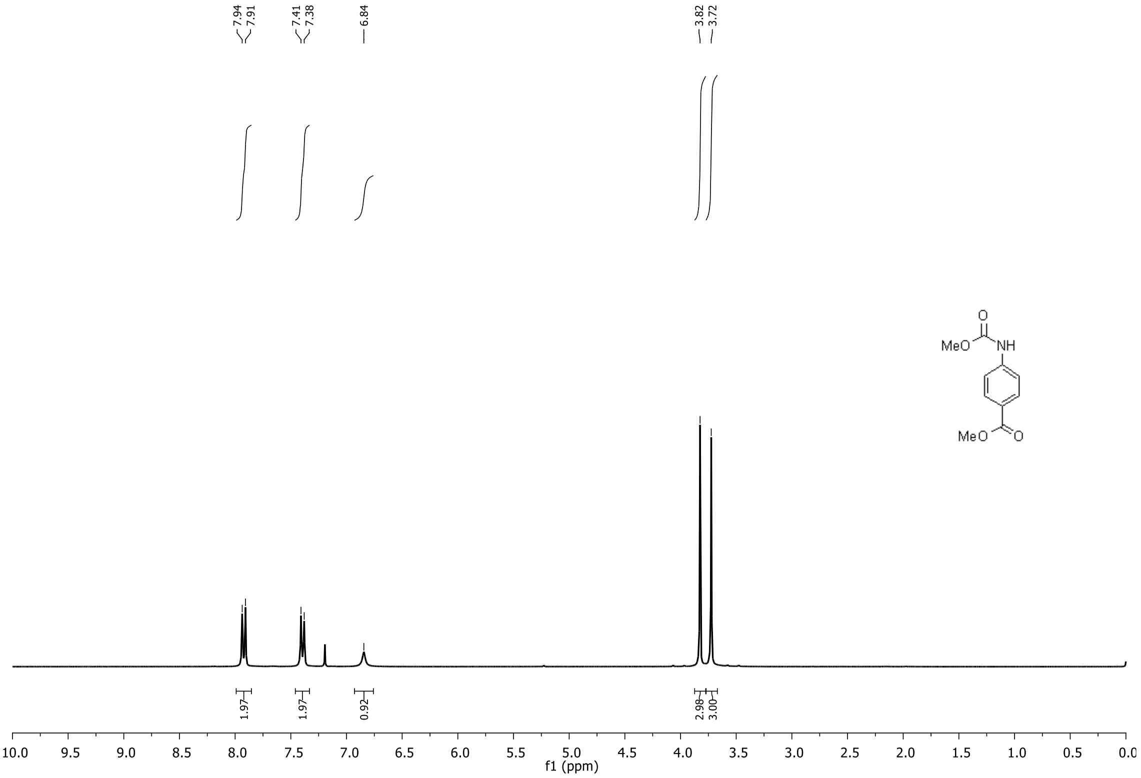

%
100
75
50
25
0
O
MeO
NH
OMe
39
41
52
59
67
78
92
95
106
119
122
134
138
149
164
166
181
183
195
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

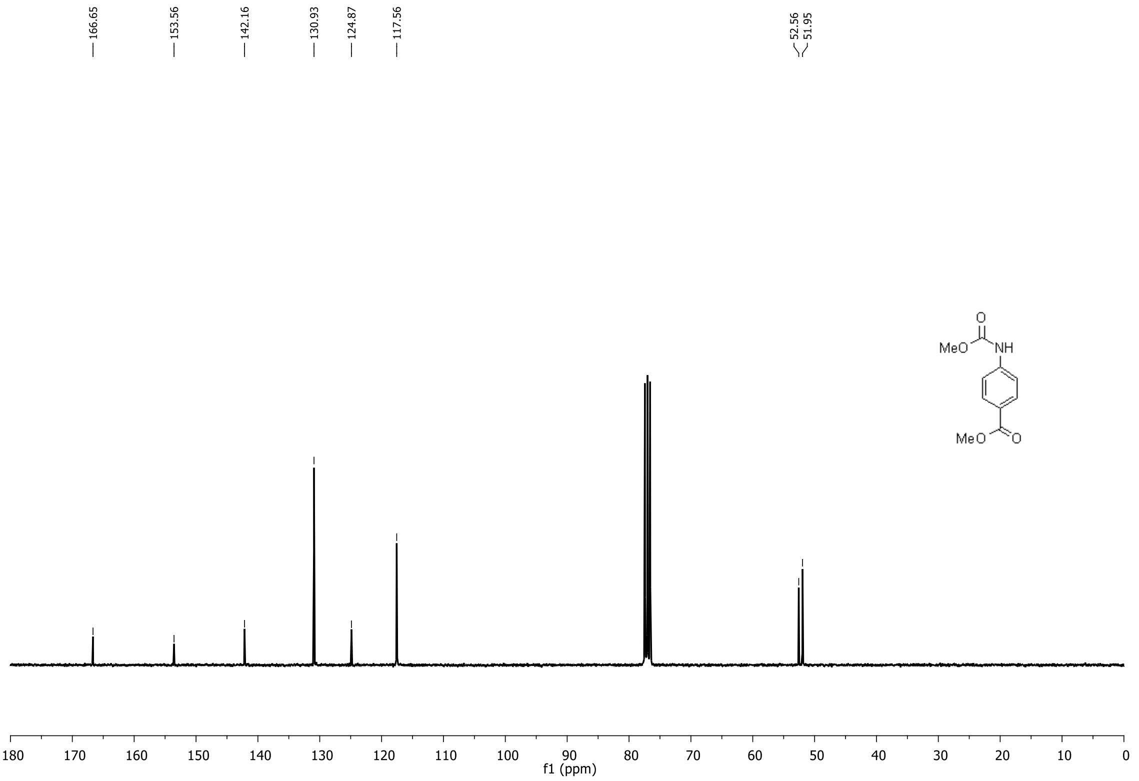

8.09
8.06
7.28
7.27
7.25
7.25
7.21
7.21
7.18
7.16
7.16
7.07
6.94
6.93
6.91
6.91
6.89
6.88
3.72
MeO
O
NH
Cl
0.97
0.96
1.11
0.93
1.06
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

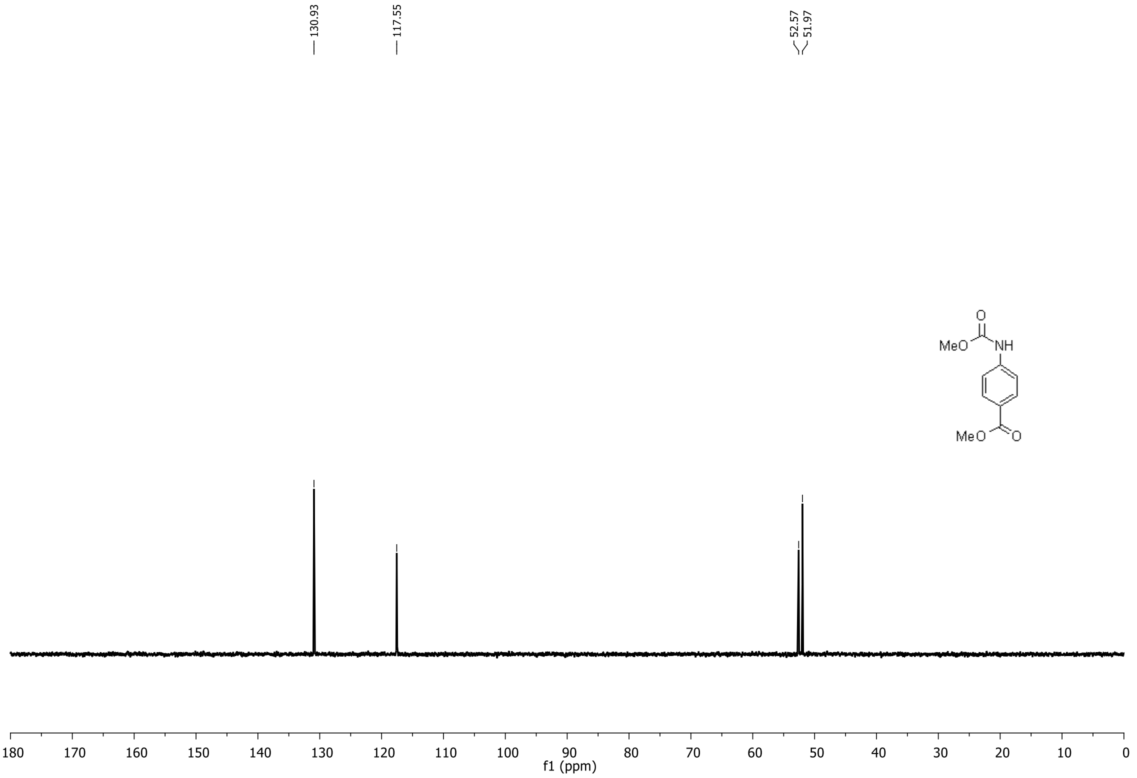

153.64
134.72
129.04
127.74
123.73
122.09
119.94
52.53
MeO
O
NH
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

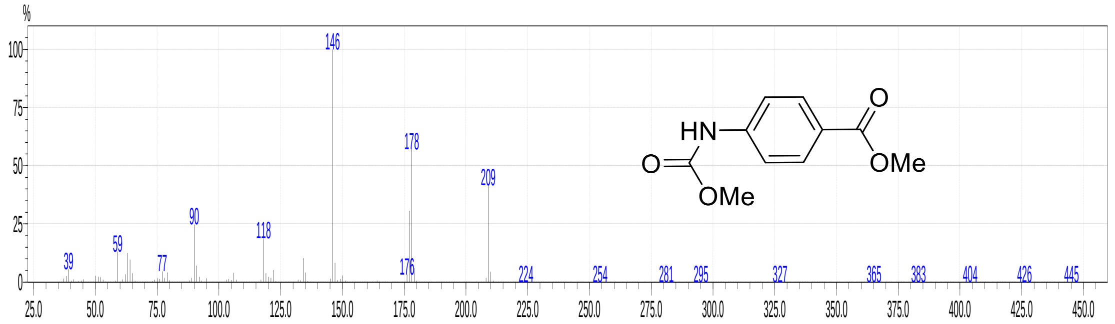

129.04
127.75
123.73
119.93
52.54
O
MeO
NH
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

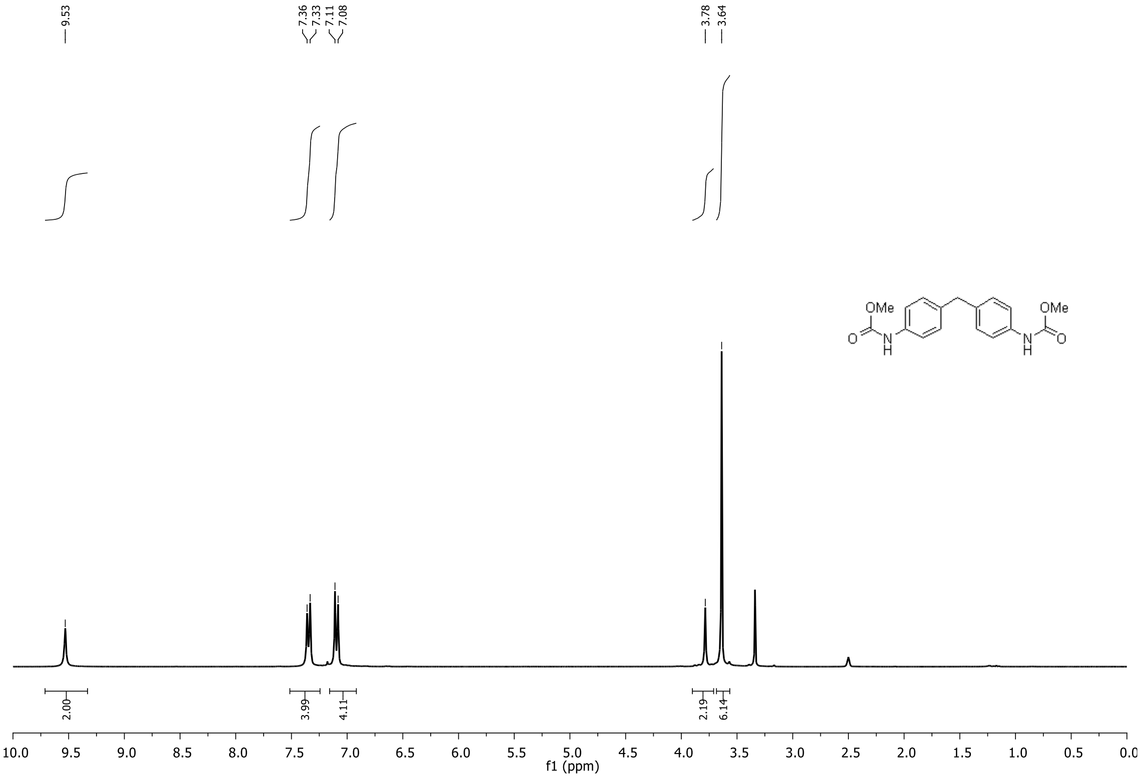

%
100
75
50
25
0
150
185
99
126
59
77
39
155
200
222
252
281
306
322
331
368
385
405
440
O
MeO
NH
Cl
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0

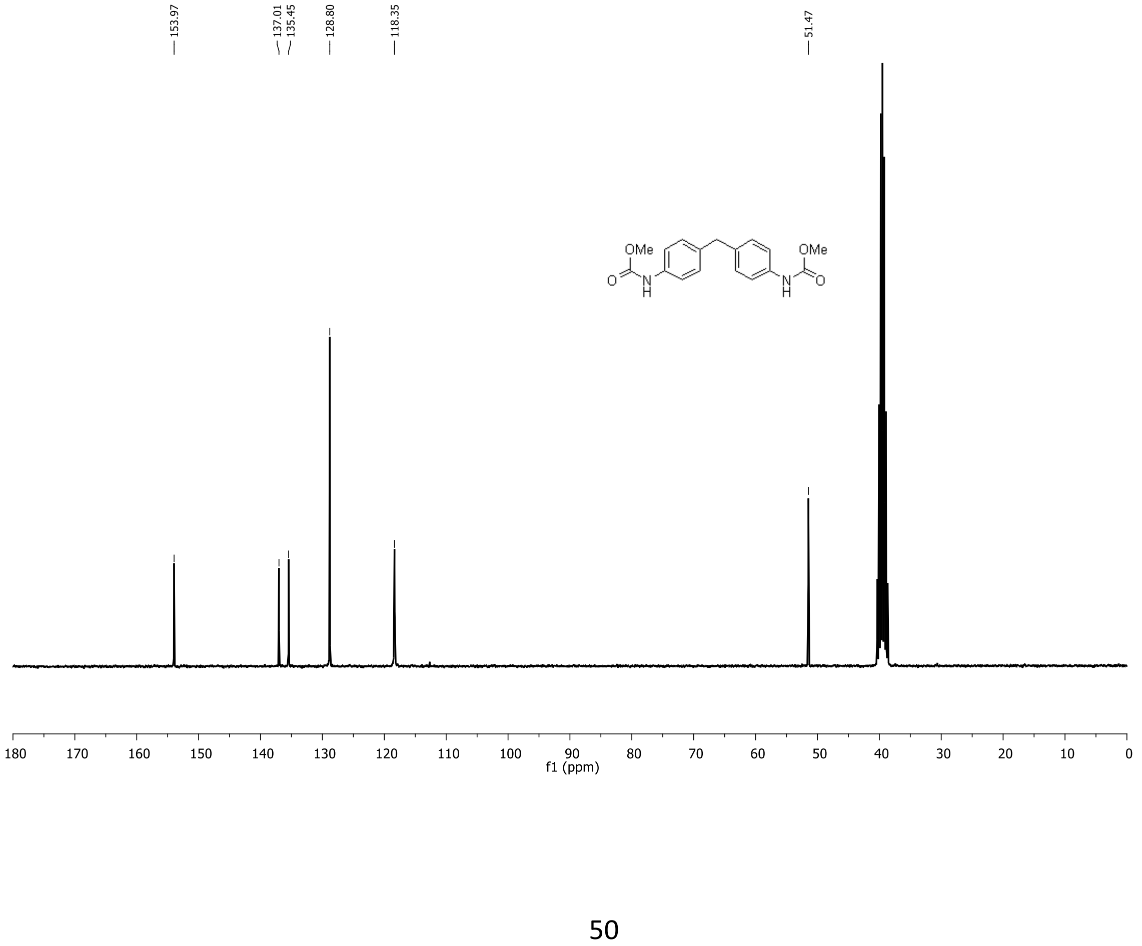

7.94
7.91
7.41
7.38
6.84
3.82
3.72
MeO
O
NH
MeO
O
1.97
1.97
0.92
2.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

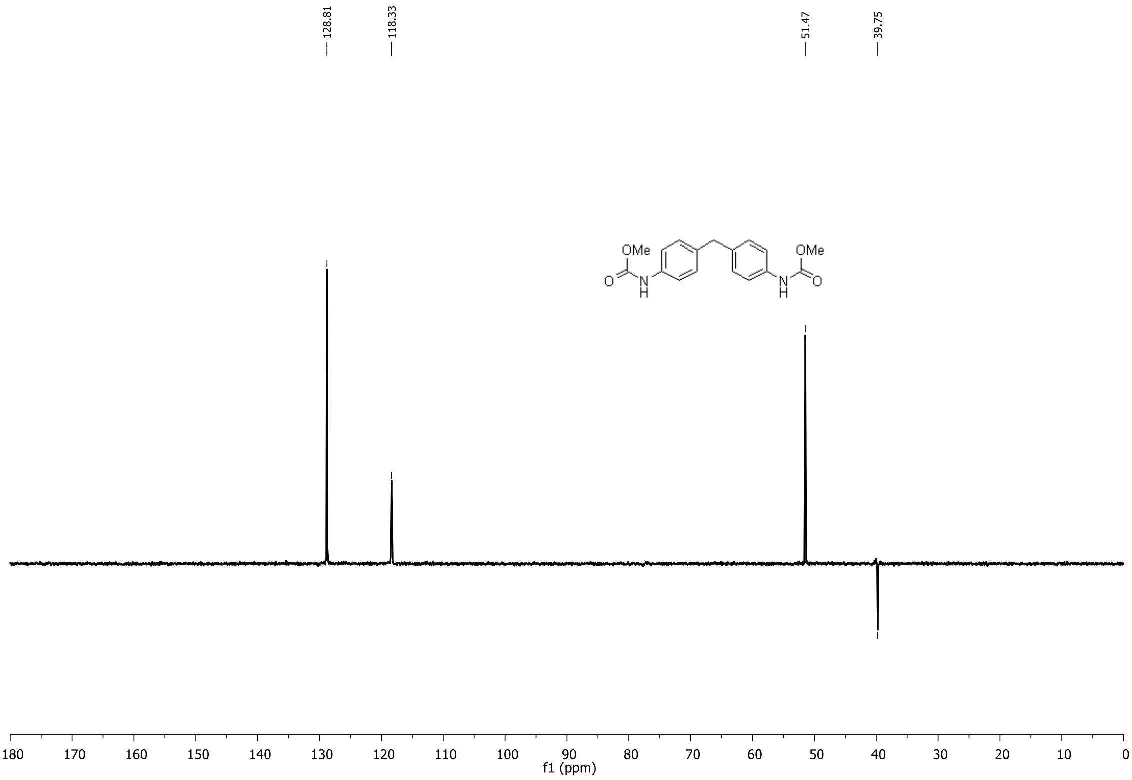

166.65
153.56
142.16
130.93
124.87
117.56
52.56
51.95
MeO
O
NH
MeO
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

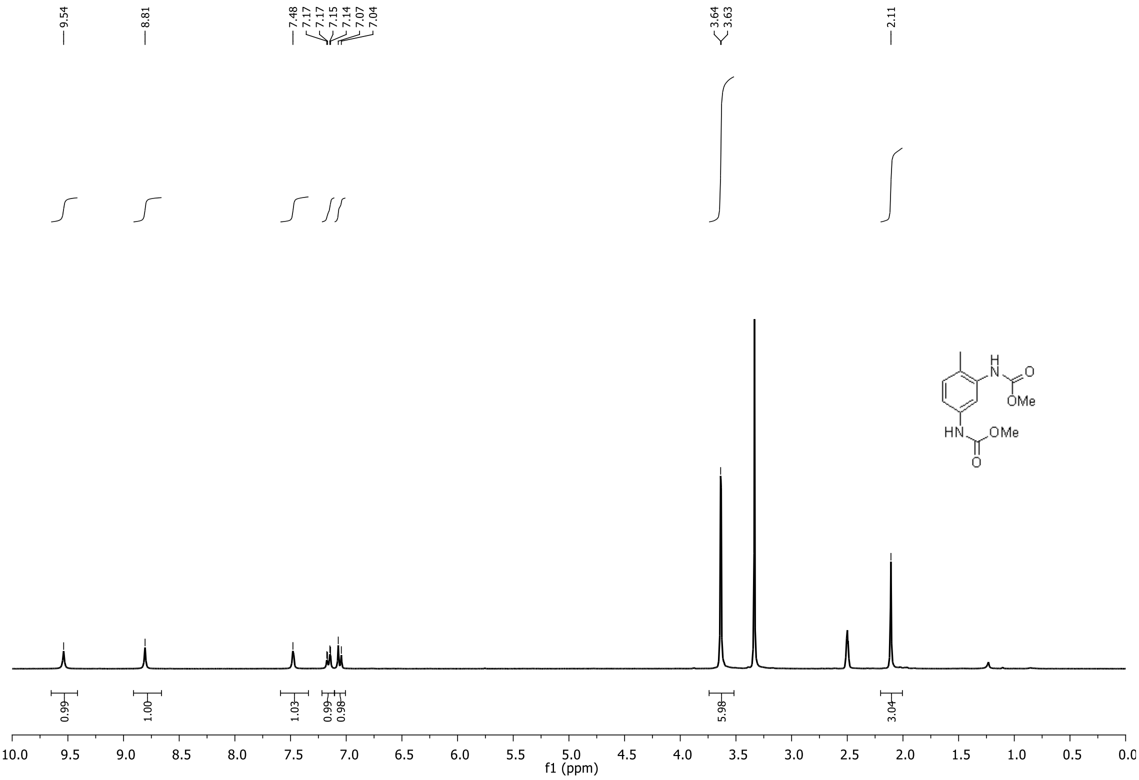

130.93
117.55
52.57
51.97
MeO
O
NH
MeO
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

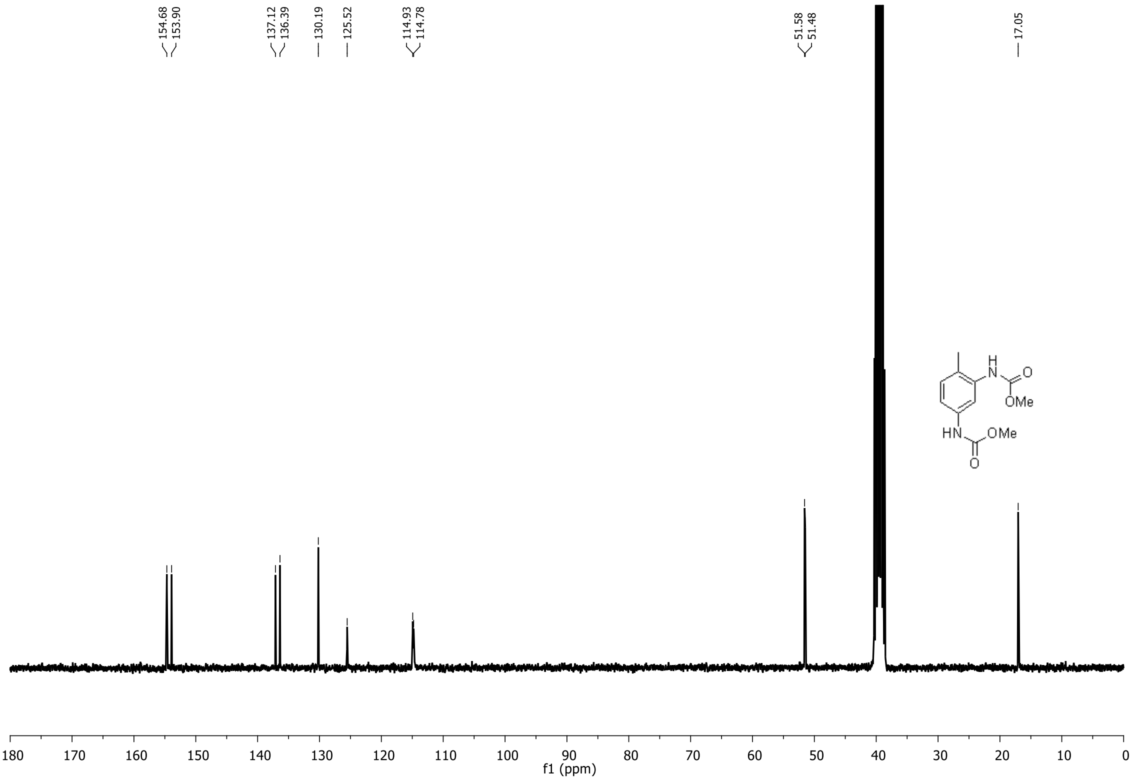

%
100
75
50
25
0
146
178
209
90
118
59
39
77
176
224
254
281
295
327
365
383
404
426
445
HN
O
OMe
O
OMe
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0

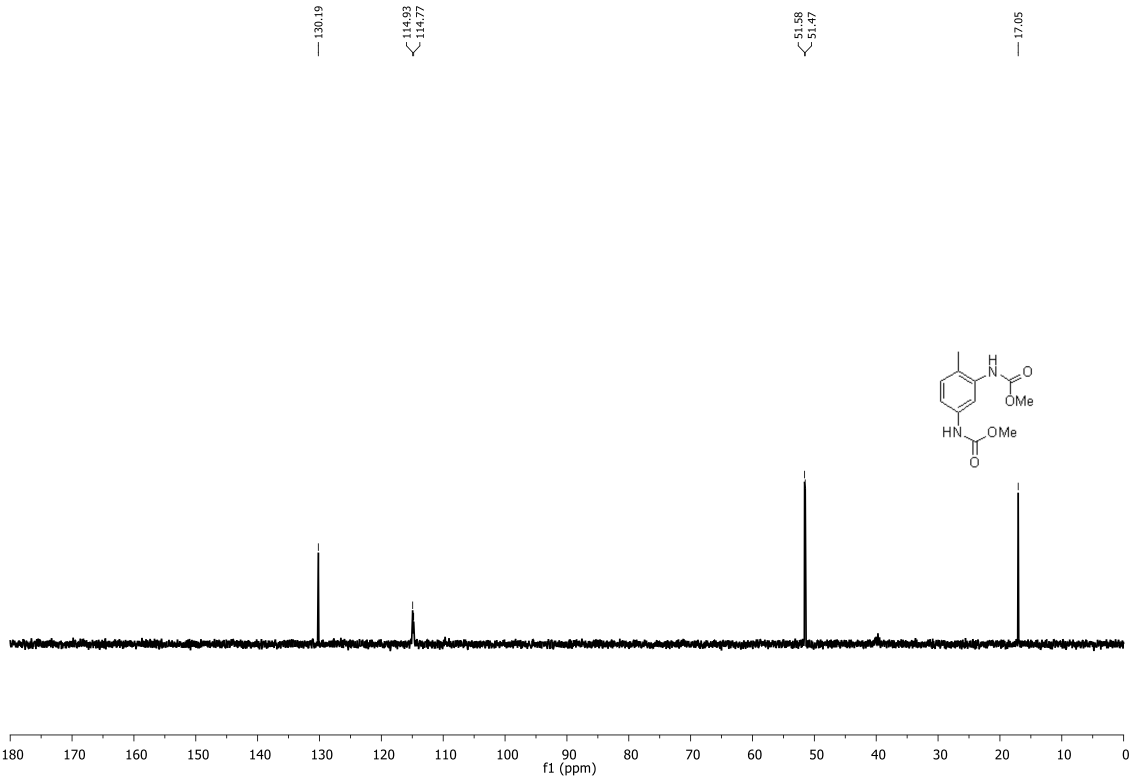

9.53
7.36
7.33
7.11
7.08
3.78
3.64
2.00
3.99
4.11
2.19
6.14
OMe
O
N
H
OMe
N
H
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

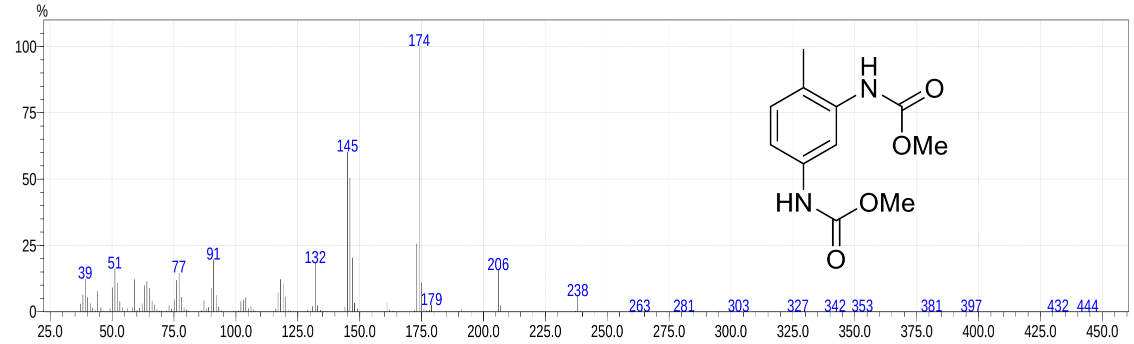

153.97
137.01
135.45
128.80
118.35
51.47
OMe
O
N
H
OMe
N
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


128.81
118.33
51.47
39.75
OMe
O
N
H
OMe
N
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.54
8.81
7.48
7.17
7.17
7.15
7.14
7.07
7.04
3.64
3.63
2.11
0.99
1.00
1.03
0.99
0.98
5.98
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
H
N
O
OMe
HN
OMe
O


154.68
153.90
137.12
136.39
130.19
125.52
114.93
114.78
51.58
51.48
17.05
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
H
N
O
OMe
HN
OMe
O


130.19
114.93
114.77
51.58
51.47
17.05
H
N
O
OMe
HN
OMe
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


%
100
75
50
25
0
174
145
39
51
77
91
132
179
206
238
263
281
303
327
342
353
381
397
432
444
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
H
N
O
OMe
HN
OMe
O

References:

1. M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert and A. L. Goodwin, *Nat. Commun.*, 2014, **5**, 4176.
2. Y. Liu, R. C. Klet, J. T. Hupp and O. Farha, *Chem. Commun.*, 2016, **52**, 7806-7809.
3. J. He, X. Duan and C. Li, *Materials Chemistry and Physics*, 2001, **71**, 221-225.
4. Z. D. Crane, P. J. Nichols, T. Sammakia and P. J. Stengel, *J. Org. Chem.*, 2011, **76**, 277-280.