

Supporting Information

All Organic Porous Heterogeneous Composite with Antagonistic Sites as Cascade Catalyst for Continuous Flow Reaction

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Section S1: Materials, General Characterizations and Physical Measurements

S1.1. Materials: Starting materials, Benzyl chloride, FeCl₃, formaldehyde dimethyl acetal (FDA), 1-Methylimidazole, were purchased from Sigma-Aldrich. NaOH, THF, 1,2-Dichloroethane (DCE) and remaining solvents were obtained locally. These chemicals were used without further purification.

S1.2. General Characterizations and Physical Measurements:

S1.2.1 Fourier transform infrared spectroscopy (FT-IR): The IR spectra were recorded using NICOLET 6700 FT-IR spectrophotometer using KBr pellet in 550-4000 cm⁻¹ range.

S1.2.2 Thermogravimetric analysis (TGA): Thermogravimetric analyses were performed using Perkin-Elmer STA 6000 TGA analyzer by heating the samples from 40 to 800 °C under N₂ atmosphere with a heating rate of 10 °C min.

S1.2.3 Field emission scanning electron microscopy (FESEM): The morphology of the materials was investigated with a Zeiss Ultra Plus field-emission scanning electron microscope (FESEM) with an integral charge compensator and embedded EsB and AsB detectors (Oxford X-max instruments 80 mm² (Carl Zeiss NTS, GmbH). The elemental analysis was carried out using voltage of 15 KV equipped with an EDX detector. Data acquisition was performed with an accumulation time of >600s.

S1.2.4 Transmission electron microscopy (TEM): For high-resolution TEM analysis, all the samples were dispersed in isopropanol (0.5 mg/mL) and sonicated for 15 minutes. Then, the samples were left undisturbed for 2 minutes, and the upper part of the solution was taken for preparing TEM samples on a lacey carbon-coated copper grid (Electron Microscopy Science). TEM imaging and STEM-EDS were performed on the HRTEM (JEM-2200FS, JEOL) operating at acceleration voltage of 200 kV.

S1.2.5 Solid-state nuclear magnetic resonance (NMR) spectroscopy: Solid-state ¹³C cross-polarization-magic angle spinning (CP-MAS) spectra were acquired on a Bruker 500 MHz NMR spectrometer with a CP-MAS probe. Carbon chemical shifts are expressed in parts per million (δ scale). The ¹³C chemical shifts were externally referenced to tetramethylsilane (δ = 0.0 ppm).

S1.2.6 Proton (¹H) nuclear magnetic resonance (NMR) spectroscopy: All ¹H spectra were recorded either on Bruker 400 MHz and Jeol 400 MHz spectrometers. The chemical shifts (δ) in ppm were referenced to the residual signal of deuterium solvents (¹H NMR CDCl₃). The multiplicities of the peaks are s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet).

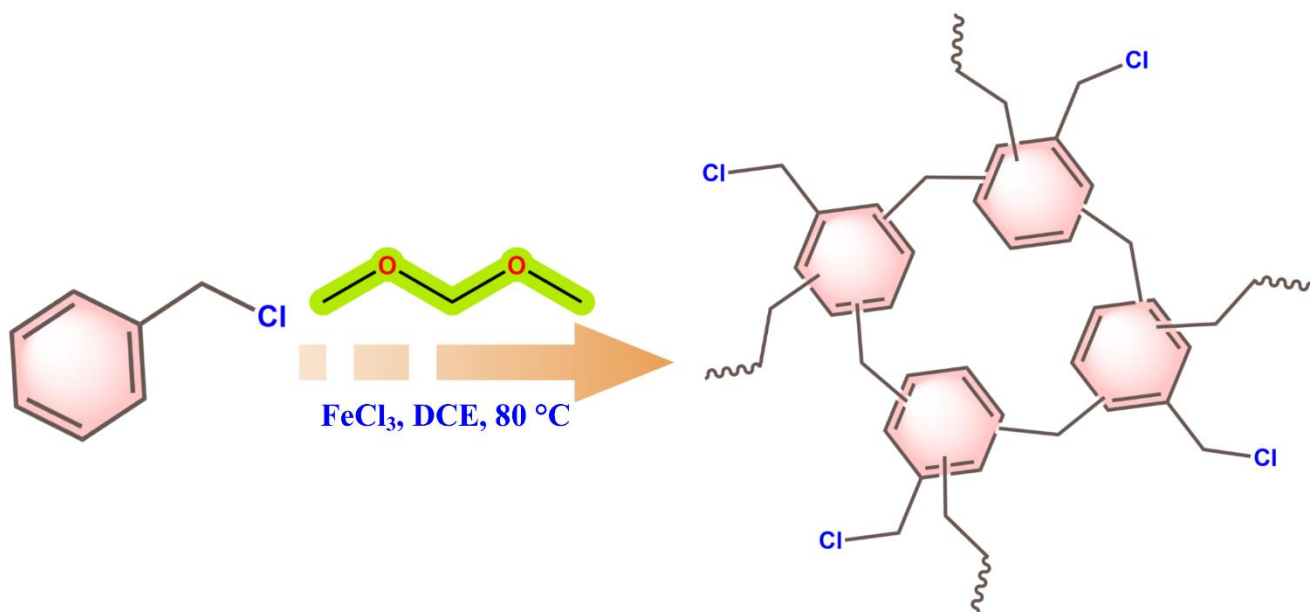
S1.2.7 Powder X-ray diffraction (PXRD): Powder X-ray diffraction (PXRD) patterns were performed on a Bruker D8 Advanced X-ray diffractometer at room temperature using Cu Kα radiation (λ = 1.5406 Å) at a scan speed of 0.5 ° min⁻¹ and a step size of 0.01° in 2θ.

S1.2.8 Nitrogen adsorption-desorption isotherm measurements: N₂ gas adsorption measurements were performed using BelSorp-Max instrument (Bel Japan). Prior to adsorption measurements, the activated samples were heated at 120 °C under vacuum for 12 hours using BelPrepvacII.

S1.2.9 X-ray photoelectron spectroscopy (XPS): As-obtained powder samples was stuck to conductive paste and then measured by X-ray photoelectron spectroscopy using K-Alpha+ model (Thermo Fischer Scientific, UK) with Al K α source.

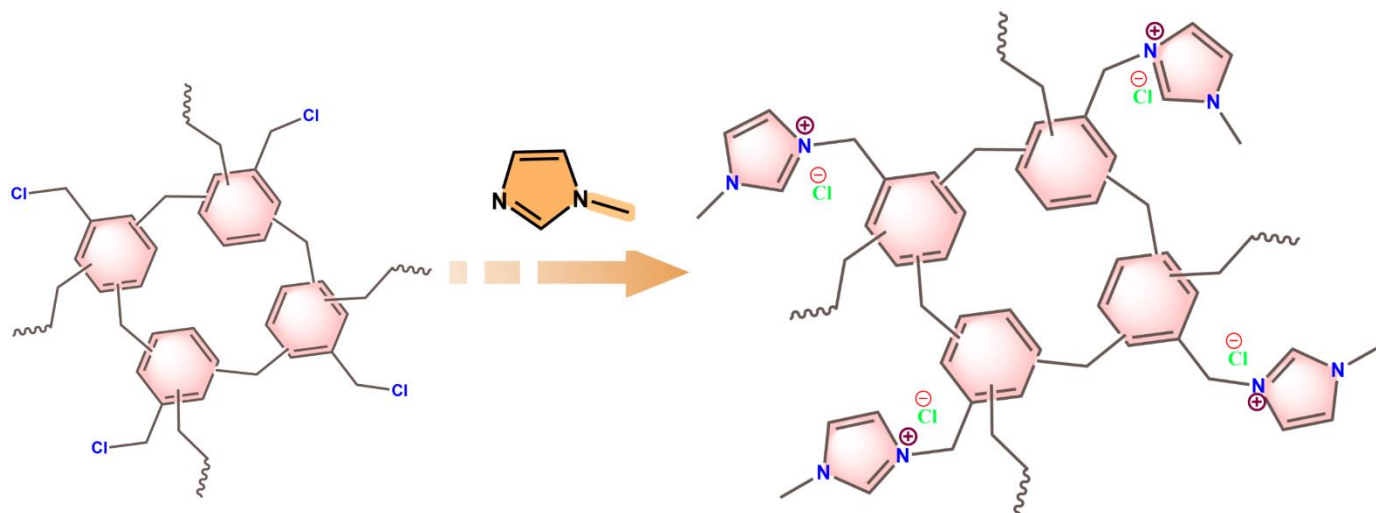
S1.2.10 Temperature-programmed desorption (TPD) measurements: The temperature programmed desorption (TPD) study was done using CHEMBET™ TPR/TPD, QUANTACHROME.

Section S2: Detail synthetic procedures of HCP120-Cl, HCP 120-MI@Cl and HCP 120-MI@OH



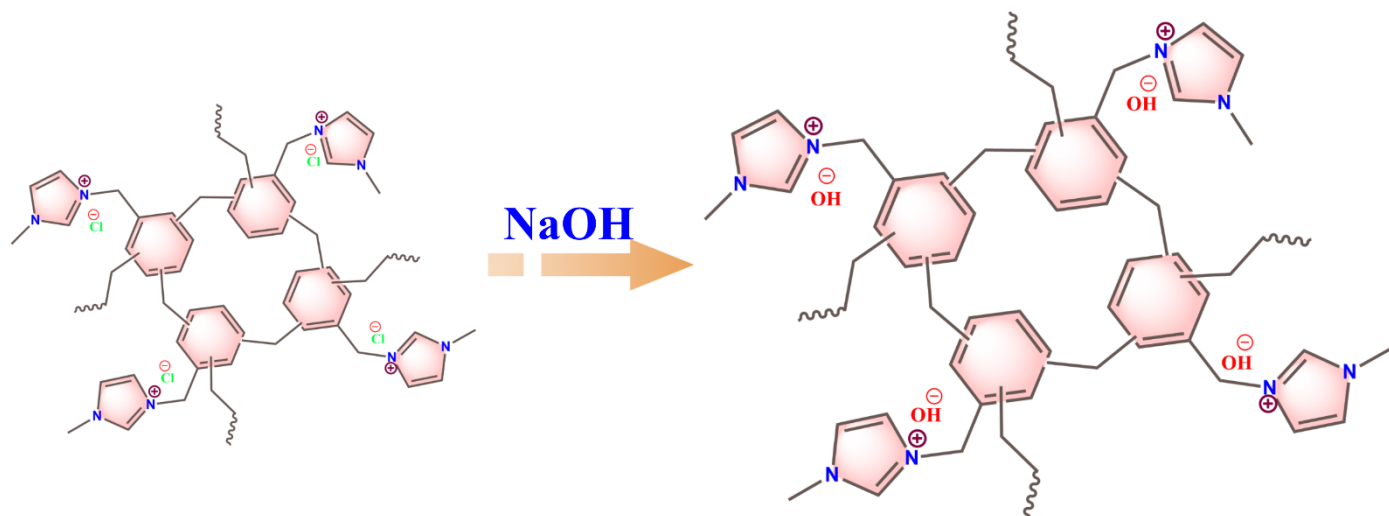
Scheme S1: Synthesis of HCP120-Cl

S2.1 Synthesis of HCP120-Cl: HCP120-Cl was synthesized by following our previous report (Scheme-1).¹ Yield: 346 mg (~91%).



Scheme S2: Synthesis of HCP 120-MI@Cl

S2.2 Synthesis of HCP120-MI@Cl: Activated HCP 120-Cl (300 mg) was taken in a round bottom flask and to that 30 ml of acetonitrile (ACN) was added (Scheme-3). This was followed by dropwise slow addition of 3 mL 1-methyl imidazole (MI) and further allowed to react under stirring for 48 hrs. at reflux temperature. On completion of the reaction dark brown precipitate was filtered off and washed with copious amount of water for several times to remove excess MI. Then the precipitate was again washed with DMF, methanol, water, chloroform, dichloromethane and tetrahydrofuran (THF) repeatedly. Thus obtained dark brown colored solid material (HCP 120-MI@Cl) was subject to Soxhlet extraction in MeOH for 24 h to remove the high boiling solvents from the porous network of HCP 120-MI@Cl. The solvent exchanged phase was further heated at 140 °C under vacuum overnight to obtain the guest free activated material and with this phase further works have been carried out Yield: 352 mg (~ 92%).

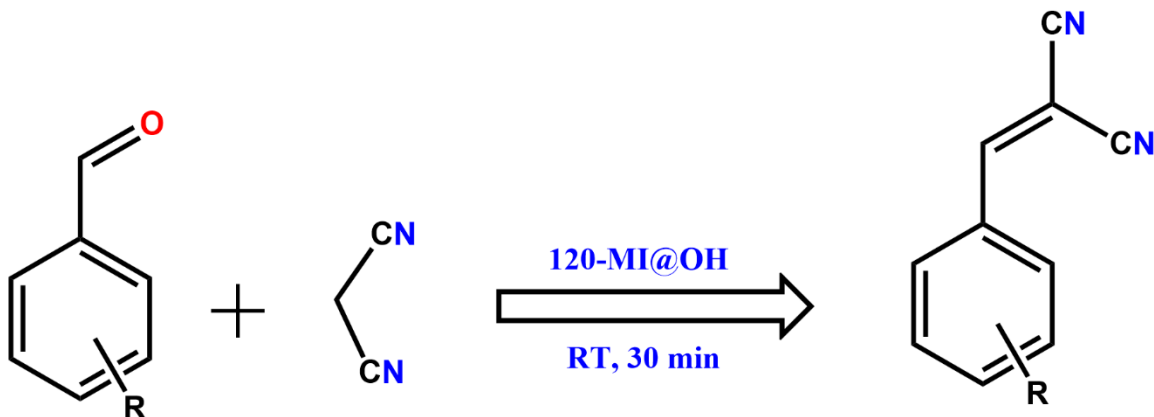


Scheme S3: Synthesis of HCP120-MI@OH

S2.3 Synthesis of HCP120-MI@OH: 100 mg of activated 120-MI@Cl and 250 mg NaOH were suspended in 10 mL H₂O. The resultant mixture was stirred at room temperature for 72 h. The mixture was then filtrated under reduced pressure and the obtained solid was washed with H₂O until neutral. Afterwards, the solid was dried in vacuo at 120 °C to yield 120-MI@OH (92 mg).

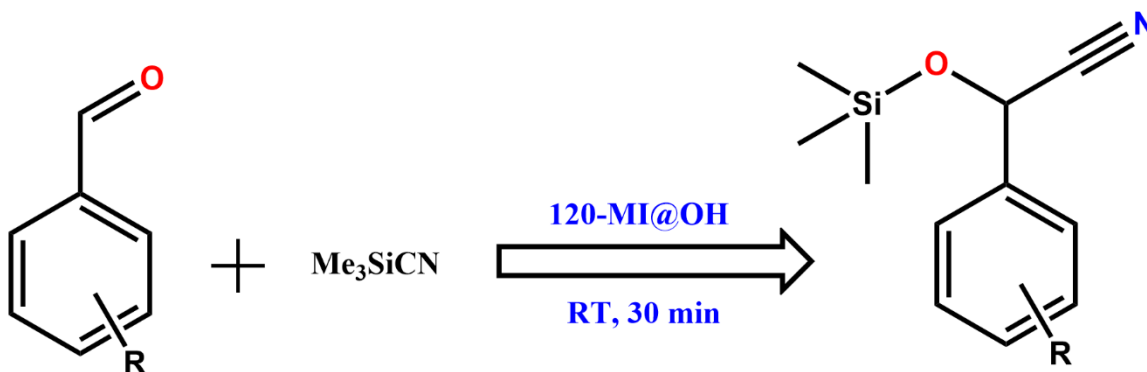
Section S3: General experimental procedures

S3.1 HCP 120-MI@OH catalyzed Knoevenagel Condensation:



To a 10 mL reaction tube were sequentially added aldehyde (0.8 mmol, 1 equiv.), H₂O (4 mL), malononitrile (0.8 mmol, 1 equiv.), and the heterogeneous catalyst HCP 120-MI@OH (5 mg). The reaction mixture was then stirred at room temperature for 0.5 h. After extraction with CH₂Cl₂ (3 × 10 mL), the combined organic phase was dried over Na₂SO₄. After evaporation of the solvent under vacuum, the crude product was analyzed ¹H NMR using 1,3,5 trimethoxybenzene as the internal standard to determine product yield.

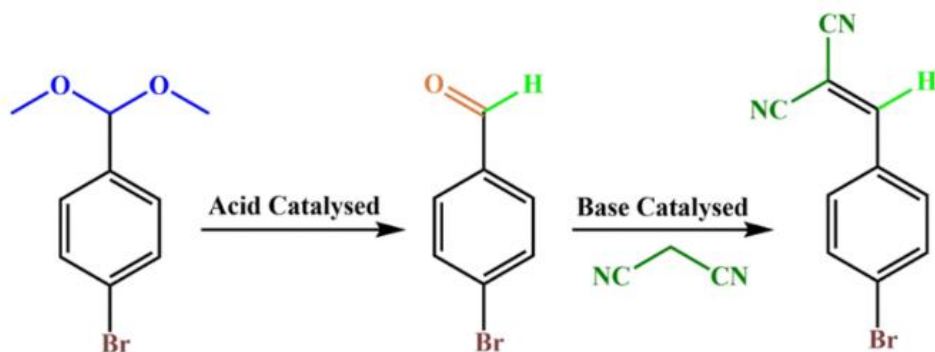
S3.2 HCP 120-MI@OH catalyzed Cyanosilylation:



Me₃SiCN (2.0 mmol), carbonyl substrate (1.0 mmol) and catalyst 120-MI@OH (5 mg) were placed into a screw cap vial. The reaction mixture was vigorously stirred at room temperature for

0.5 h. After the reaction was completed, the crude product was extracted with CH_2Cl_2 (3×5 mL), and the solvent was evaporated. Finally, the conversion was determined by ^1H NMR using 1,3,5 trimethoxybenzene as the internal standard.

S3.3 HCP 120-MI@OH catalyzed One-Pot Cascade Catalysis Reaction:



The one-pot deacetalization-Knoevenagel condensation reaction was performed in a 10 mL reaction tube equipped with a temperature controller and magnetic drive. A typical process is as follows: 5 mg of HCP 120-MI@OH catalyst together with a mixture of 4-bromobenzaldehyde dimethyl acetal (0.5 mmol), malononitrile (0.5 mmol) was put into the reactor. Then, 5 ml water (H_2O) was added as solvent and the reaction mixture was heated at 60°C for 2 hrs. To test the reaction conversion, the compositions of starting reagent, intermediate product and the final product 3 were measured by ^1H NMR in CDCl_3 . Comparing the integral of the phenylic proton from the final product benzylidene ethyl cyanoacetate (7.72 ppm) with the phenylic proton of the 4-bromobenzaldehyde dimethyl acetal (5.35 ppm) and 4-bromobenzaldehyde (9.96 ppm), the conversions of the starting reagent acetal and the intermediate product aldehyde were calculated by ^1H NMR using 1,3,5 trimethoxybenzene as the internal standard (see the example in Figure S15).

S3.4 Scaled-up Cascade Catalysis: The scaled up deacetalization-Knoevenagel condensation cascade catalysis was carried out by increasing the reactant, solvent as well as the catalyst amount. Typically, benzaldehyde dimethyl acetal (6.1 mL, 40 mmol), malononitrile (2.64

g, 40 mmol) and 150 mL water (H₂O) was added to a round bottom flask and was heated for 2 h at 60 °C. To test the reaction conversion, the formation of the final product and its purity ¹H NMR was performed in CDCl₃. Isolated product yield 5.54 g (89%)

S3.4 Continuous flow-through Cascade Catalysis:



A mixture of benzaldehyde dimethylacetal (1.82 mL, 12.0 mmol), H₂O (5 mL), malononitrile (792.8 mg, 12.0 mmol) in C₂H₅OH solution (40 mL) was pumped through the spiral transparent glass tube reactor which is evenly charged with 120-MI@OH beads (0.2 g) at 60 °C with a flow rate of 0.4 mL min⁻¹.

Section S4: Structural and morphological characterizations

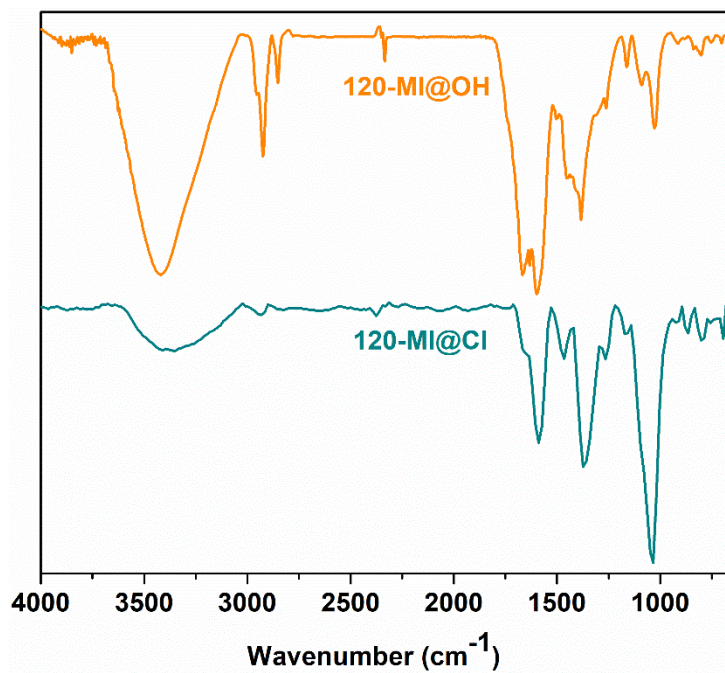


Figure S1: Infra-red (IR) spectra of 120-MI@Cl (cyan) and 120-MI@OH (orange).

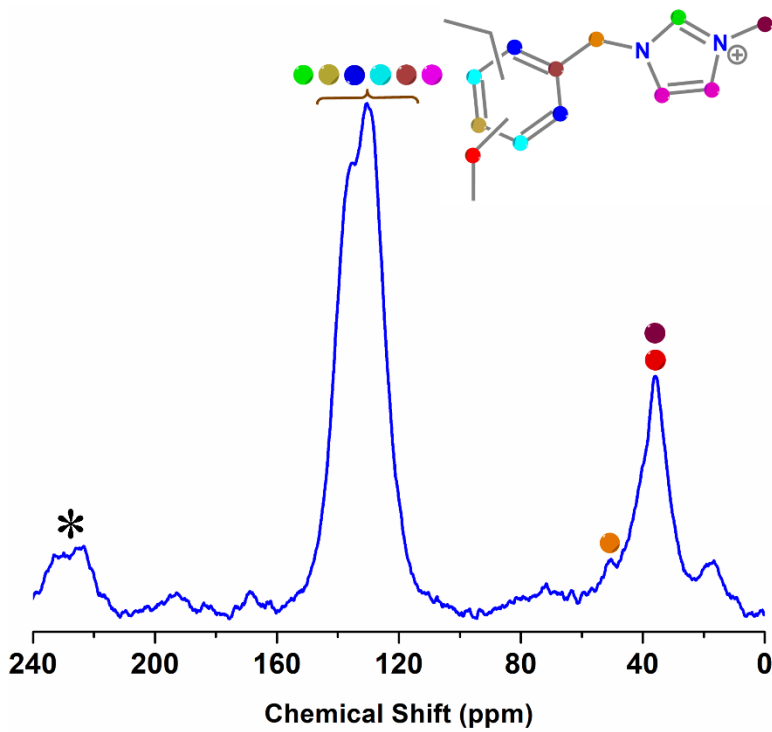


Figure S2: Solid-state ^{13}C CP-MAS NMR spectrum of polymer 120-MI@Cl.

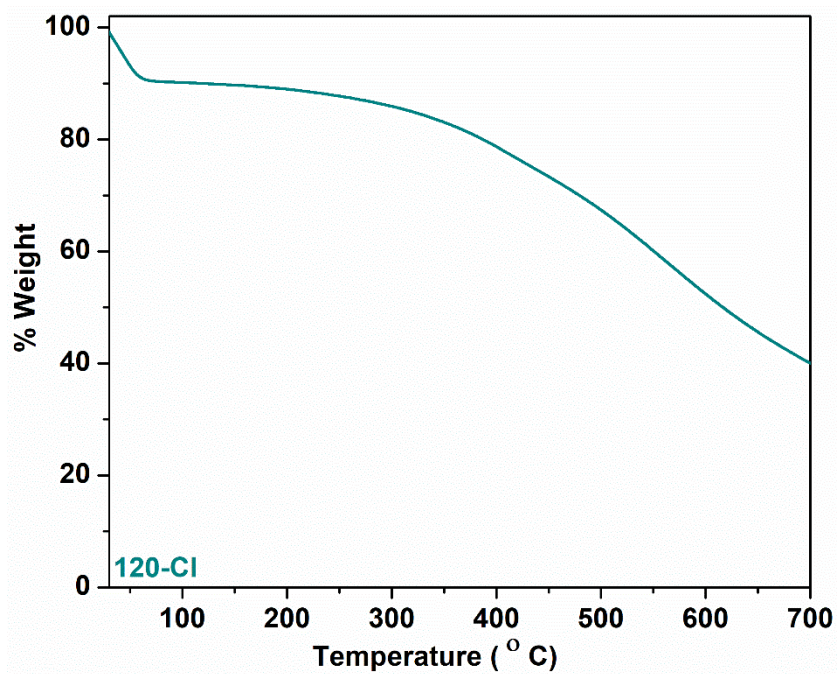


Figure S3: Thermogravimetric profile for pristine 120-Cl (cyan).

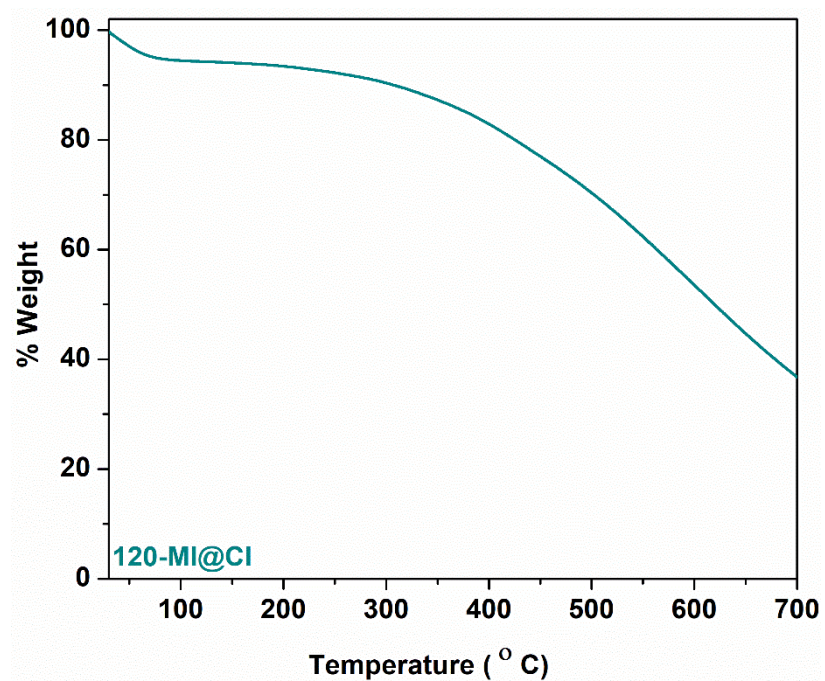


Figure S4: Thermogravimetric profile for pristine 120-MI@Cl (cyan).

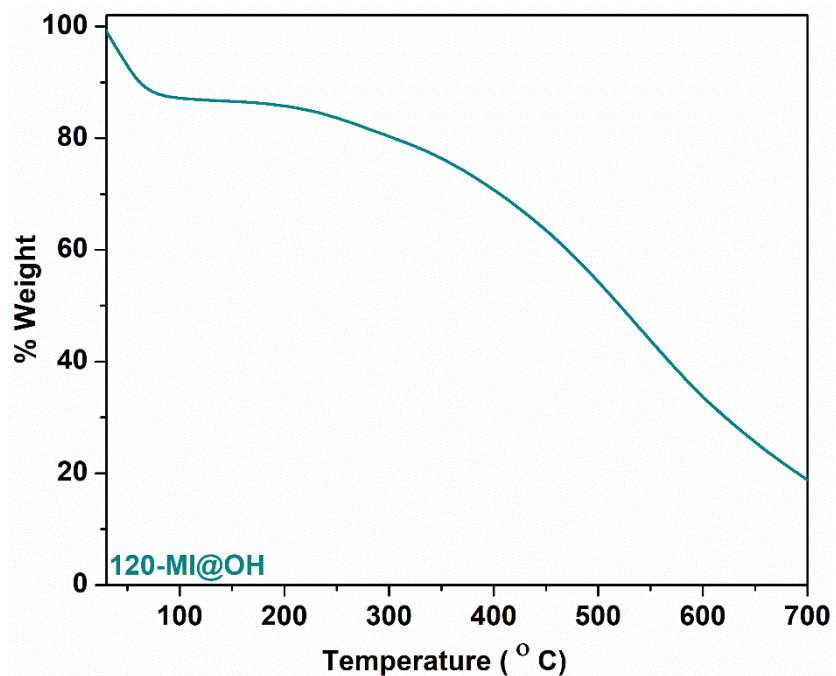


Figure S5: Thermogravimetric profile for pristine 120-MI@OH (cyan).

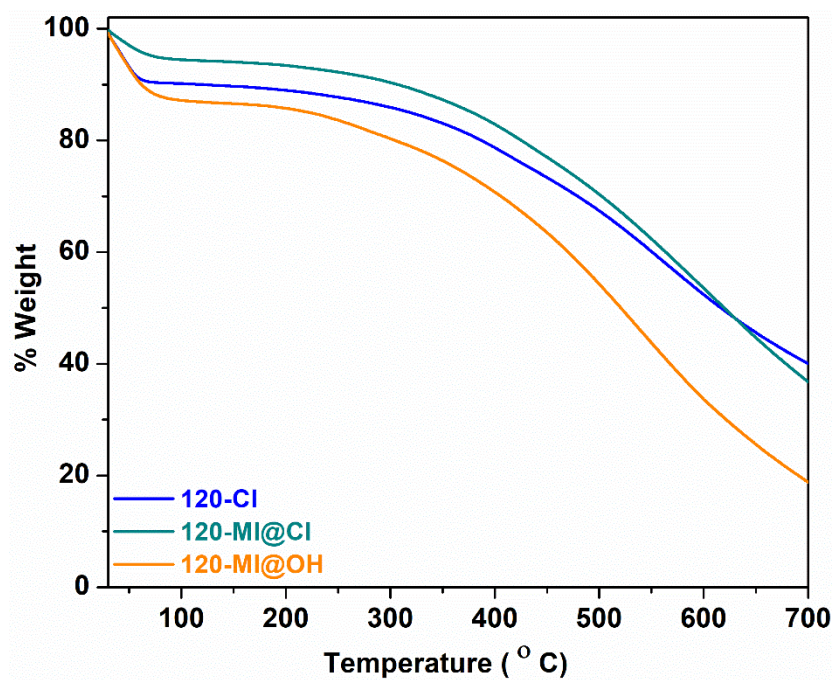


Figure S6: Thermogravimetric profile for pristine 120-Cl (blue), 120-MI@Cl (cyan) and 120-MI@OH (orange).

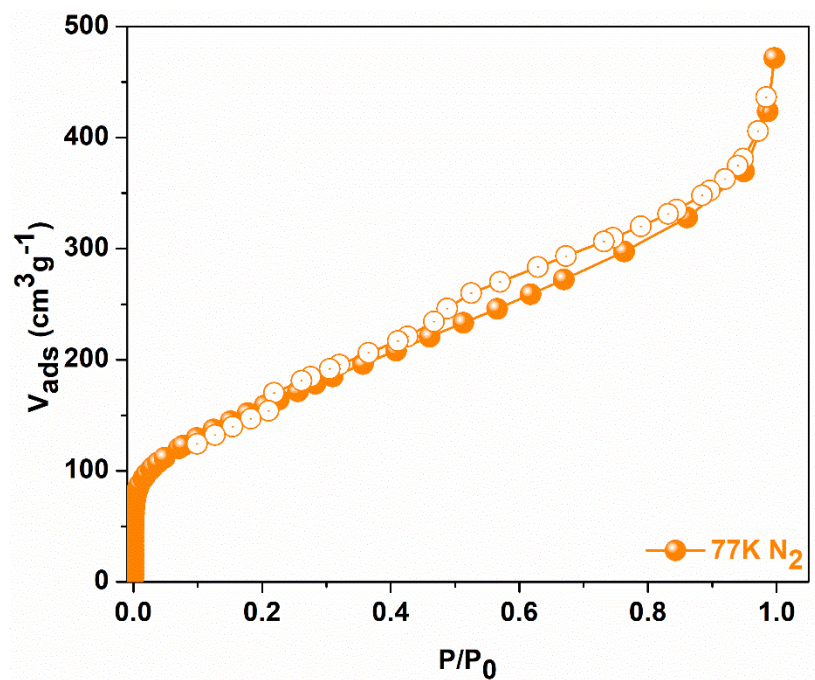


Figure S7: N₂ adsorption profile at 77 K for 120-MI@Cl

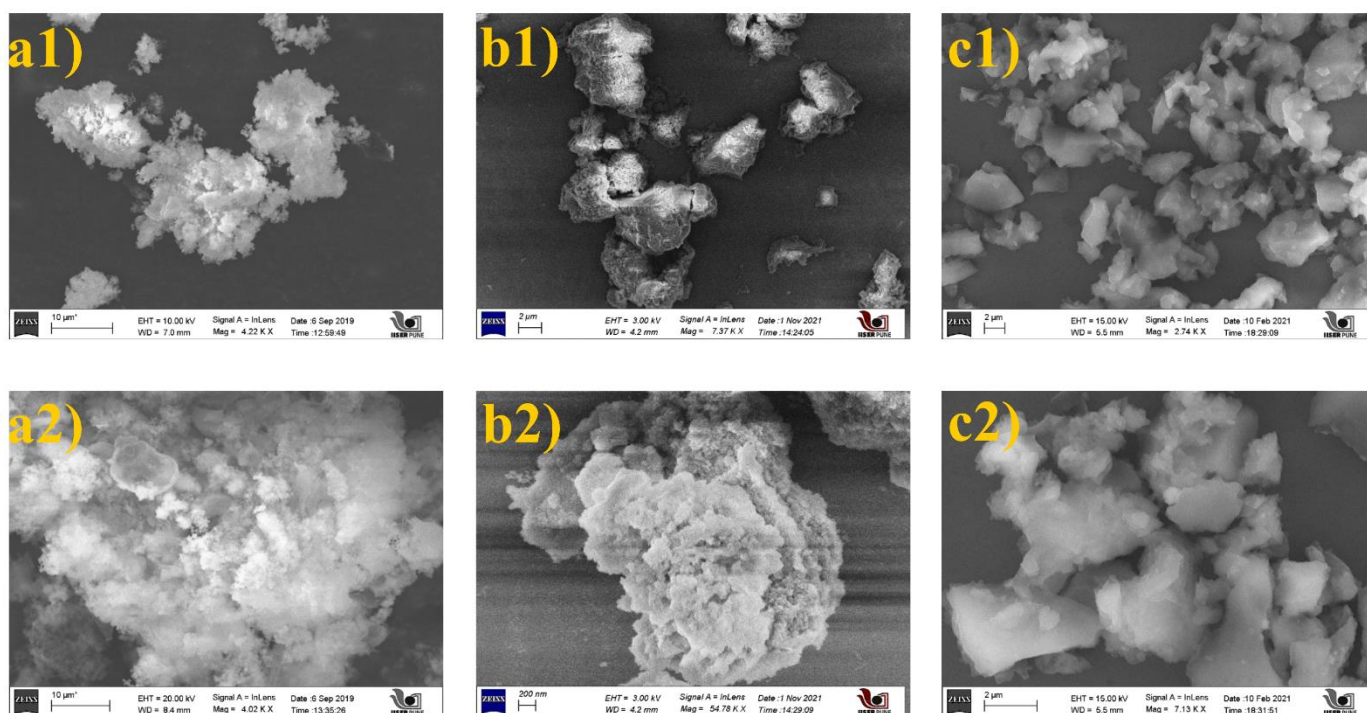


Figure S8: Magnified FESEM images of (a1-a2) 120-Cl, (b1-b2) 120-MI@Cl and (c1-c2) 120-MI@OH, scale bar = 1-2 μ M

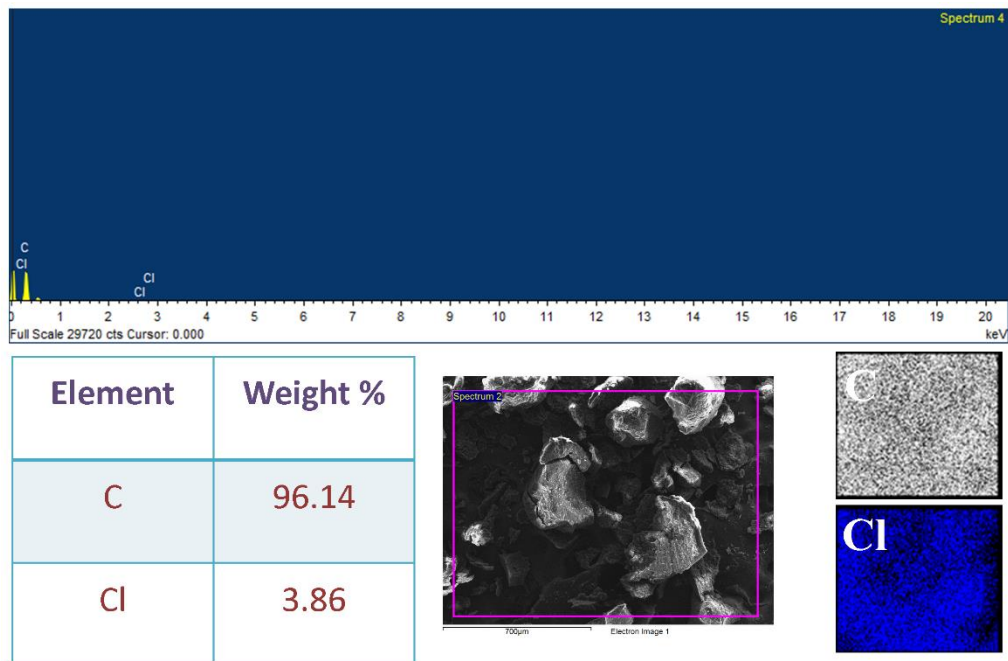


Figure S9: EDX analysis and elemental mapping of 120-Cl

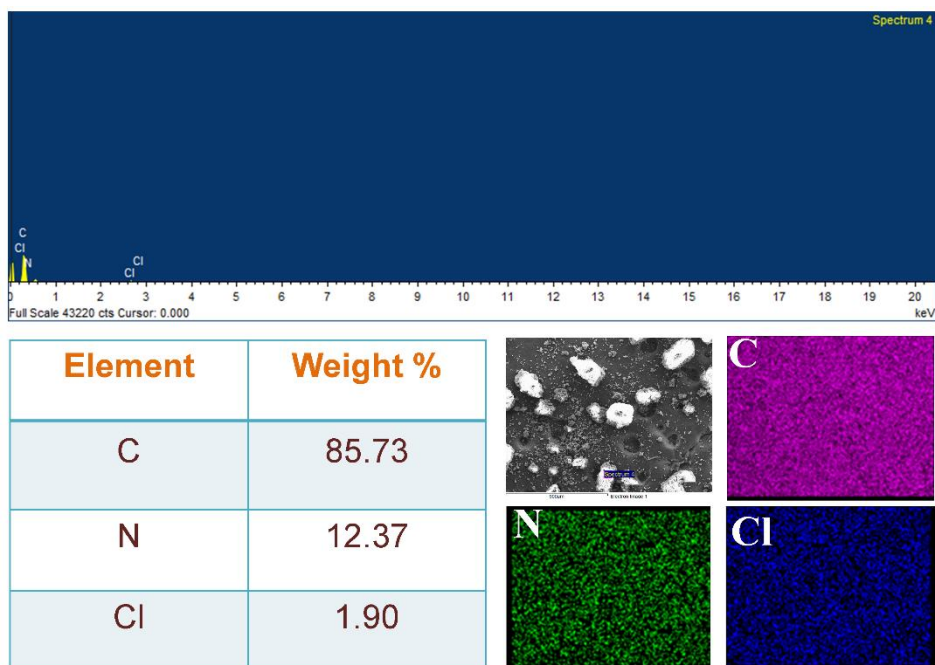


Figure S10: EDX analysis and elemental mapping of 120-MI@Cl

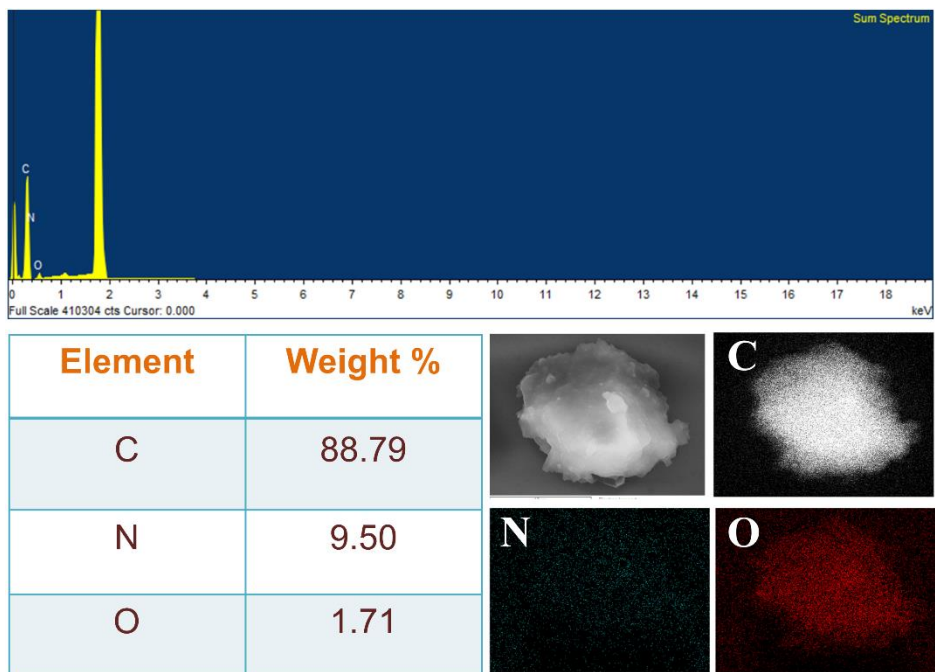


Figure S11: EDX analysis and elemental mapping of 120-MI@OH.

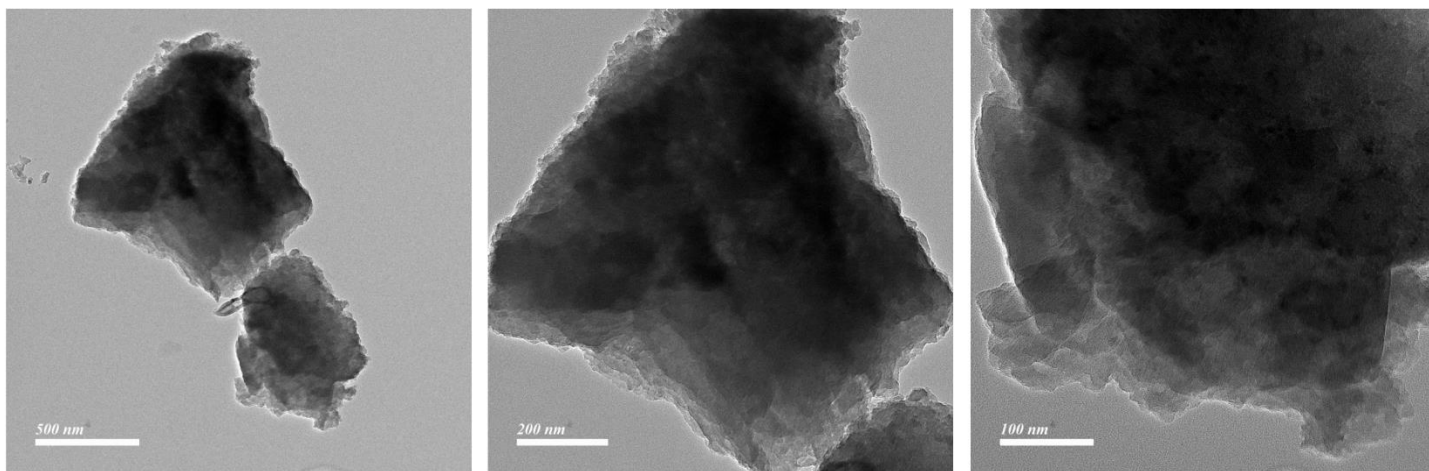


Figure S12: TEM images of 120-MI@OH.

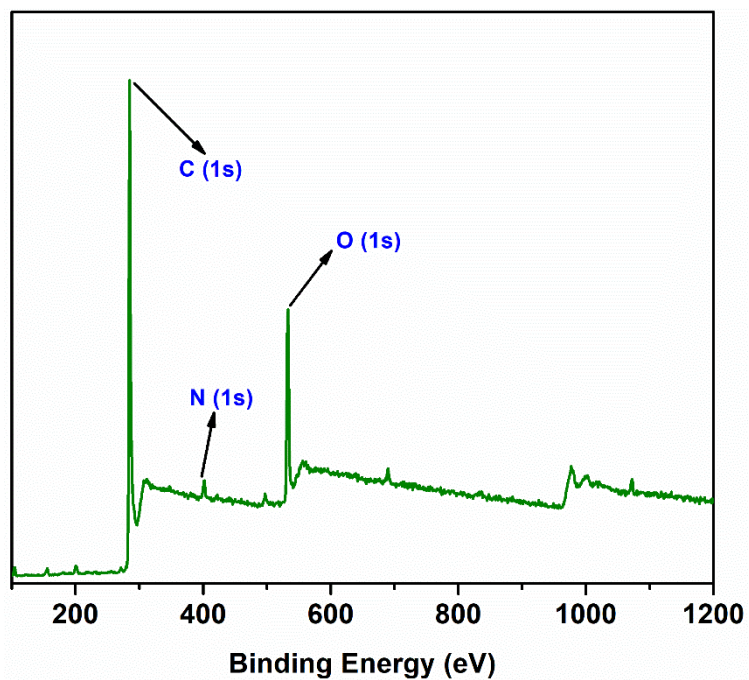


Figure S13: XPS survey scan spectra of 120-MI@OH.

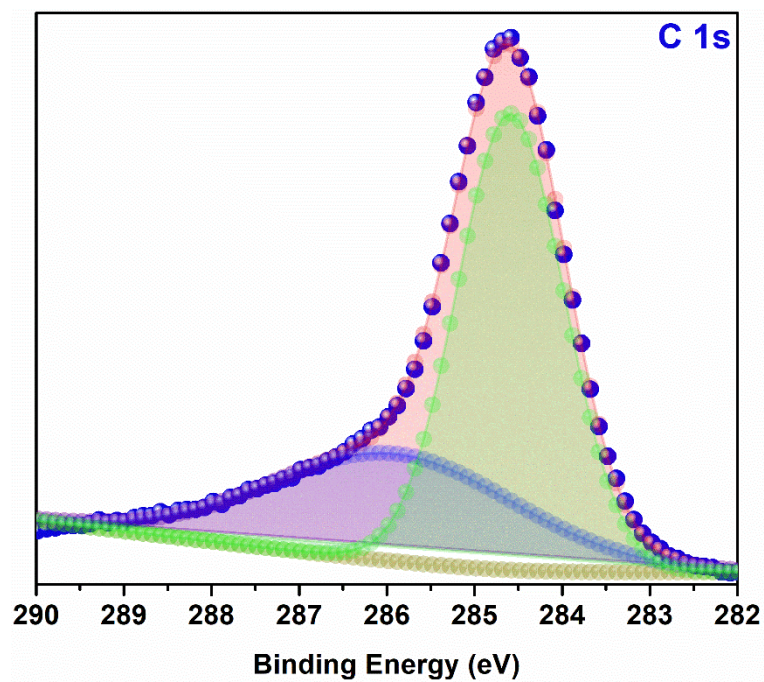


Figure S14: C 1s XPS spectrum of 120-MI@OH.

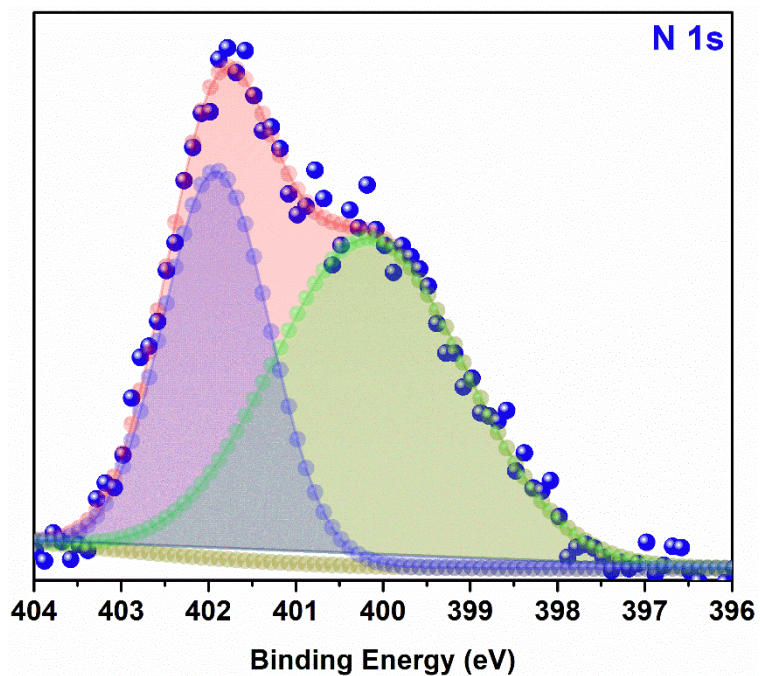


Figure S15: N 1s XPS spectrum of 120-MI@OH.

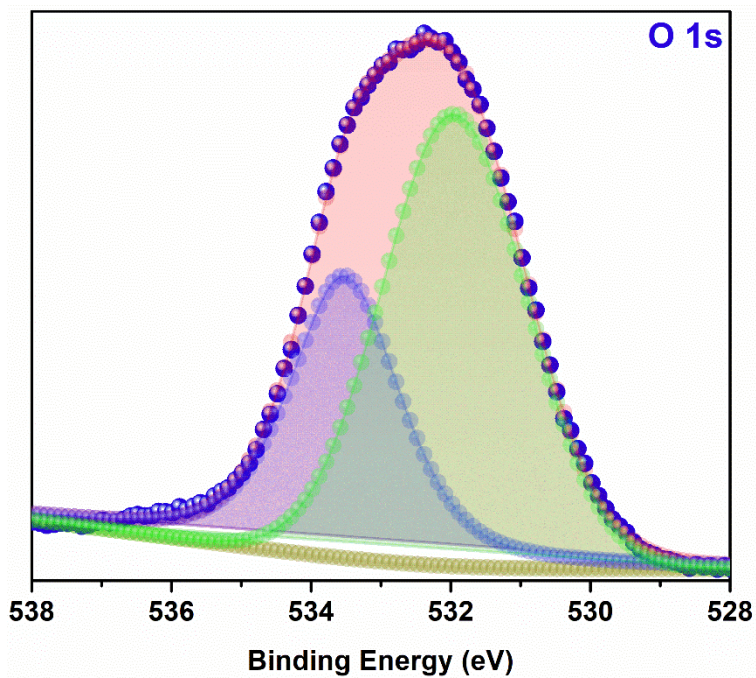


Figure S16: O 1s XPS spectrum of 120-MI@OH.

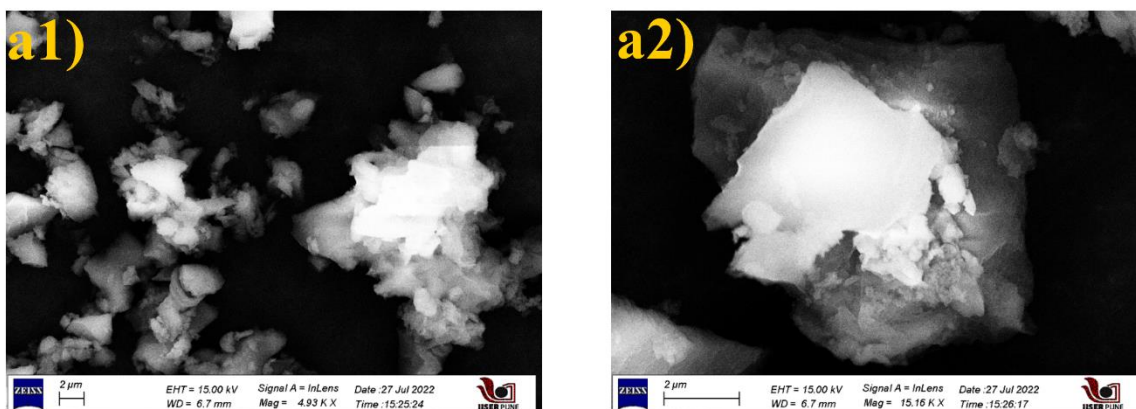


Figure S17: FESEM images of (a1-a2) spent120-MI@OH catalyst, scale bar = 2 μM

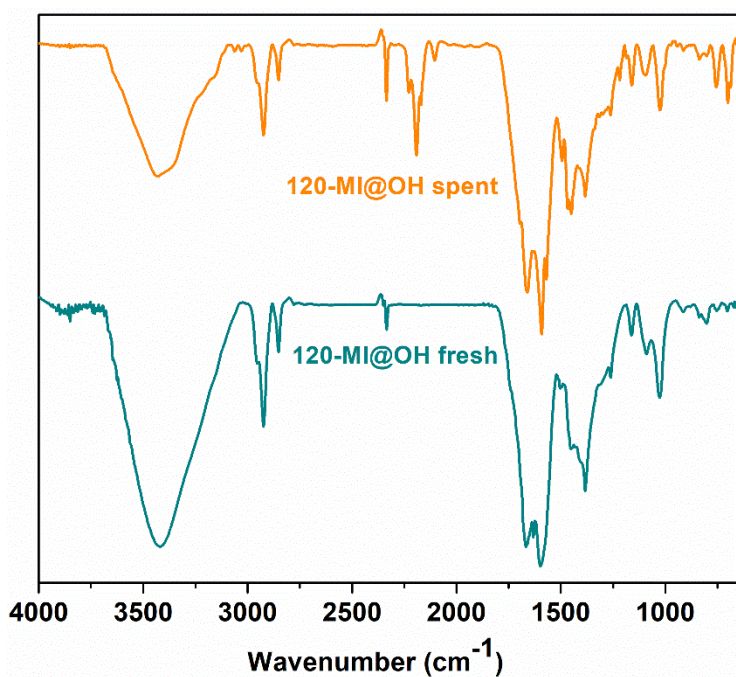


Figure S18: Infra-red (IR) spectroscopy of fresh120-MI@OH (cyan) and spent120-MI@OH (orange).

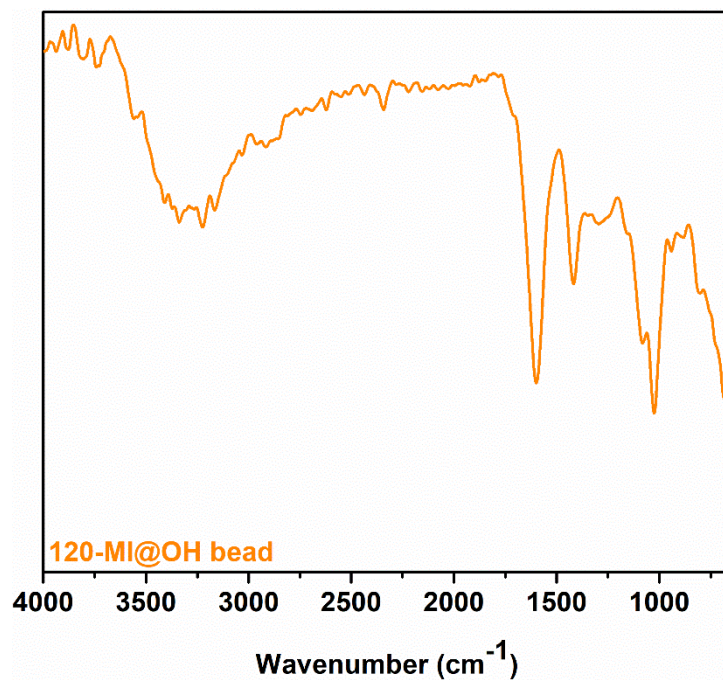


Figure S19: Infra-red (IR) spectroscopy of 120-MI@OH composite bead (orange).

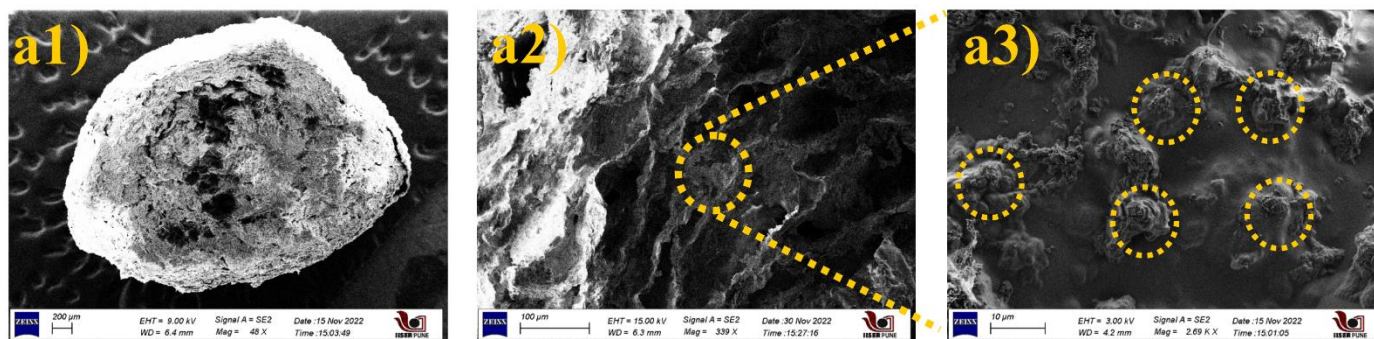


Figure S20: FESEM images of 120-MI@OH composite bead at different magnification showing the successful integration 120-MI@OH polymer inside the bead, scale bar = 200 μM (a1), 100 μM (a2) and 10 μM (a3)

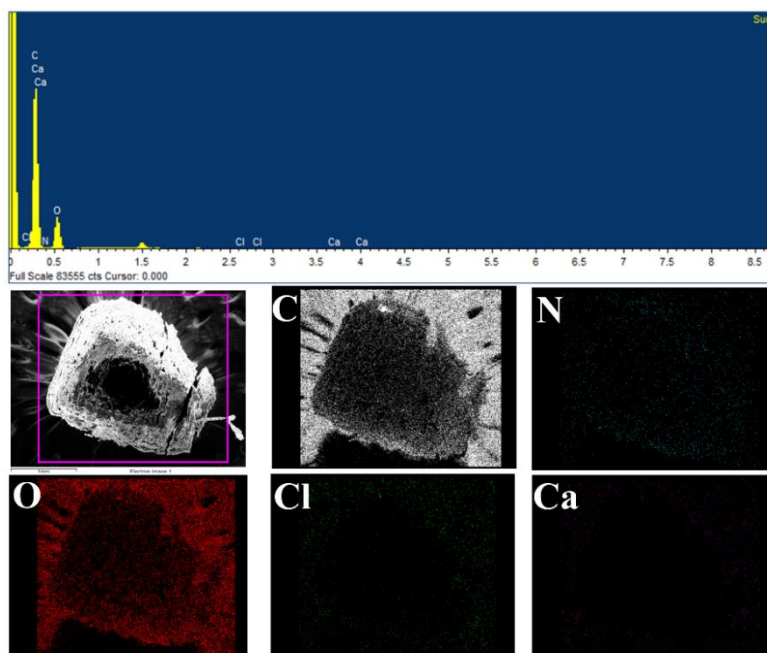


Figure S21: EDX analysis and elemental mapping of millimeter-sized 120-MI@OH composite bead.

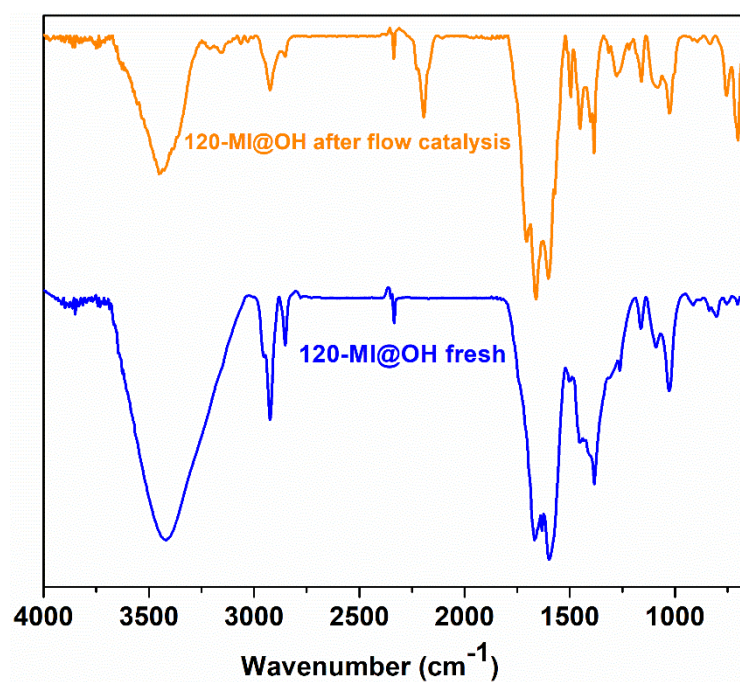


Figure S22: Infra-red (IR) spectroscopy of fresh 120-MI@OH (blue) and 120-MI@OH after flow catalysis (orange).

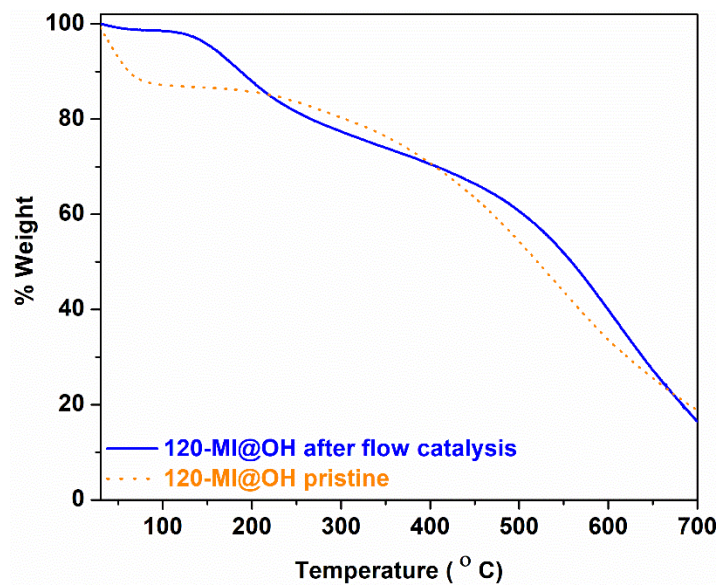


Figure S23: Thermogravimetric profile for pristine 120-MI@OH (orange) and 120-MI@OH after flow catalysis (blue).

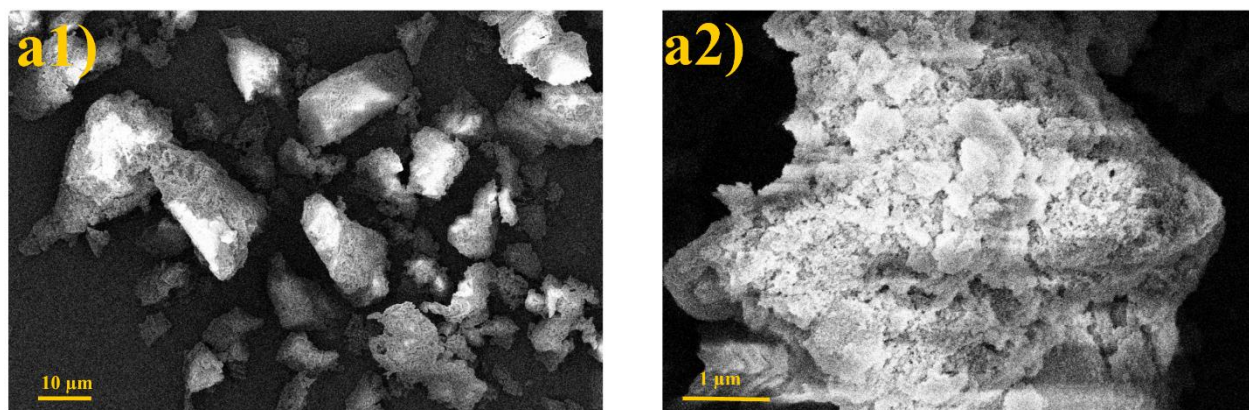


Figure S24: FESEM images of 120-MI@OH after flow catalysis.

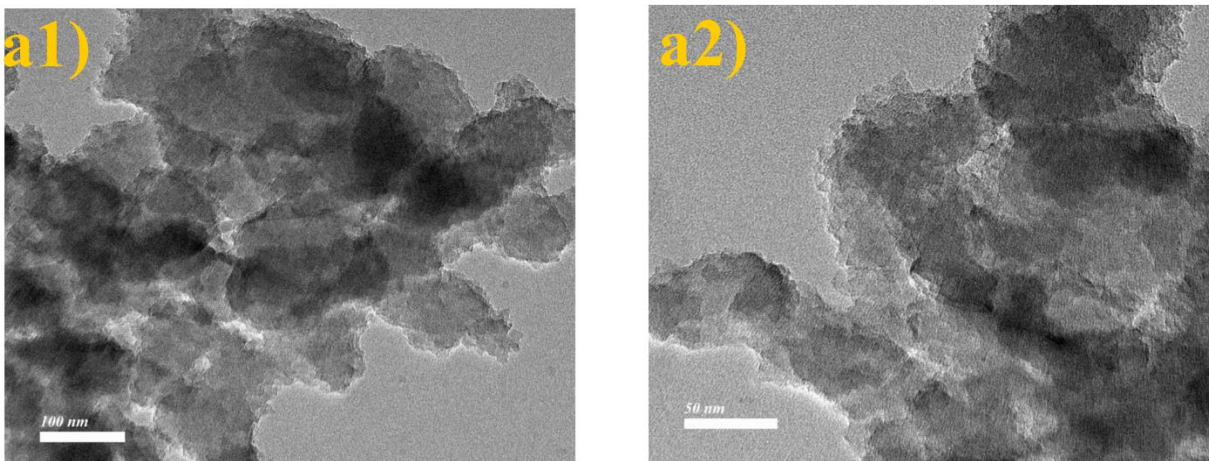


Figure S25: TEM images of 120-MI@OH after flow catalysis.

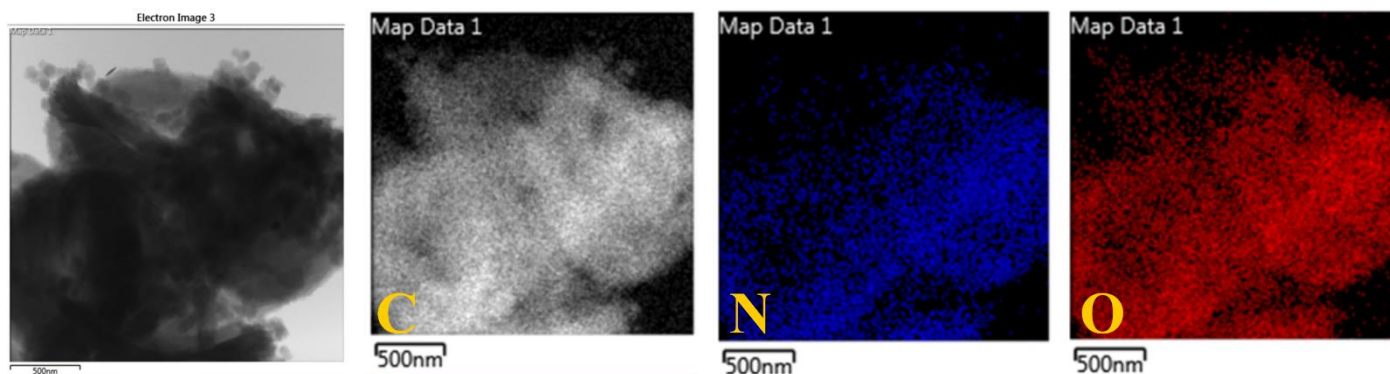


Figure S26: STEM-EDS mapping profile of 120-MI@OH after flow catalysis.

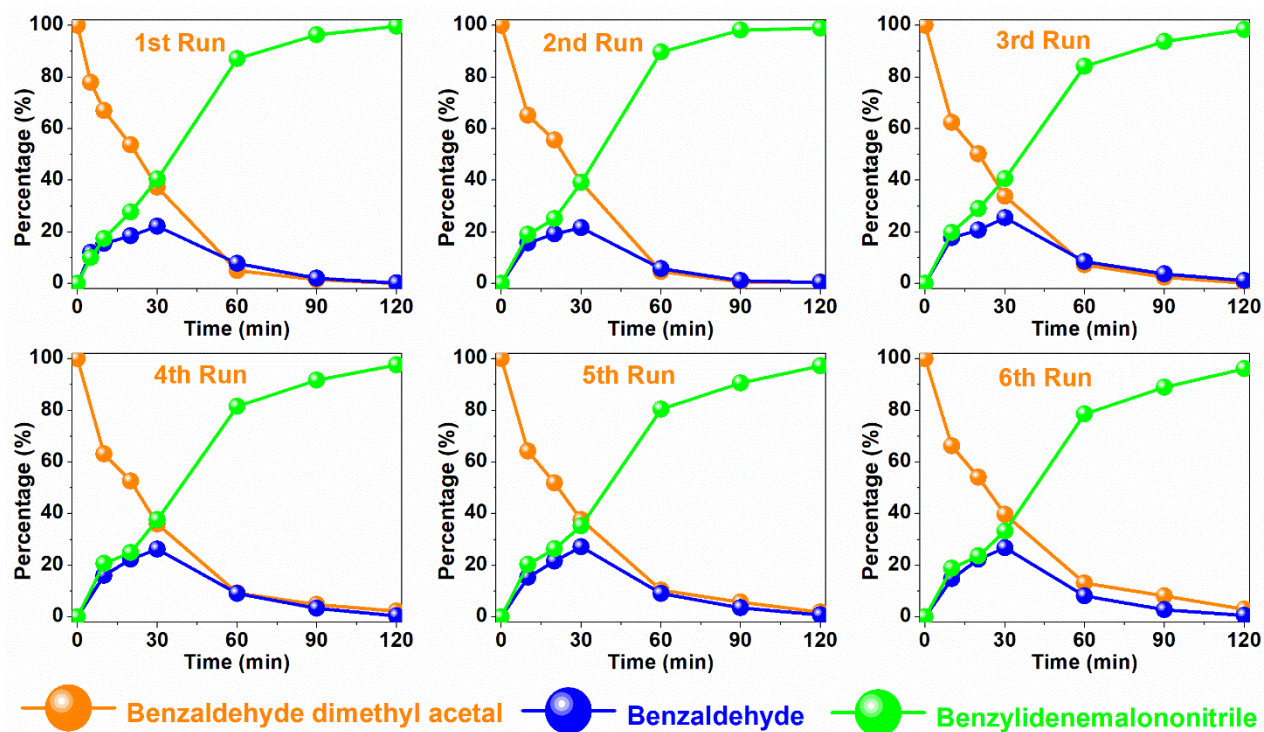


Figure S27: Kinetics monitoring of recyclable cascade catalytic reaction

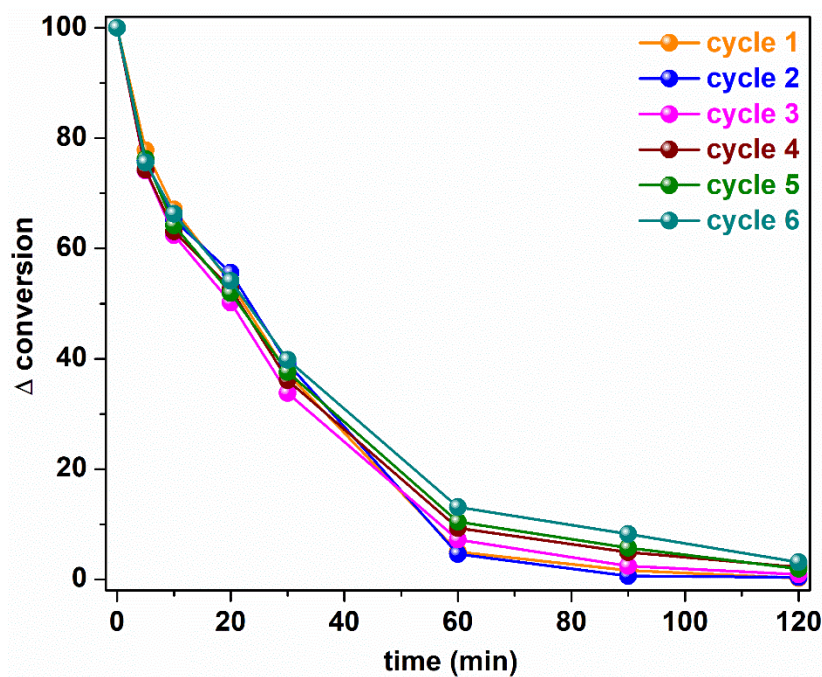


Figure S28: Δ conversion vs time plot for different cycles of one-pot cascade catalysis by 120-MI@OH.

Table S1. Control experiments for 120-MI@OH catalyzed Knoevenagel condensation reaction

Entry	Catalyst	Solvent	Temp. (°C)	Time	Yield (%) ^b
1.	120-MI@OH (5 mg)	CH ₂ Cl ₂	RT	1 h	56
2.	120-MI@OH (5 mg)	MeOH	RT	1 h	65
3.	120-MI@OH (5 mg)	H ₂ O	RT	1 h	>99
4.	120-MI@OH (5 mg)	H ₂ O	RT	0.5 h	>99
5.	120-MI@Cl (5 mg)	H ₂ O	80	2h	51
6.	No Catalyst	H ₂ O	RT	1h	6.8
7.	Supernatant Liquid of the H ₂ O suspension of 120- MI@OH	H ₂ O	RT	1h	7.3

^a Reaction conditions (Unless otherwise mentioned): a solution of the carbonyl compound (0.8 mmol, 1 equiv.), H₂O (4 mL), malononitrile (0.8 mmol, 1 equiv.), and the heterogeneous catalyst HCP 120-MI@OH (5 mg) was stirred at the indicated temperature for noted time duration. ^b Yield determined from ¹H-NMR.

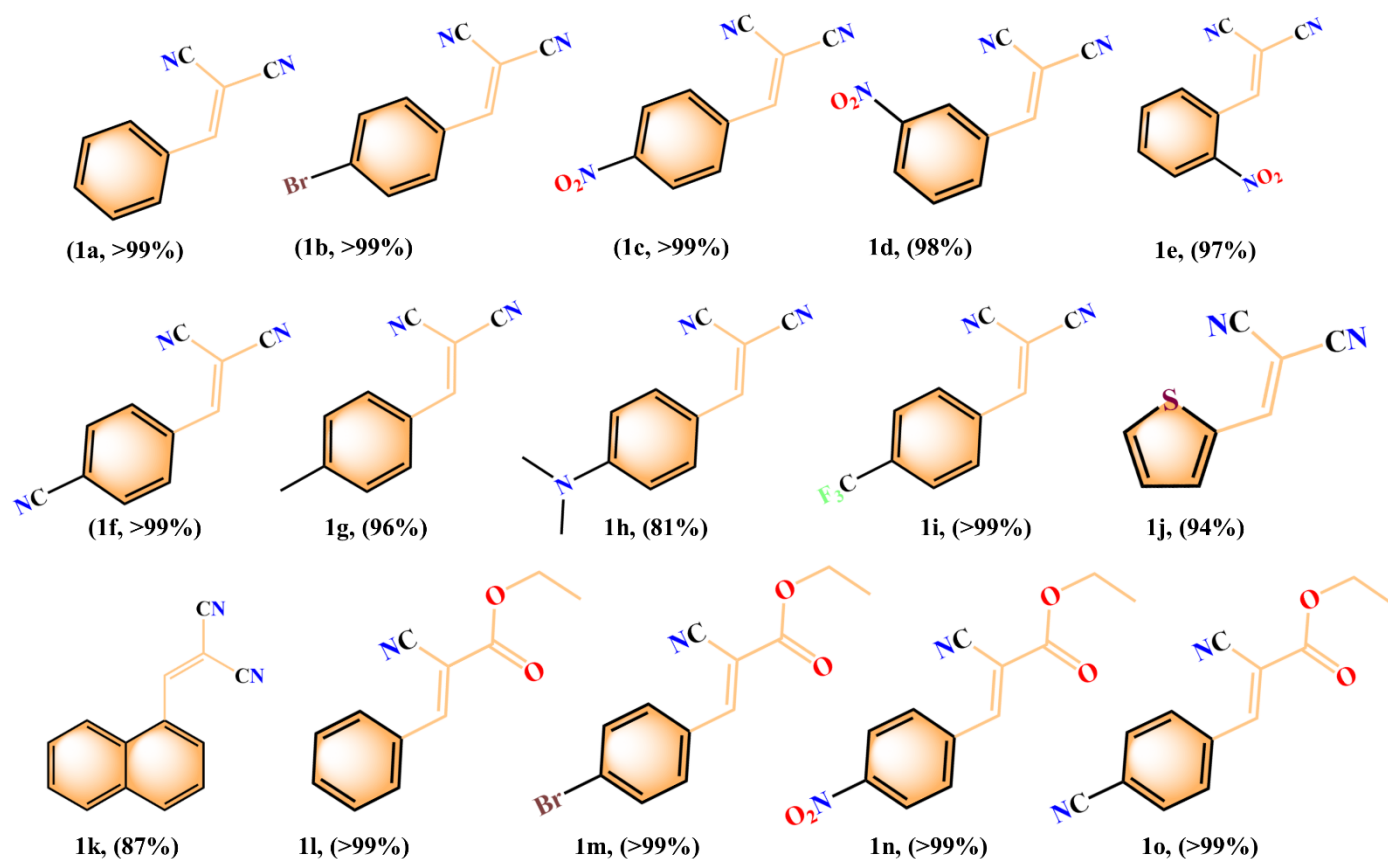


Table S2. 120-MI@OH catalyzed Knoevenagel condensation reaction at room temperature. Conditions: 0.8 mmol of carbonyl compound, 0.8 mmol malononitrile/ ethyl cyanoacetate and 5 mg of catalyst was stirred in 4 mL H₂O for 0.5 h; Yield determined from ¹H NMR

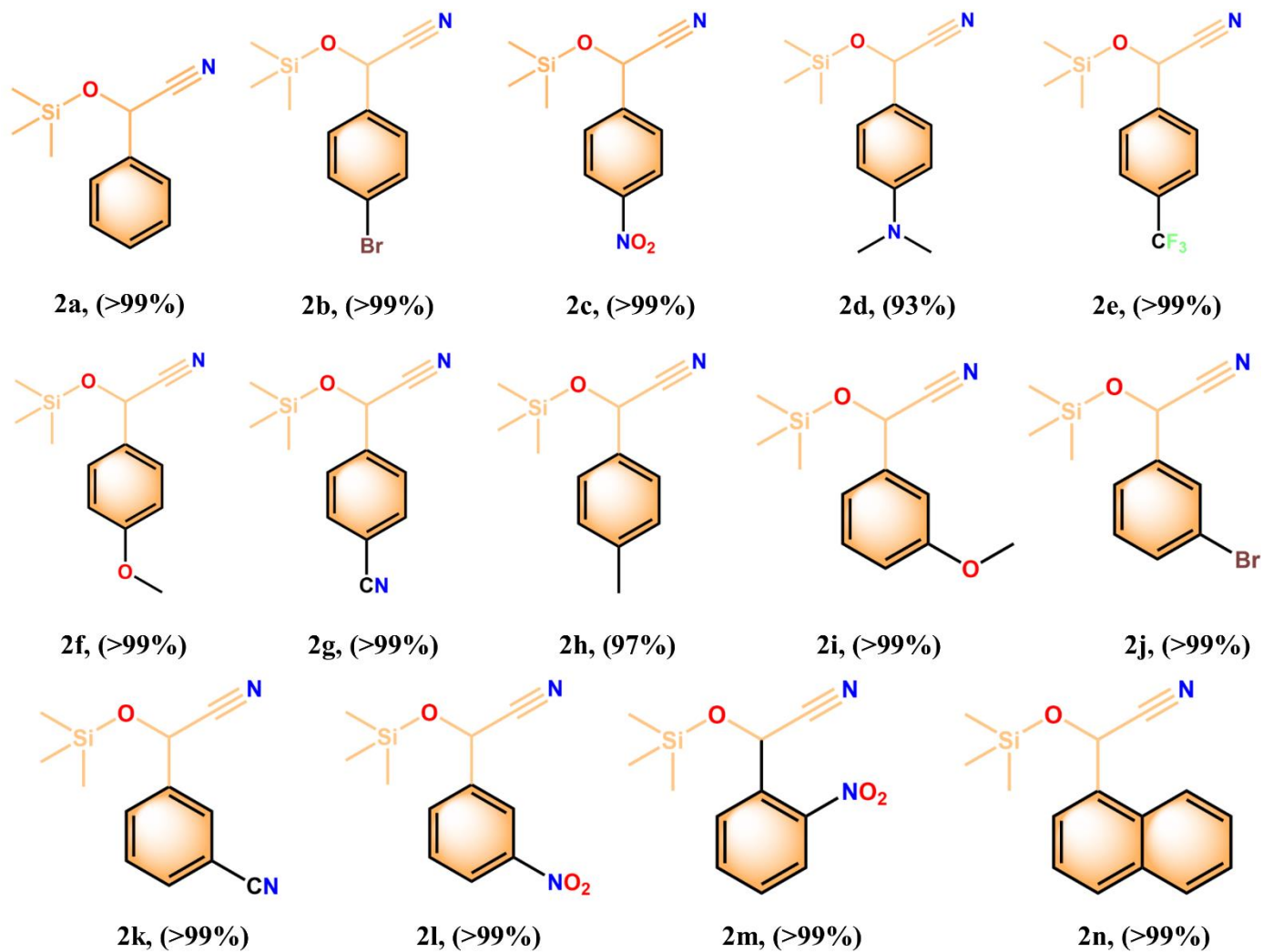


Table S3. 120-MI@OH catalyzed cyanosilylation reaction at room temperature. Conditions: Me₃SiCN (2.0 mmol), carbonyl substrate (1.0 mmol) and catalyst 120-MI@OH (5 mg) at RT for 0.5 h; Yield determined from ¹H NMR

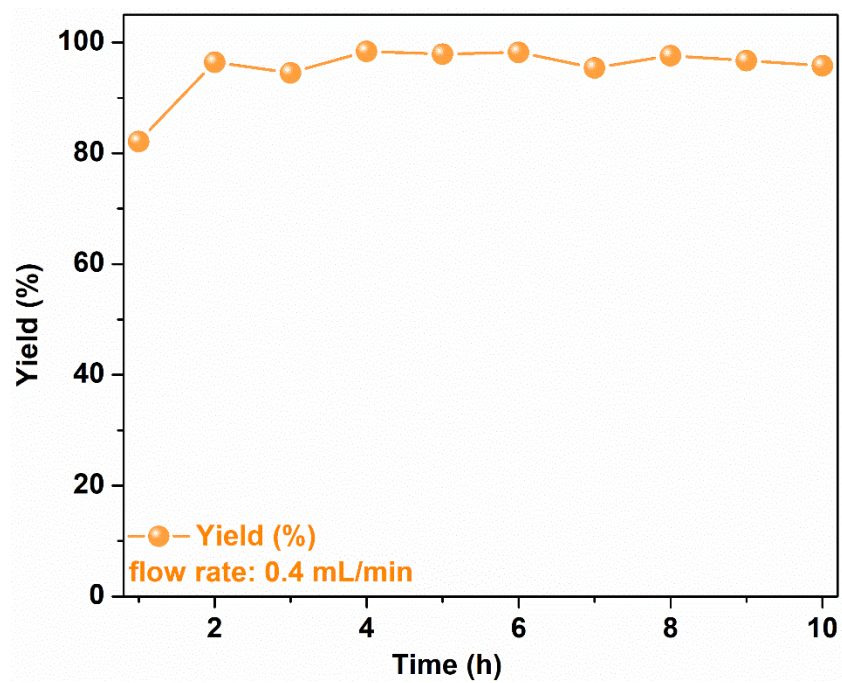


Figure S29: Yield over time of flow deacetalization-Knoevenagel condensation reactions under continuous flow condition.

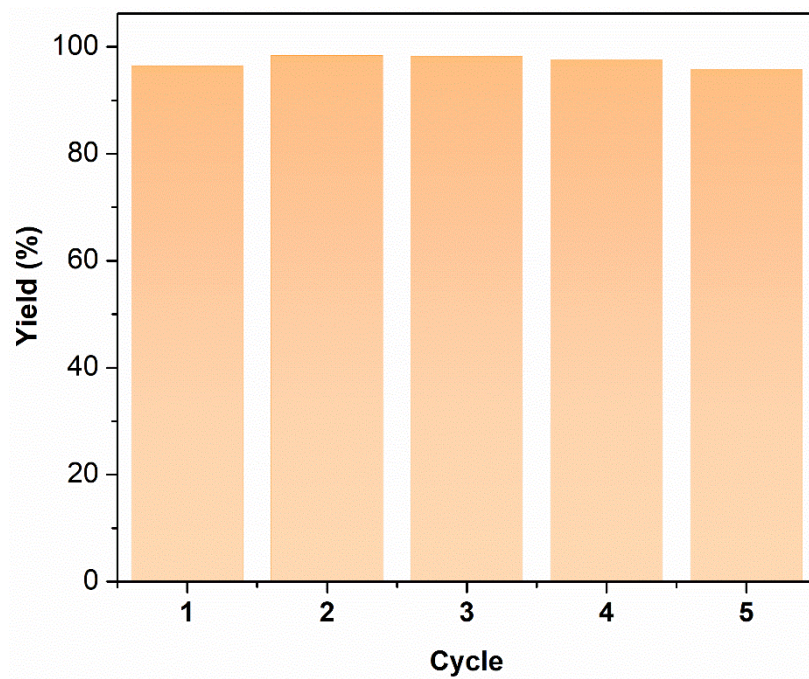
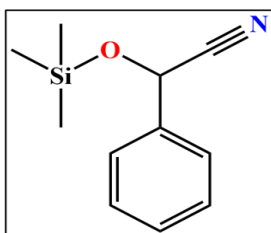


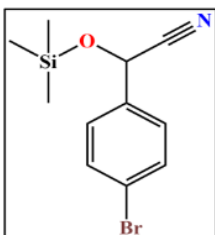
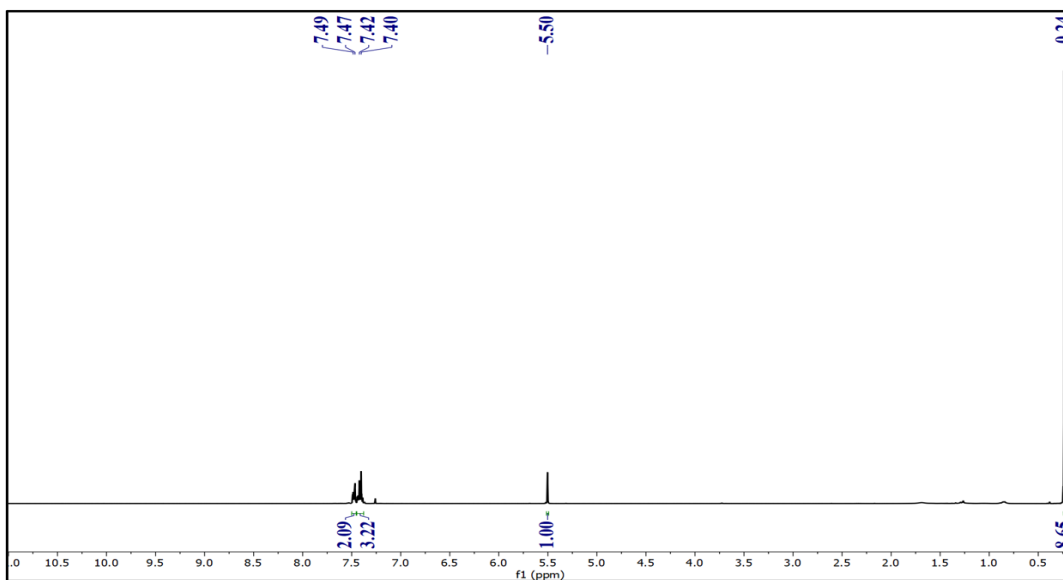
Figure S30: Recyclability test for one-pot cascade catalysis under flow.

Section S5: ^1H NMR spectra of compounds



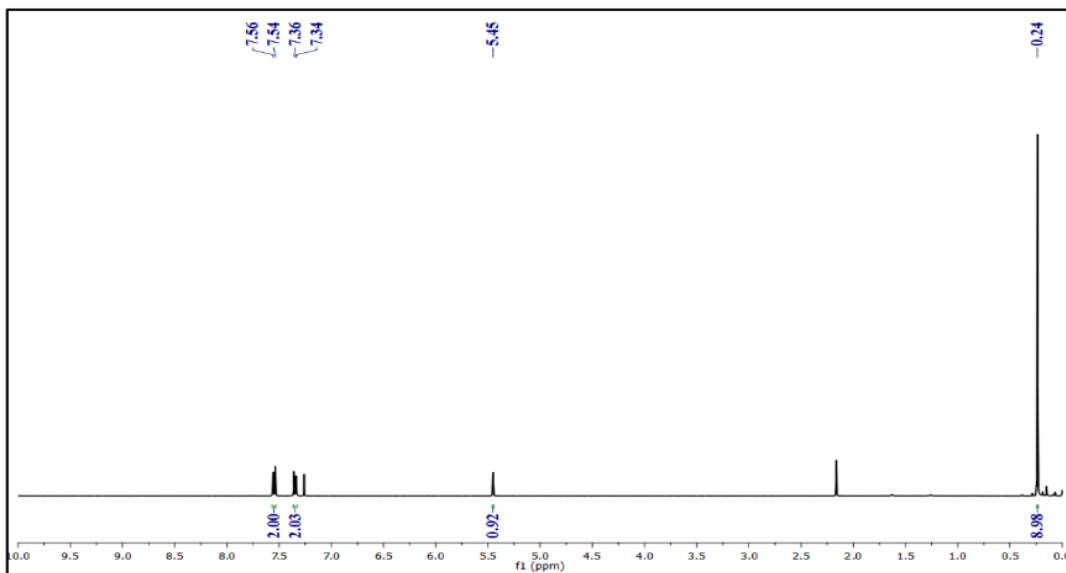
2-phenyl-2-((trimethylsilyloxy)acetonitrile):

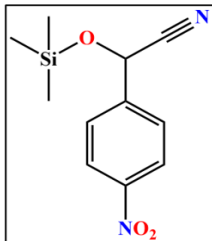
^1H -NMR (400 MHz, CDCl_3 , 25°C, TMS), δ (in ppm):
7.48 (d, 2H, ArH), 7.41 (d, $J=8$ Hz, 3H, ArH), 5.50 (s, 1H, ArH), 0.24 (s, 9H, Alkyl H)



2-(4-bromophenyl)-2-((trimethylsilyloxy)acetonitrile):

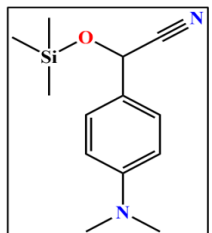
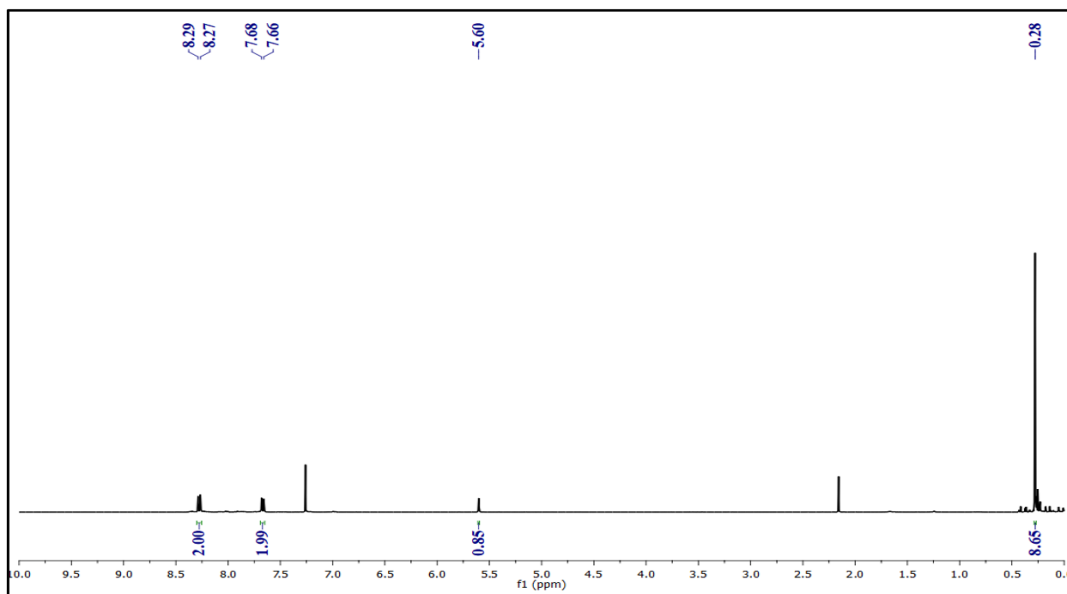
^1H -NMR (400 MHz, CDCl_3 , 25°C, TMS), δ (in ppm): 7.55 (d, $J=8$ Hz, 2H, ArH), 7.35 (d, $J=8$ Hz, 2H, ArH), 5.45 (s, 1H, ArH), 0.24 (s, 9H, Alkyl H)





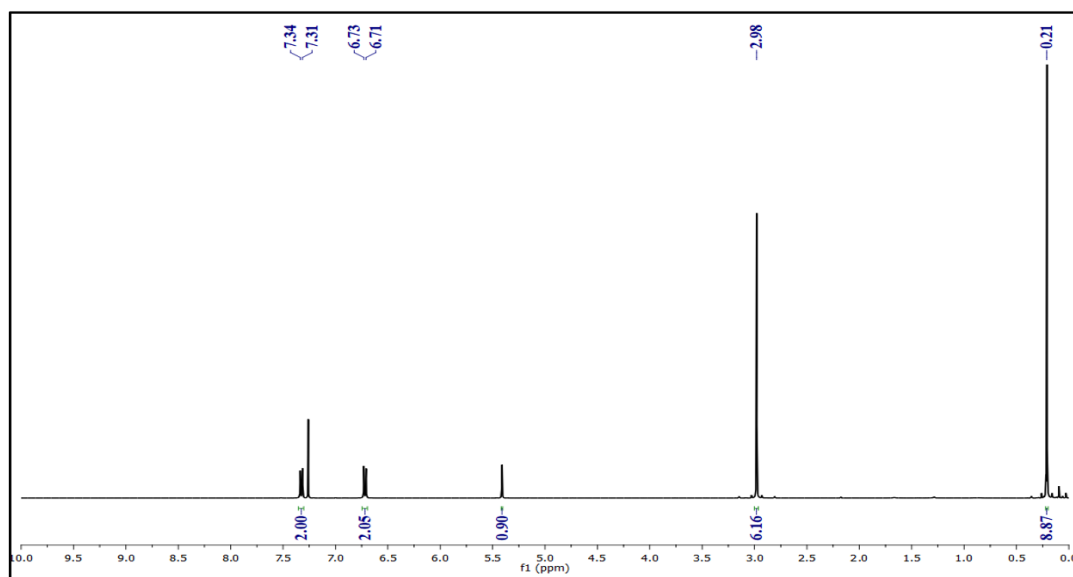
2-(4-nitrophenyl)-2-((trimethylsilyloxy)acetonitrile:

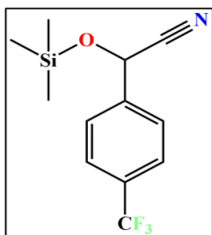
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 8.28 (d, J= 8 Hz, 2H, ArH), 7.67 (d, J= 8 Hz, 2H, ArH), 5.60 (s, 1H, ArH), 0.28 (s, 9H, Alkyl H)



2-(4-(dimethylamino)phenyl)-2-((trimethylsilyloxy)acetonitrile:

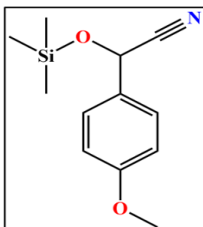
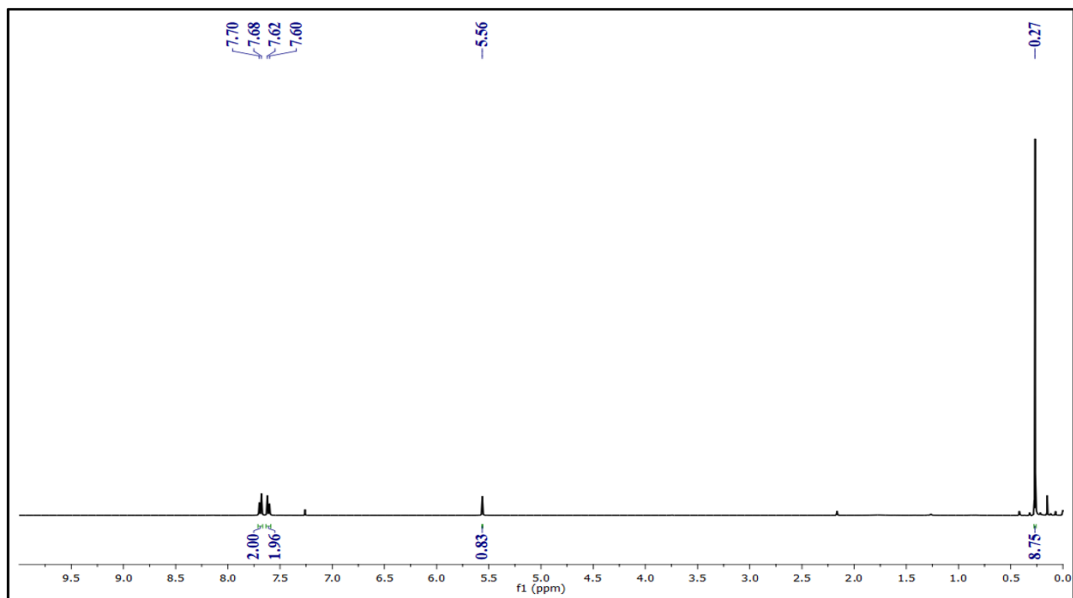
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.33 (d, J= 8 Hz, 2H, ArH), 6.72 (d, J= 8 Hz, 2H, ArH), 5.4 (s, 1H, ArH), 2.98 (s, 6H, Alkyl H), 0.21 (s, 9H, Alkyl H)





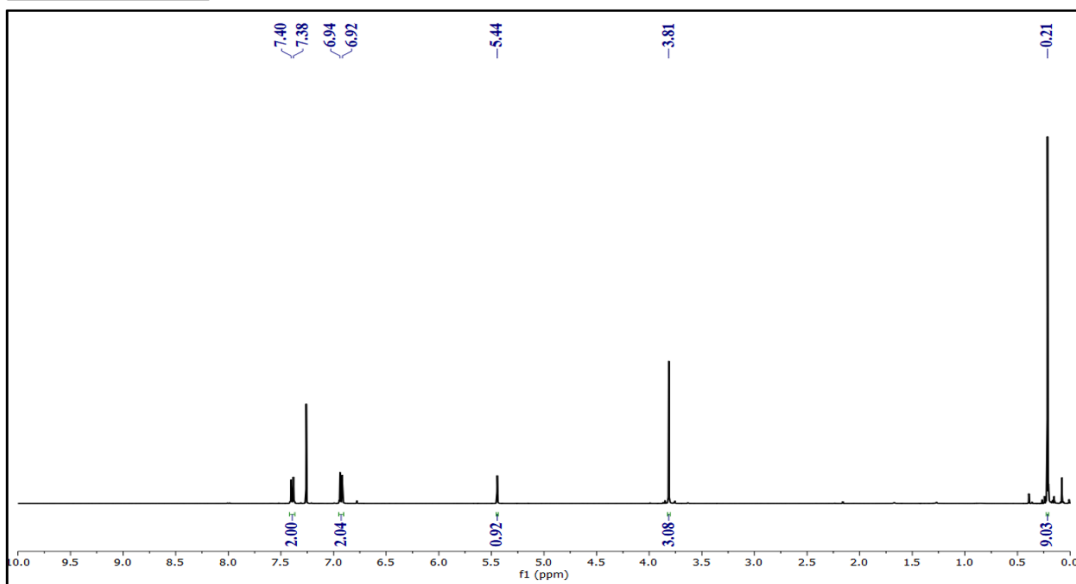
2-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)oxy)acetonitrile:

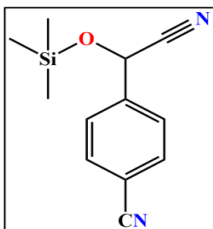
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.69 (d, J= 8 Hz, 2H, ArH), 7.61 (d, J= 8 Hz, 2H, ArH), 5.56 (s, 1H, ArH), 0.27 (s, 9H, Alkyl H)



2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile:

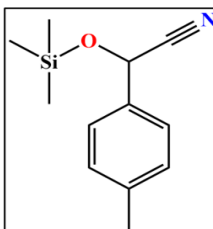
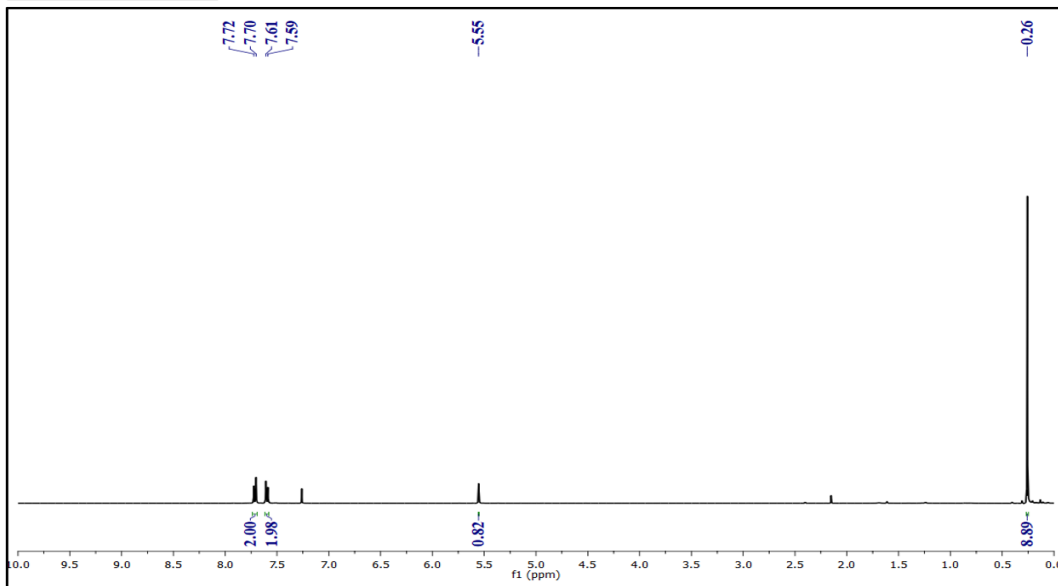
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.39 (d, J= 8 Hz, 2H, ArH), 6.93 (d, J= 8 Hz, 2H, ArH), 5.44 (s, 1H, ArH), 3.81 (s, 3H, Alkyl H), 0.21 (s, 9H, Alkyl H)





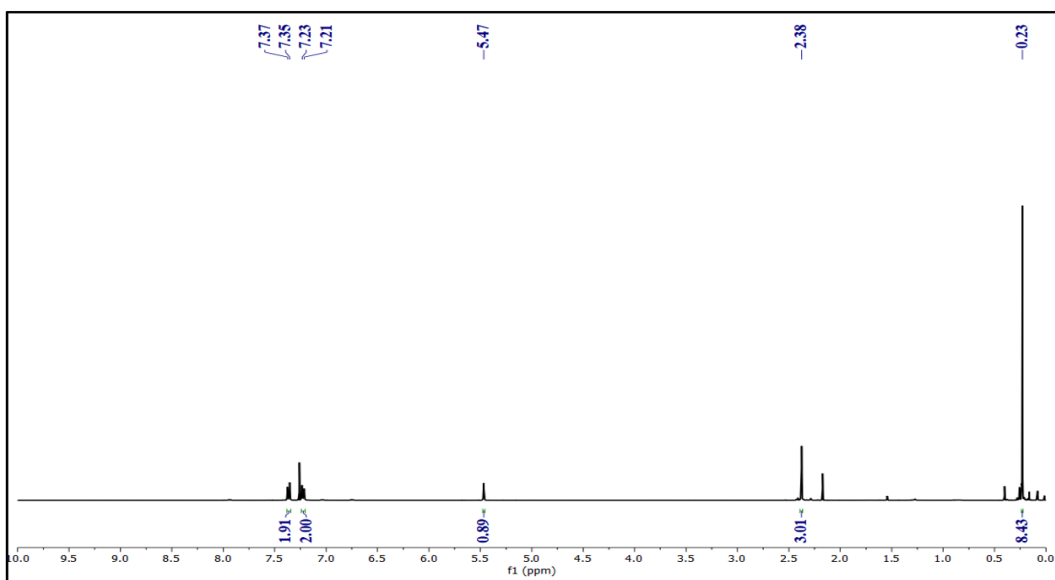
4-(cyano((trimethylsilyloxy)methyl)benzonitrile:

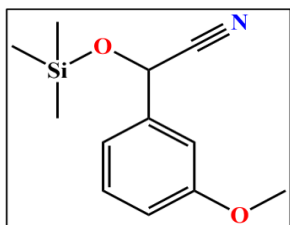
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.71 (d, J= 8 Hz, 2H, ArH), 7.60 (d, J= 8 Hz, 2H, ArH), 5.55 (s, 1H, ArH), 0.26 (s, 9H, Alkyl H)



2-(p-tolyl)-2-((trimethylsilyloxy)acetonitrile:

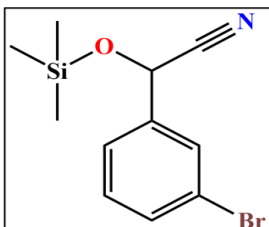
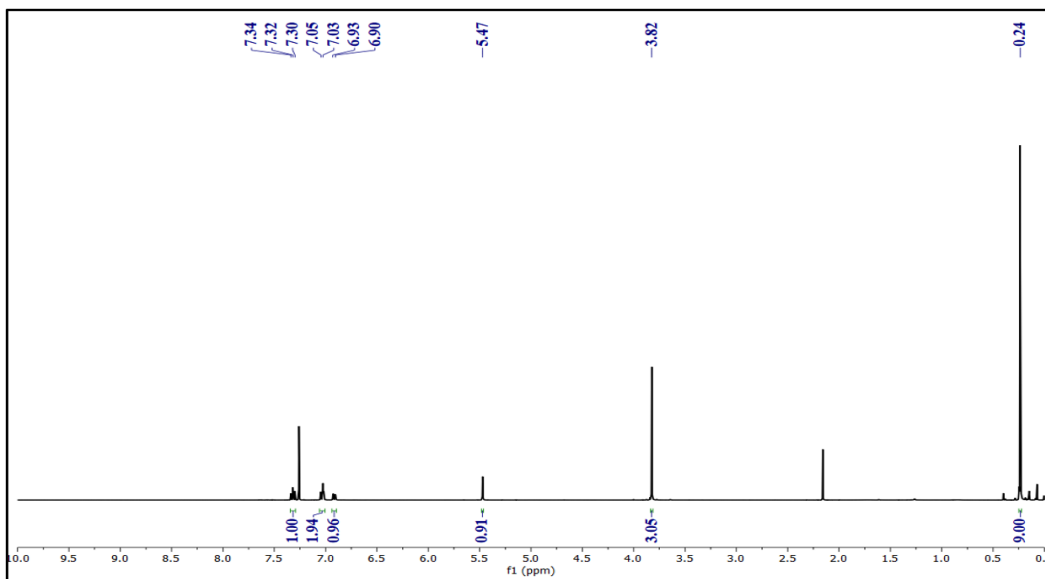
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.36 (d, 2H, ArH), 7.22 (d, J= 8 Hz, 2H, ArH), 5.47 (s, 1H, ArH), 2.28 (s, 3H, Alkyl H), 0.23 (s, 9H, Alkyl H)





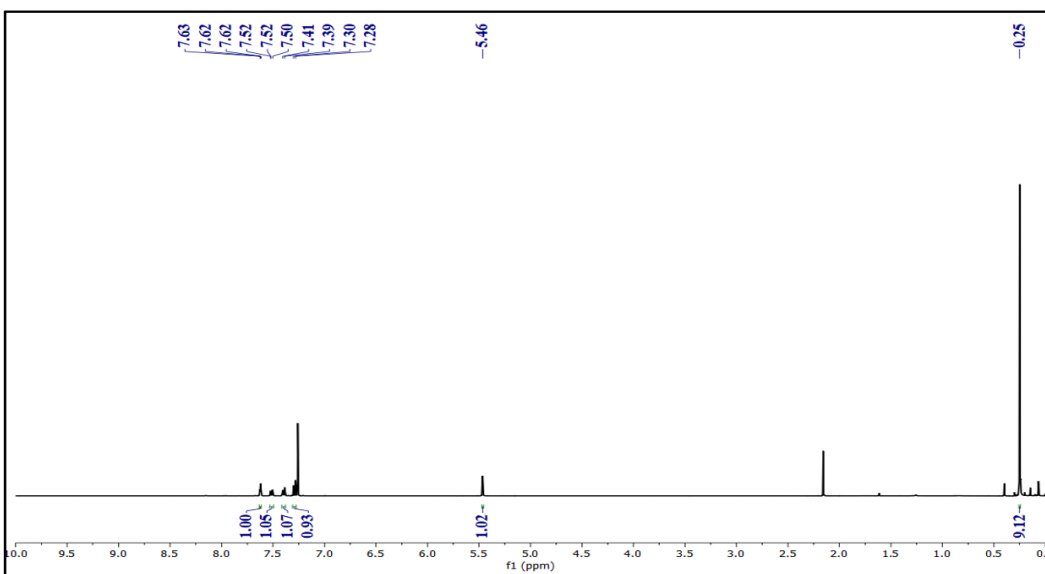
2-(3-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile:

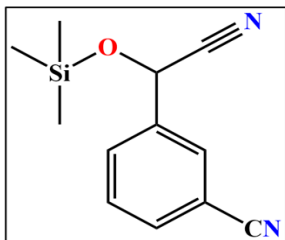
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm):
 7.32 (t, J= 8 Hz, 1H, ArH), 7.04 (d, J= 8 Hz, 2H, ArH),
 6.91 (d, J= 8 Hz, 1H, ArH), 5.47 (s, 1H, ArH), 3.05 (s,
 3H, Alkyl H), 0.24 (s, 9H, Alkyl H)



2-(3-bromophenyl)-2-((trimethylsilyl)oxy)acetonitrile:

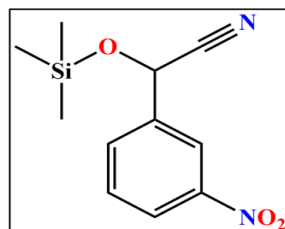
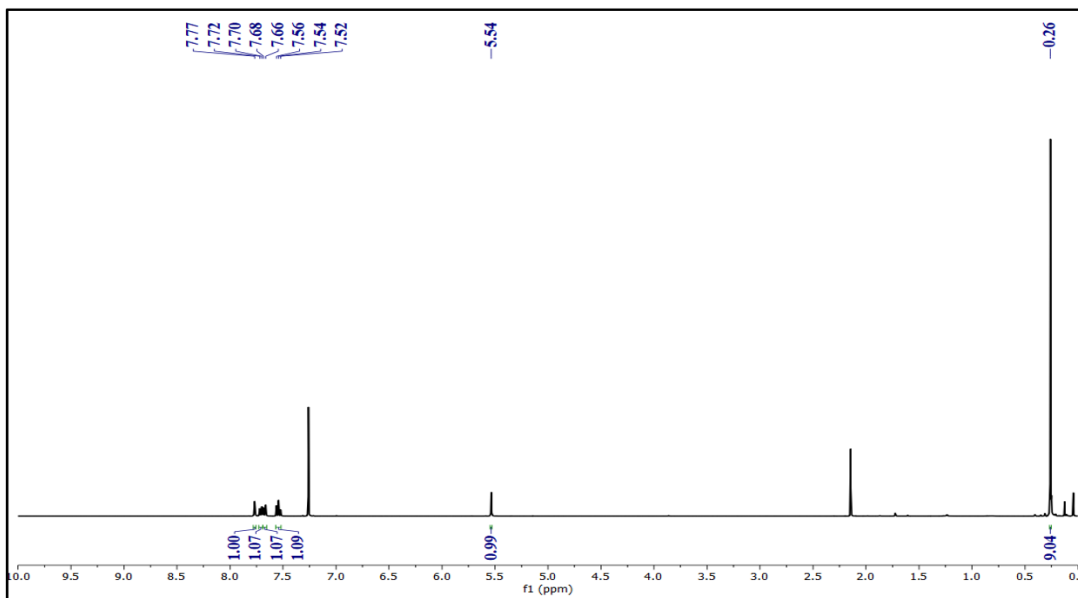
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm):
 7.62 (t, J= 8 Hz, 1H, ArH), 7.51 (t, J= 8 Hz, 1H, ArH),
 7.40 (t, J= 8 Hz, 1H, ArH), 7.31 (d, J= 8 Hz, 1H, ArH),
 5.46 (s, 1H, ArH), 0.25 (s, 9H, Alkyl H)





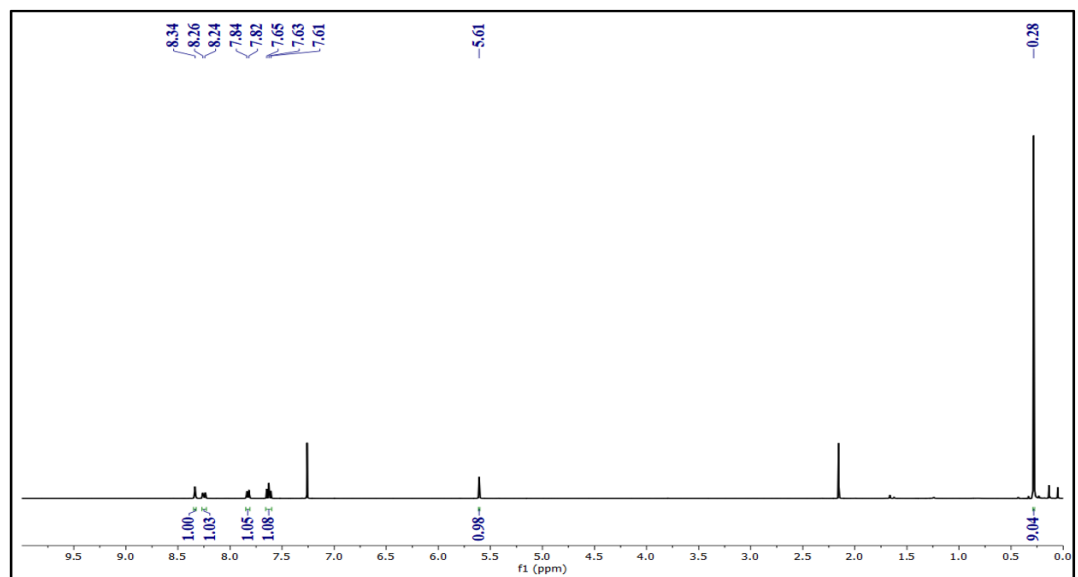
3-(cyano((trimethylsilyl)oxy)methyl)benzonitrile:

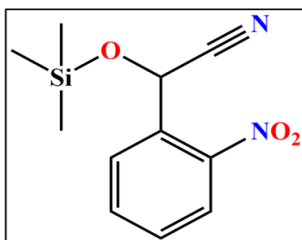
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm):
 7.77 (s, J= 8 Hz, 1H, ArH), 7.71 (d, J= 8 Hz, 1H, ArH),
 7.67 (d, J= 8 Hz, 1H, ArH), 7.54 (d, J= 8 Hz, 1H, ArH),
 5.54 (s, 1H, ArH), 0.26 (s, 9H, Alkyl H)



2-(3-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile:

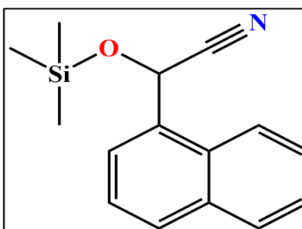
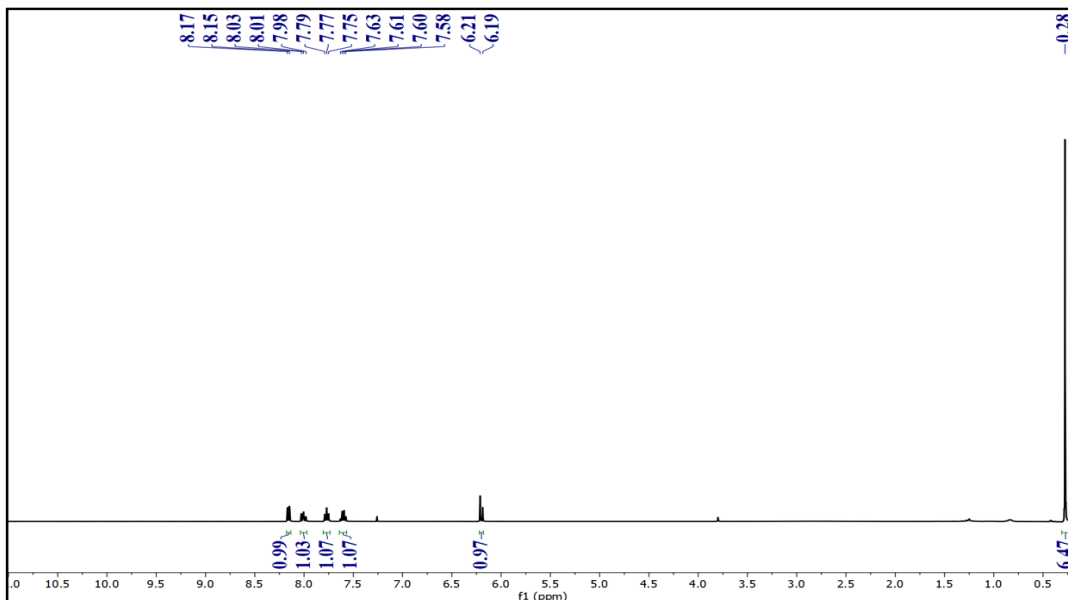
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm):
 8.34 (s, 1H, ArH), 8.25 (d, J= 8 Hz, 1H, ArH), 7.83 (d, J= 8 Hz, 1H, ArH),
 7.63 (t, J= 8 Hz, 1H, ArH), 5.61 (s, 1H, ArH), 0.28 (s, 9H, Alkyl H)





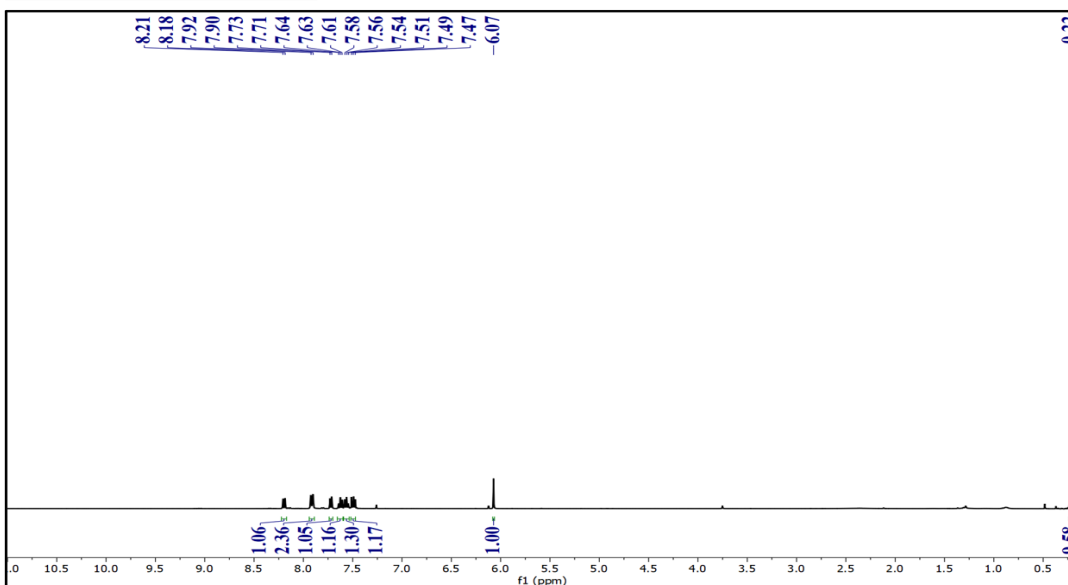
2-(2-nitrophenyl)-2-((trimethylsilyloxy)acetonitrile :

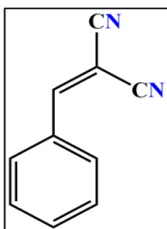
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm):
 8.16 (d, 8 Hz, 1H, ArH), 8.01 (t, J= 8 Hz, 1H, ArH),
 7.77 (t, J= 8 Hz, 1H, ArH), 7.60 (m, J= 8 Hz, 1H, ArH),
 6.20 (d, 1H, ArH), 0.28 (s, 9H, Alkyl H)



2-(naphthalen-1-yl)-2-((trimethylsilyloxy)acetonitrile :

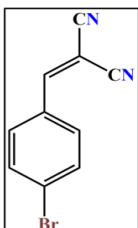
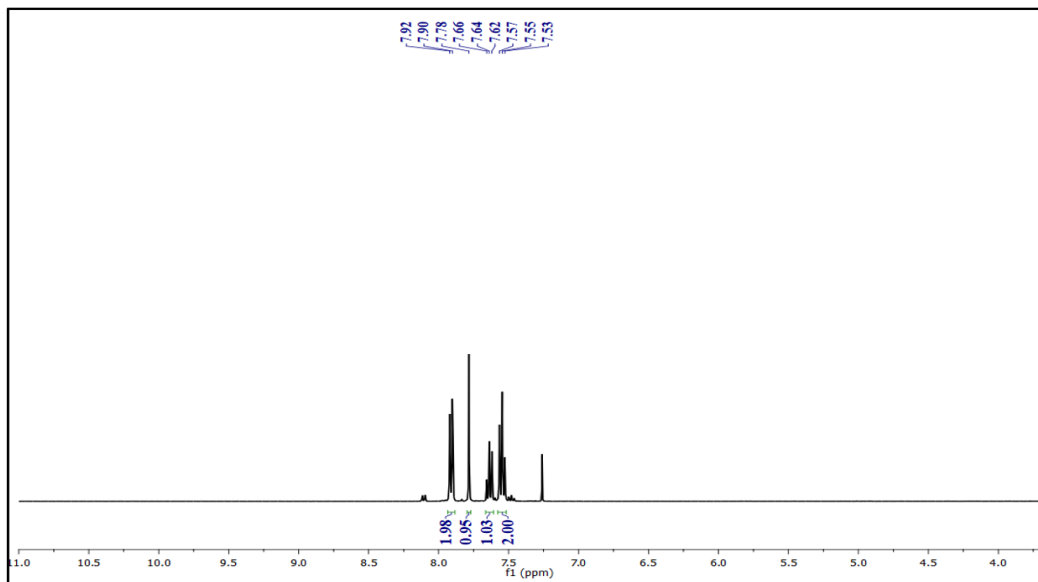
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm):
 8.20 (d, 8 Hz, 1H, ArH), 7.91 (d, J= 8 Hz, 2H, ArH),
 7.72 (d, J= 8 Hz, 1H, ArH), 7.63 (t, J= 8 Hz, 1H, ArH),
 7.56 (t, J= 8 Hz, 1H, ArH), 7.49 (t, J= 8 Hz, 1H, ArH),
 6.07 (s, 1H, ArH), 0.22 (s, 9H, Alkyl H)





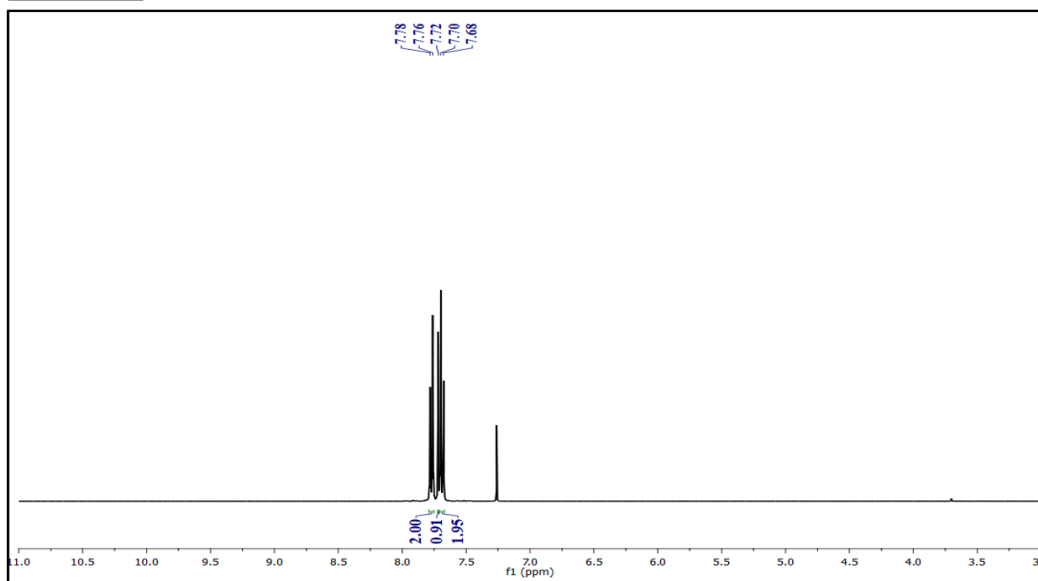
2-benzylidenemalononitrile:

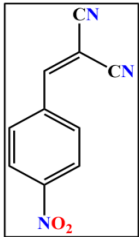
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.91 (d, $J=8$ Hz, 2H, ArH), 7.78 (s, 1H, ArH), 7.64 (t, $J=8$ Hz, 1H, ArH), 7.55 (t, 2H, $J=8$ Hz, ArH)



2-(4-bromobenzylidene)malononitrile:

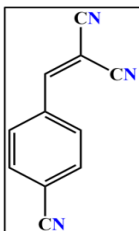
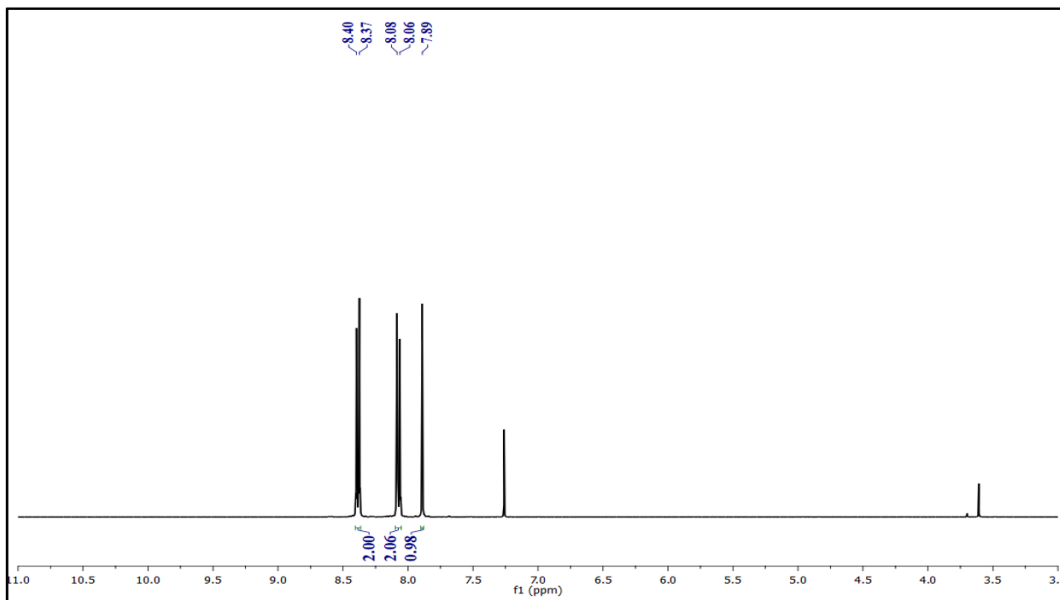
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.77 (d, $J=8$ Hz, 2H, ArH), 7.72 (s, 1H, ArH), 7.69 (d, 2H, $J=8$ Hz, ArH)





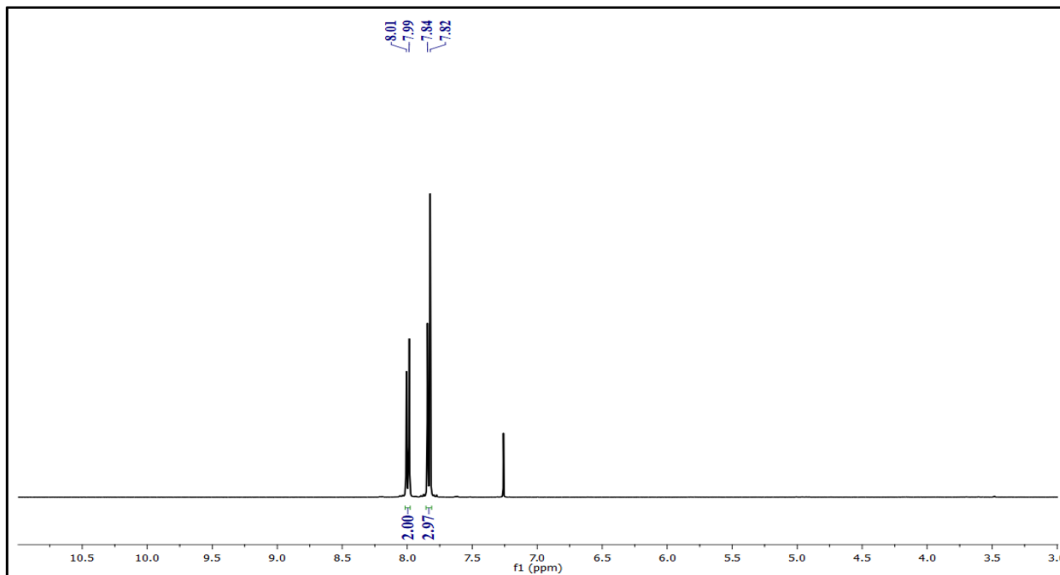
2-(4-nitrobenzylidene)malononitrile:

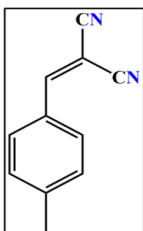
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.39 (d, $J=8$ Hz, 2H, ArH), 8.07 (d, 2H, $J=8$ Hz, ArH), 7.89 (s, 1H, ArH)



2-(4-cyanobenzylidene)malononitrile:

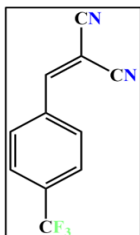
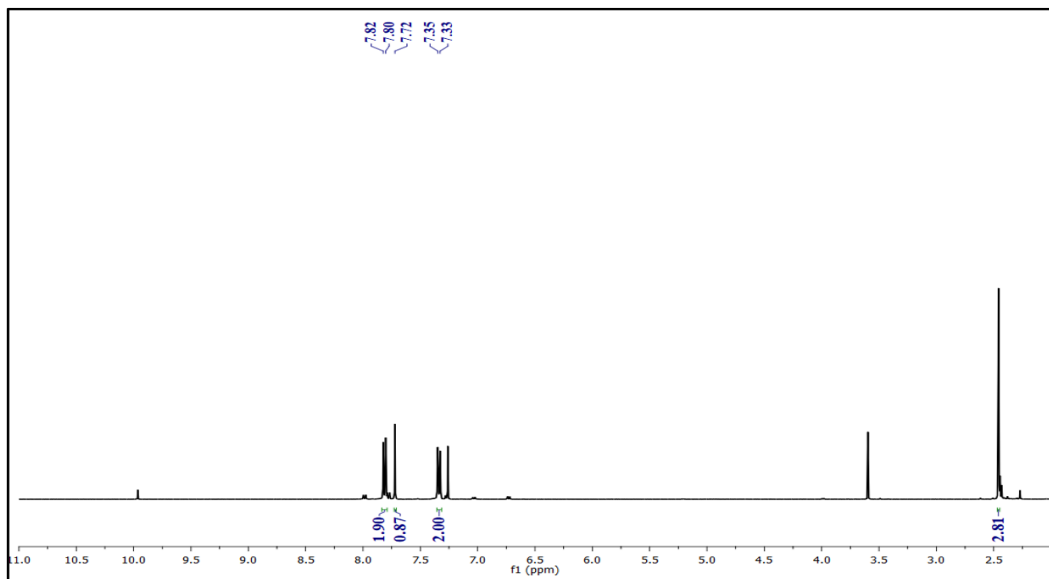
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.00 (d, $J=8$ Hz, 2H, ArH), 7.83 (d, 2H, $J=8$ Hz, ArH), 7.82 (s, 1H, ArH)





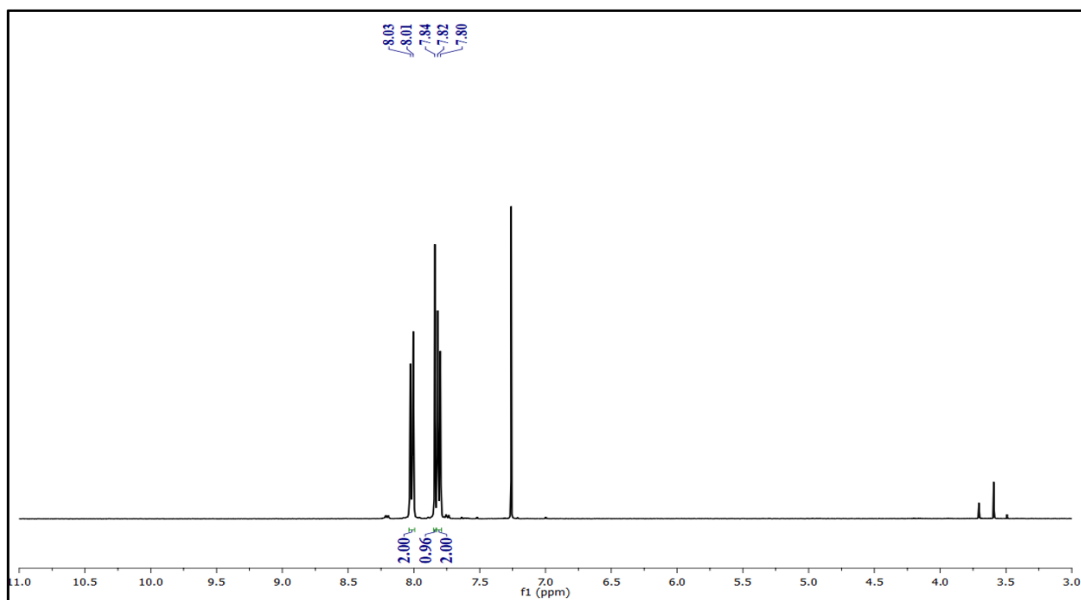
2-(4-methylbenzylidene)malononitrile:

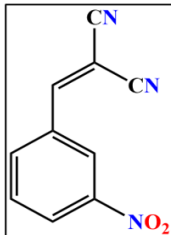
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.81 (d, $J = 8$ Hz, 2H, ArH), 7.72 (s, 1H, ArH), 7.34 (d, 2H, $J = 8$ Hz, ArH), 2.49 (s, 3H, Alkyl H)



2-(4-(trifluoromethyl)benzylidene)malononitrile:

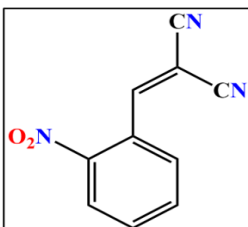
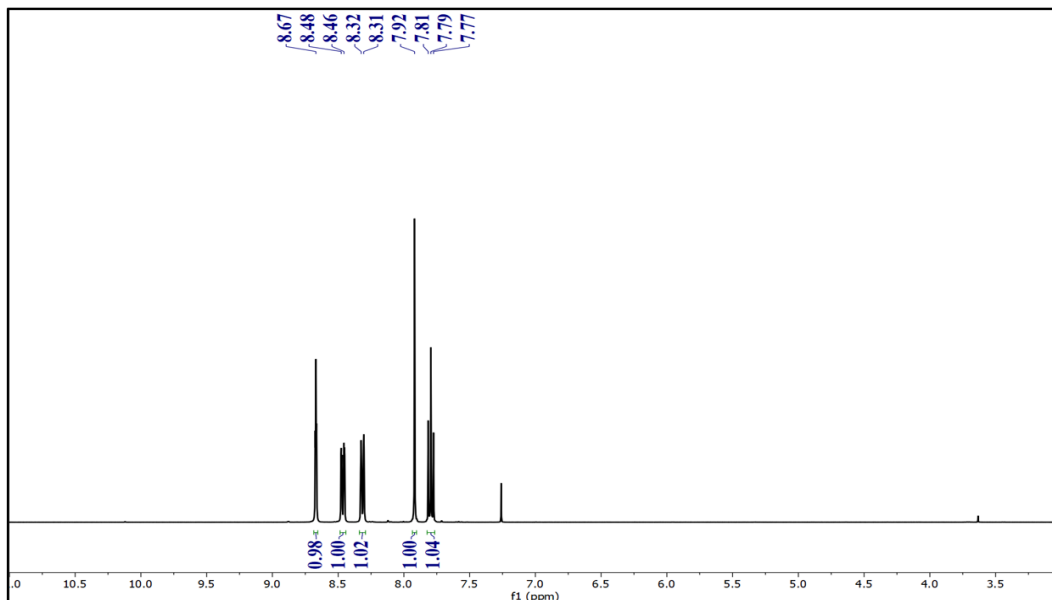
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.02 (d, $J = 8$ Hz, 2H, ArH), 7.84 (s, 1H, ArH), 7.81 (d, 2H, $J = 8$ Hz, ArH)





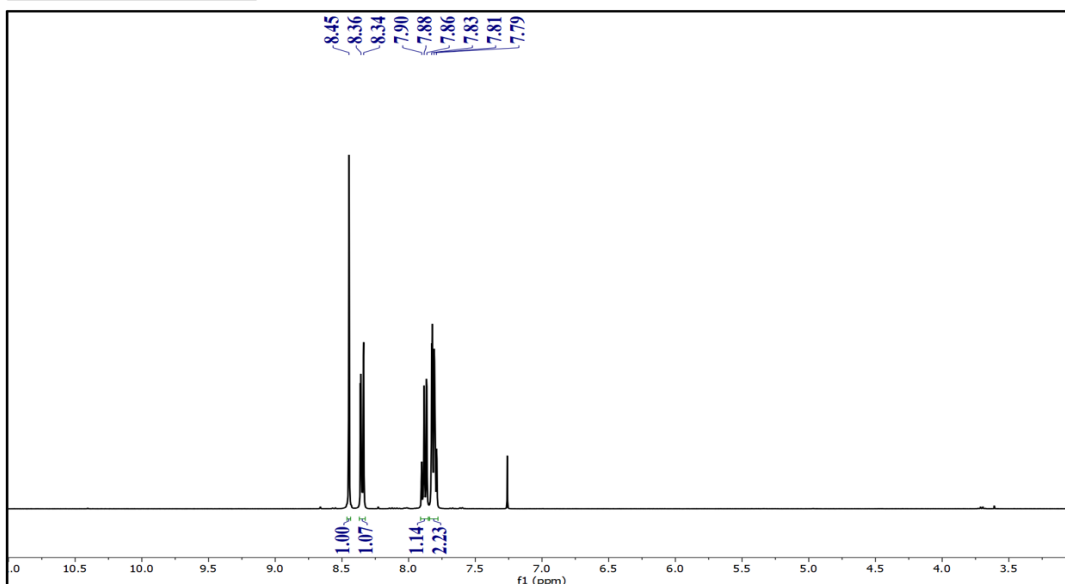
2-(3-nitrobenzylidene)malononitrile:

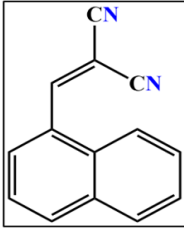
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.67 (s, 1H, ArH), 8.47 (d, 1H, $J=8$ Hz ArH), 8.31 (d, 1H, $J=8$ Hz, ArH), 7.92 (s, 1H, ArH), 7.79 (t, 1H, $J=8$ Hz, ArH)



2-(2-nitrobenzylidene)malononitrile:

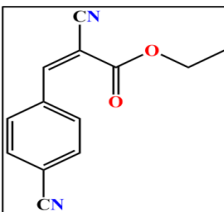
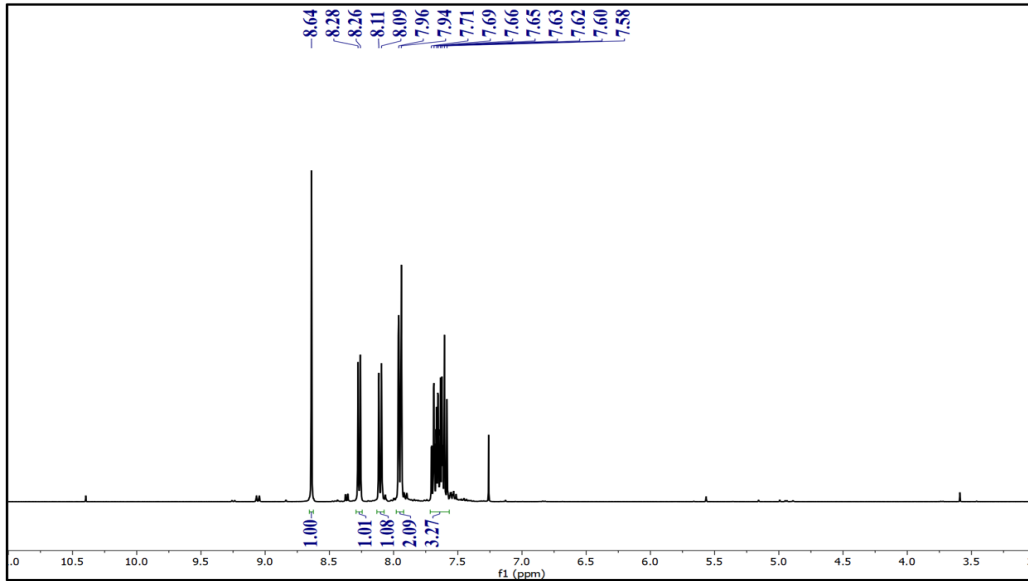
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.45 (s, 1H, ArH), 8.35 (d, 1H, $J=8$ Hz ArH), 7.88 (t, 1H, $J=8$ Hz, ArH), 7.81 (t, 2H, $J=8$ Hz, ArH)





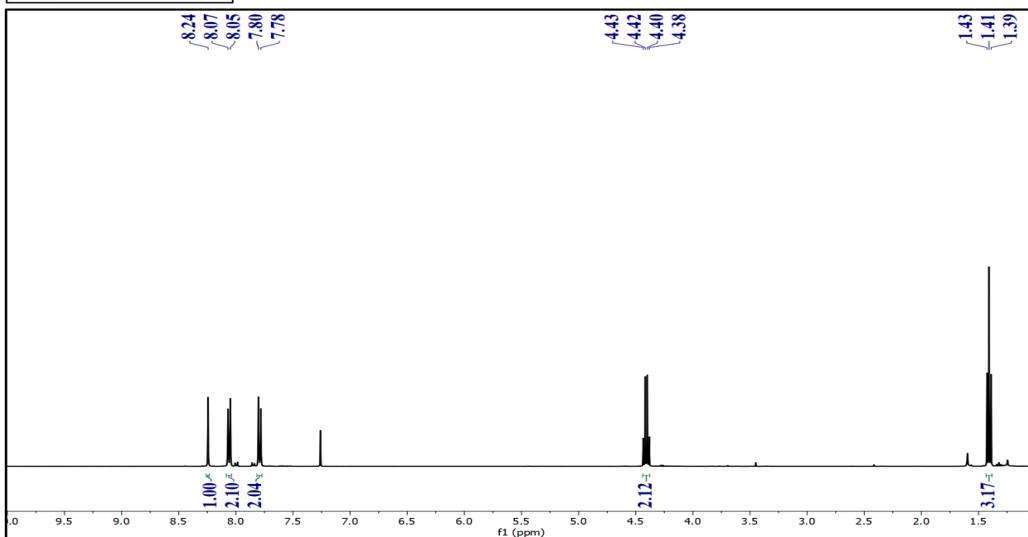
2-(naphthalen-1-ylmethylene)malononitrile:

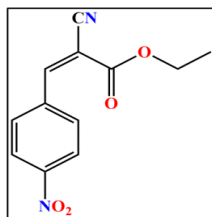
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.64 (s, 1H, ArH), 8.27 (d, 1H, $J = 8$ Hz ArH), 8.10 (d, 1H, $J = 8$ Hz, ArH), 7.95 (d, 2H, $J = 8$ Hz, ArH), 7.64 (m, 3H, $J = 8$ Hz, ArH)



Ethyl-2-cyano-3-(4-cyanophenyl)acrylate:

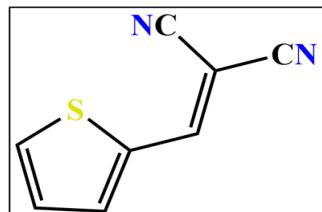
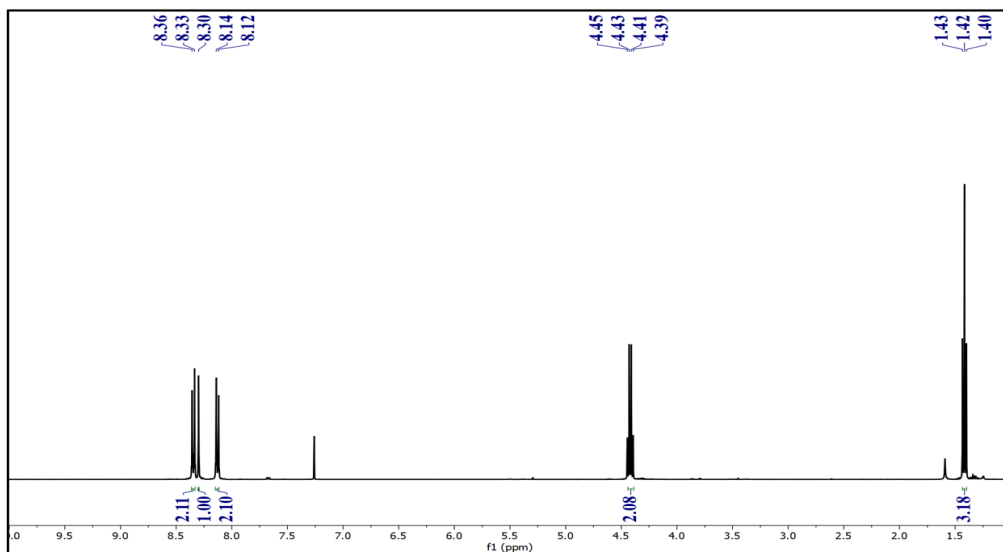
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.24 (s, 1H, ArH), 8.06 (d, $J = 8$ Hz, 2H, ArH), 7.79 (d, $J = 8$ Hz, 2H, ArH), 4.41 (m, $J = 8$ Hz, 2H), 1.41 (t, $J = 8$ Hz, 3H)





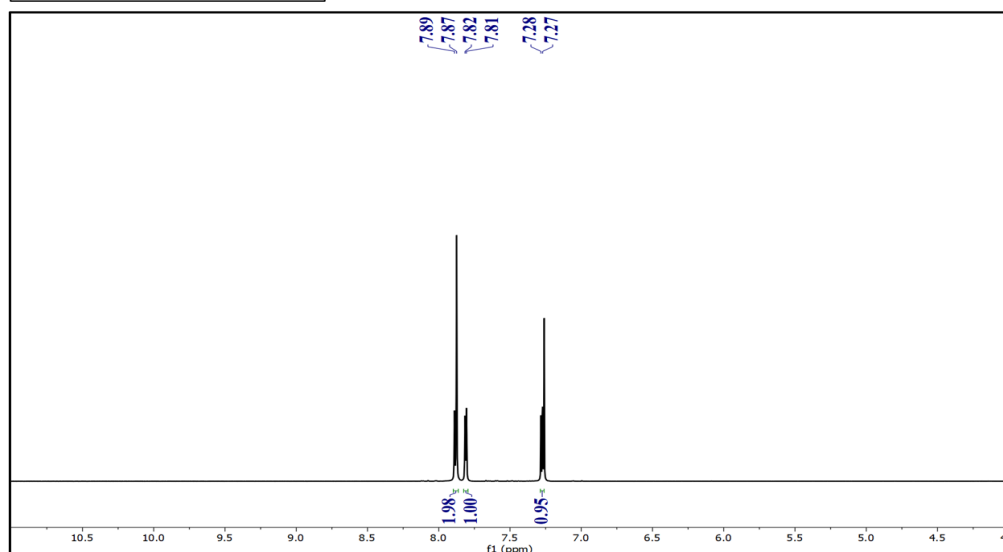
Ethyl-2-cyano-3-(4-nitrophenyl)acrylate:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.35 (d, $J=8$ Hz, 2H, ArH), 8.30 (s, 1H, ArH), 8.13 (d, $J=8$ Hz, 2H, ArH), 4.42 (m, $J=8$ Hz, 2H), 1.42 (t, $J=8$, Hz 3H)

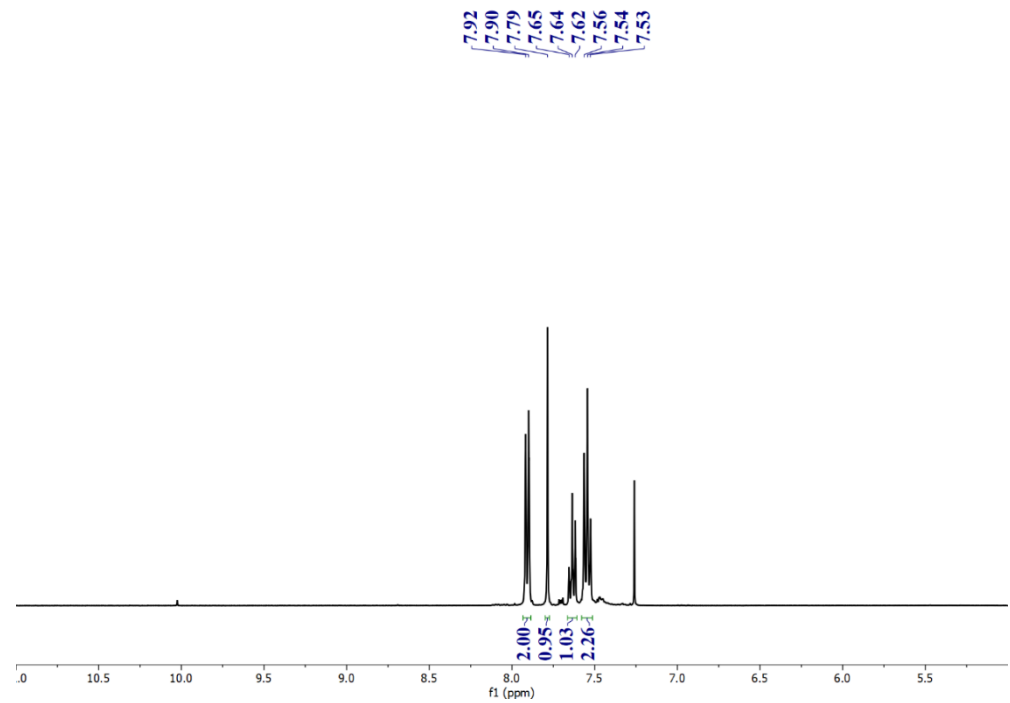
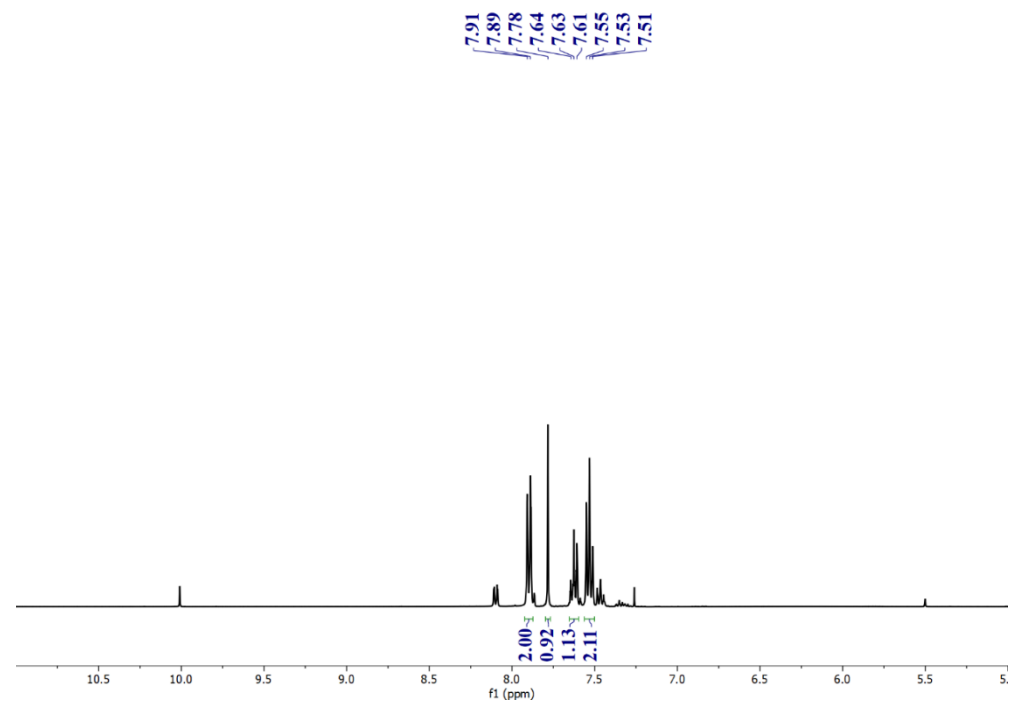


2-(thiophen-2-ylmethylene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.89 (s, 1H, ArH), 7.87 (s, 1H, ArH), 7.81 (d, $J=8$ Hz, 1H, ArH), 7.26 (t, 1H, ArH)



Section S6: ^1H NMR spectra of continuous flow cascade catalysis



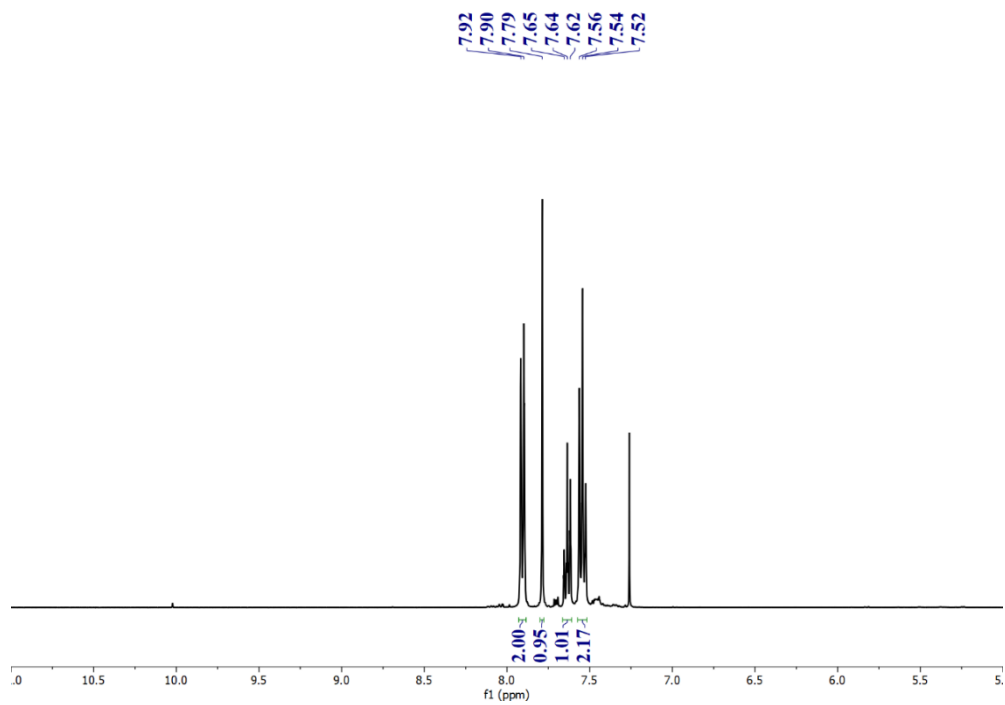


Figure S23: ^1H NMR spectra (CDCl_3) of the cascade catalysis under continuous flow (Run 3)

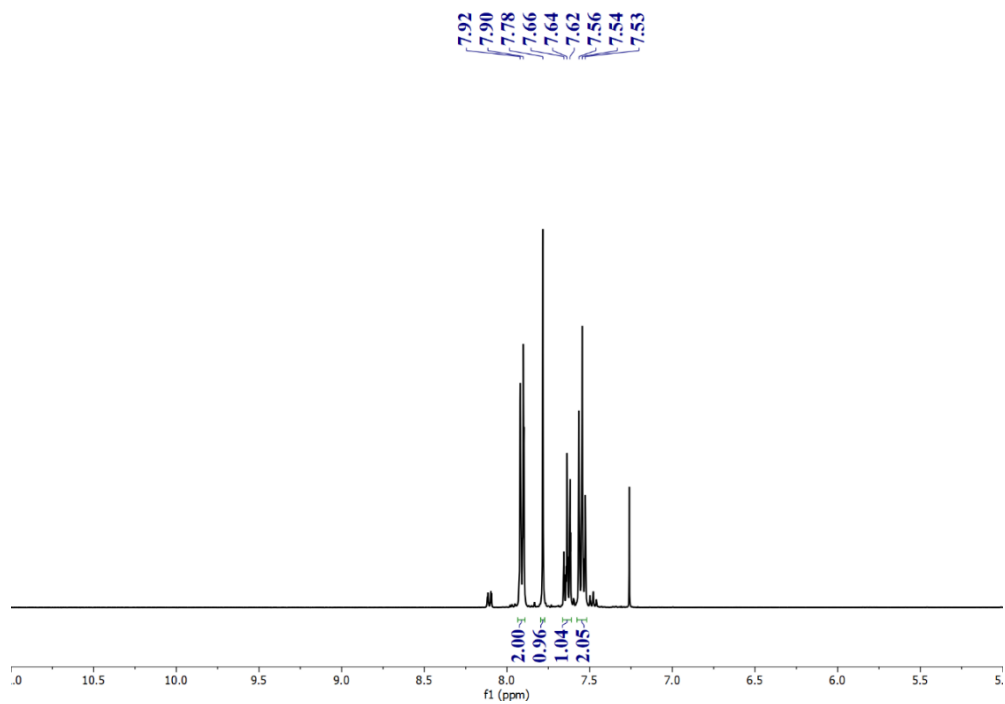


Figure S24: ^1H NMR spectra (CDCl_3) of the cascade catalysis under continuous flow (Run 4)

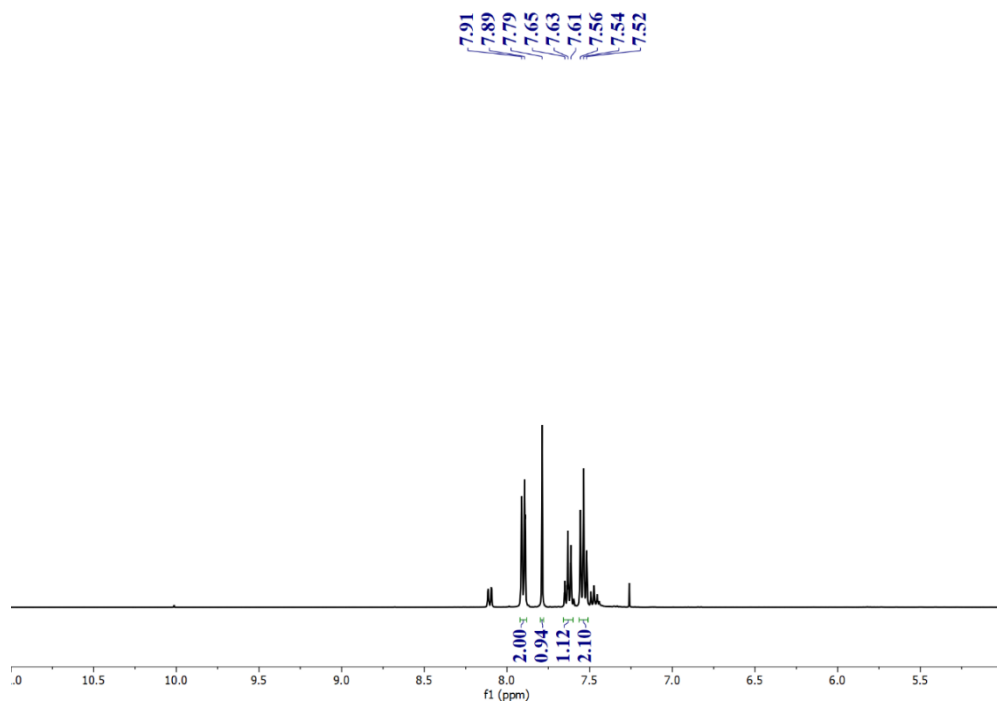


Figure S25: ^1H NMR spectra (CDCl_3) of the cascade catalysis under continuous flow (Run 5)

Table S4. Substrate scope for 120-MI@OH catalyzed one-pot cascade reaction

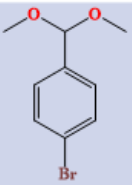
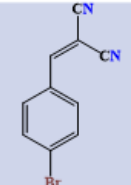
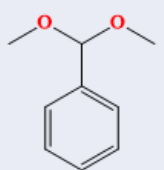
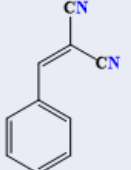
Entry	Substrate	Product	Yield
1			>99 %
2			>99 %

Table S5. One-pot cascade catalysis activity, parameters comparison of 120-MI@OH with other previously reported organic polymers

Type	Catalyst	Reaction condition (Temp./ Solvent)	Duration	Yield (%)	Reusability (Cycles)	Flow catalysis	Reference
Polymer/ COF	120-MI@OH	60 °C, H₂O	2 h	> 99	5	Yes	This Work
	HisAA-220	80 °C, MeCN	4 h	77	5	No	2
	3D DL-COF-1	RT, CDCl ₃	20 h	98	3	No	3
	2,3-DhaTph	80 °C, Toluene	1 h	96	5	No	4
	PPAF-SO ₃ H + PPAF-NH ₂	90 °C, Toluene	1 h	87	7	No	5
	TAPB-DMTP-PA-COF	75°C, Solvent-free	5 h	99	15	Yes	6
	PPAF-SO ₃ H-NH ₂	90 °C, Toluene	1 h	100	8	No	7
	HCPs-SO ₃ H/CH ₂ NH ₂	90 °C, Toluene	7 h	95	3	No	8
	PPVBS/HPONNs + PVBMAP/HPONNs	80 °C, Toluene	2 h	98	12	No	9
	P(DVB-NH ₂ -0.5-StSO ₃ H)	80 °C, Toluene	24 h	99	5	No	10
	CBAP-1(EDA-SO ₃ H)	70 °C, Toluene	2h	100	7	No	11

References:

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