Supporting Information

Synthesis of Secondary and Tertiary Amine-Containing MOFs: C-N Bond Cleavage during MOF Synthesis

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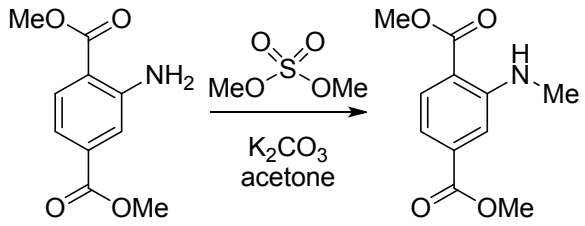
I. General Methods.

Concentration of solution was carried out by using a rotary evaporator with a water aspirator, and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on FT AM 400 or 500 (400 MHz or 500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on FT AM 400 or 500 (100 MHz or 125 MHz) and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d* and a septet at 39.52 ppm of DMSO-d_6.

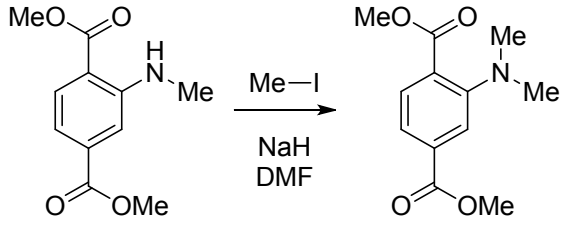
II. Ligand Synthesis



*Dimethyl-2-(methylamino)terephthalate (**2**)*

Dimethyl-2-aminoterephthalate (1 g, 5 mmol) and potassium carbonate (2.07 g, 15 mmol), dimethyl sulfate (1.4 mL, 15 mmol) were dissolved in acetone (15 mL). The mixture was stirred under reflux condition (60 ^{o}C) for overnight. Once conversion was complete (by TLC), the solvent was evaporated. And then water was added to dissolve all of the inorganic salt. The solution was three times extracted with ethyl acetate. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The solid mixture was separated by silica gel column chromatography (10% EtOAc/*n*-Hexane) and the desired compound, dimethyl 2-(methylamino)terephthalate (**2**, 560 mg, 50%), were obtained as a yellow solid.

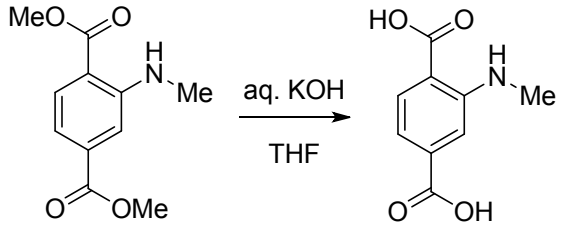
^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.93 (1H, d, *J* = 8.3 Hz), 7.35 (1H, d, *J* = 1.5 Hz), 7.21 (1H, dd, *J* = 8.3, 1.6 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 2.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.6, 167.0, 151.5, 135.3, 131.8, 115.2, 113.4, 112.4, 52.4, 51.9, 29.9. ESI-MS(+) *m/z* calcd. For $C_{11}H_{14}NO_4$ $[M+H]^+$: 224.0917, found $[M+H]^+$: 224.0917.



*Dimethyl-2-(dimethylamino)terephthalate (**3**)*

Sodium hydride (1 g of 60% suspension in oil, 25 mmol) was washed with hexanes and suspended in DMF (2.5 mL) at 0 °C under nitrogen atmosphere. A solution of **1** (1.12 g, 5 mmol) in DMF (5 mL) was then added drop-wise and the reaction mixture was stirred at 0 °C for 1 h. Methyl iodide (1.6 mL, 25 mmol) was then added and stirring continued at room temperature for 4 h. The reaction was quenched by addition of water and the resulting mixture was extracted with EtOAc. The organic phase was washed with brine. The solution was then dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The solid mixture was separated by silica gel column chromatography (10% EtOAc/*n*-Hexane) and the desired compound, dimethyl 2-(dimethylamino)terephthalate (**3**, 1.07 g, 90%), were obtained as a yellow solid.

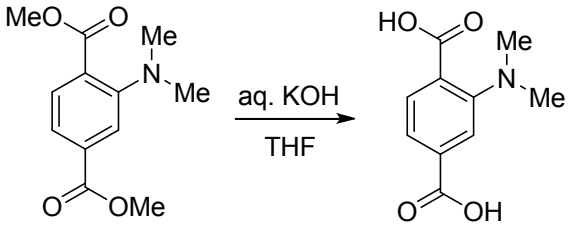
^{1}H NMR ($CDCl_3$, 400 MHz, ppm.): δ 7.70 (1H, d, J = 8.0 Hz), 7.68 (1H, s), 7.53 (1H, dd, J = 8.0, 1.1 Hz), 3.93 (s, 3H), 3.92 (s, 3H), 2.92 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.7, 166.9, 152.0, 133.3, 131.6, 124.5, 119.2, 117.8, 52.4, 43.5, 29.8. ESI-MS(+) *m/z* calcd. For $C_{12}H_{16}NO_4$ $[M+H]^+$: 238.1074, found $[M+H]^+$: 238.1074.



*2-(Methylamino)terephthalic acid (**4**)*

1 (558 mg, 2.5 mmol) was dissolved in 12.5 mL of THF. To this, 12.5 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 °C) for 3 h. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**4**, 460 mg, 93%) as a yellow solid.

^{1}H NMR (DMSO-d_6, 400MHz, ppm.): δ 7.86 (1H, d, J = 8.2 Hz), 7.21 (1H, d, J = 1.4 Hz), 7.09 (1H, dd, J = 8.2, 1.5 Hz), 2.87 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 169.5, 167.3, 151.4, 135.9, 132.0, 114.4, 113.2, 111.5, 29.3 . ESI-MS(+) *m/z* calcd. For $C_9H_{10}NO_4$ $[M+H]^+$: 196.0604, found $[M+H]^+$: 196.0604.



*2-(Dimethylamino)terephthalic acid (**5**)*

2 (475 mg, 2 mmol) was dissolved in 10 mL of THF. To this, 10 mL of a 4% KOH aqueous solution was added drop-wise. The mixture was stirred under reflux condition (66 ^{o}C) for 3 h. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. The solution was stored overnight in a refrigerator. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (**5**, 300 mg, 71%) as a pale yellow solid.

^{1}H NMR (DMSO-d_6, 400 MHz, ppm.): δ 8.03 (1H, d, J = 1.4 Hz), 7.95 (1H, d, J = 8.0 Hz), 7.76 (1H, dd, J = 8.0, 1.5 Hz), 2.9 (s, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 167.2, 166.4, 150.3, 134.9, 131.0, 127.3, 125.0, 121.0, 39.5. ESI-MS(+) *m/z* calcd. For $C_{10}H_{12}NO_4$ $[M+H]^+$: 210.0761, found $[M+H]^+$: 210.0761.

III. MOF Synthesis

IRMOF Synthesis

The IRMOF series was prepared and activated using a modified method from what has been previously described.[S1]

IRMOF-3

2-Aminoterephthalic acid (15 mg, 0.082 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (65 mg, 0.22 mmol) were dissolved in 2 mL of DMF. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then held for 18 h and then cooled to room temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

IRMOF-3-NHMe

4 (16 mg, 0.082 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (65 mg, 0.22 mmol) were dissolved in 2 mL of DMF. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then held for 18 h and then cooled to room temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24h.

IRMOF-3-NMe_2

5 (17 mg, 0.082 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (65 mg, 0.22 mmol) were dissolved in 2 mL of DMF. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 120 °C. The temperature was then held for 18 h and then cooled to room temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24h.

UiO-66 Synthesis

The UiO-66 series was prepared and activated using a modified method from what has been previously described.[S2]

UiO-66-NH_2

2-Aminoterephthalic acid (63 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 °C for 24 h. The microcrystalline powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 10 mL DMF three times. Then the solid was soaked with fresh 10 mL methanol. This process was repeated for three days.

UiO-66-NHMe

4 (68 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 °C for 24 h. The microcrystalline powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 10 mL DMF three times. Then the solid was soaked with fresh 10 mL methanol. This process was repeated for three days.

UiO-66-NMe_2

5 (73 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 °C for 24 h. The microcrystalline powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 10 mL DMF three times. Then the solid was soaked with fresh 10 mL methanol. This process was repeated for three days.

DMOF-1 Synthesis

The DMOF series was prepared and activated using a modified method from what has been previously described.[S3]

DMOF-1-NH_2

2-Aminoterephthalic acid (91 mg, 0.5 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.5 mmol) were dissolved in 25 mL of DMF. To this mixture, 1,4-diazabicyclo[2.2.2]octane (dabco, 90 mg, 0.8 mmol) was added. Upon adding, a white precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 120 °C. The temperature was then held for 12 h and then cooled to room temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF-1-NHMe

4 (98 mg, 0.5 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.5 mmol) were dissolved in 12.5 mL of DMF. To this mixture, dabco (90 mg, 0.8 mmol) was added. Upon adding, a white precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at a rate of 1 °C/min from room temperature to 100 °C. The temperature was then held for 12 h and then cooled to room temperature at a rate of 1 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF-1-NMe_2

5 (105 mg, 0.5 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.5 mmol) were dissolved in 12.5 mL of DMF.

To this mixture, dabco (90 mg, 0.8 mmol) was added. Upon adding, a white precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 °C/min from room temperature to 100 °C. The temperature was then held for 12 h and then cooled to temperature at a rate of 2.5 °C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

IV. MOF characterization

Digestion and Analysis by ^{1}H NMR of IRMOF-3 and DMOF-1 Series

Approximately 10 mg of IRMOF-3 or DMOF-1 material was dried under vacuum and digested with sonication in 590 μL of DMSO-d_6 and 10 μL of DCl.

Digestion and Analysis by ^{1}H NMR of UiO-66 Series

Approximately 10 mg of UiO-66 material was dried under vacuum and digested with sonication in 500 μL of CD_3OD-d_4, 85 μL of DMSO-d_6 and 15 μL of HF (48% aqueous solution).

Thermal Analysis

Approximately 10 mg of DMOF was used for TGA measurements, after BET analysis (activated). Sample was analyzed under a stream of N_2 using a TGA/DSC 1 running from room temperature to 1000 °C with a scan rate of 10 °C/min.

Powder X-ray Diffraction

Approximately 10 mg of IRMOF, UiO-66 or DMOF-1 was air-dried for 1 min prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Discover with GADDS using a LynxEye detector at 40 kV, 40 mA for CuKa (1 = 1.5406 Å), with a scan speed of 1 sec/step, a step size of 0.02° in 2θ, and a 2θ range of 5-55°.

BET Surface Area Analysis

Approximately 30-50 mg of DMOF-1 sample was evacuated under vacuum for a moment at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 μmHg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials. BET surface area (m^2/g) measurements were collected at 77K by N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique.

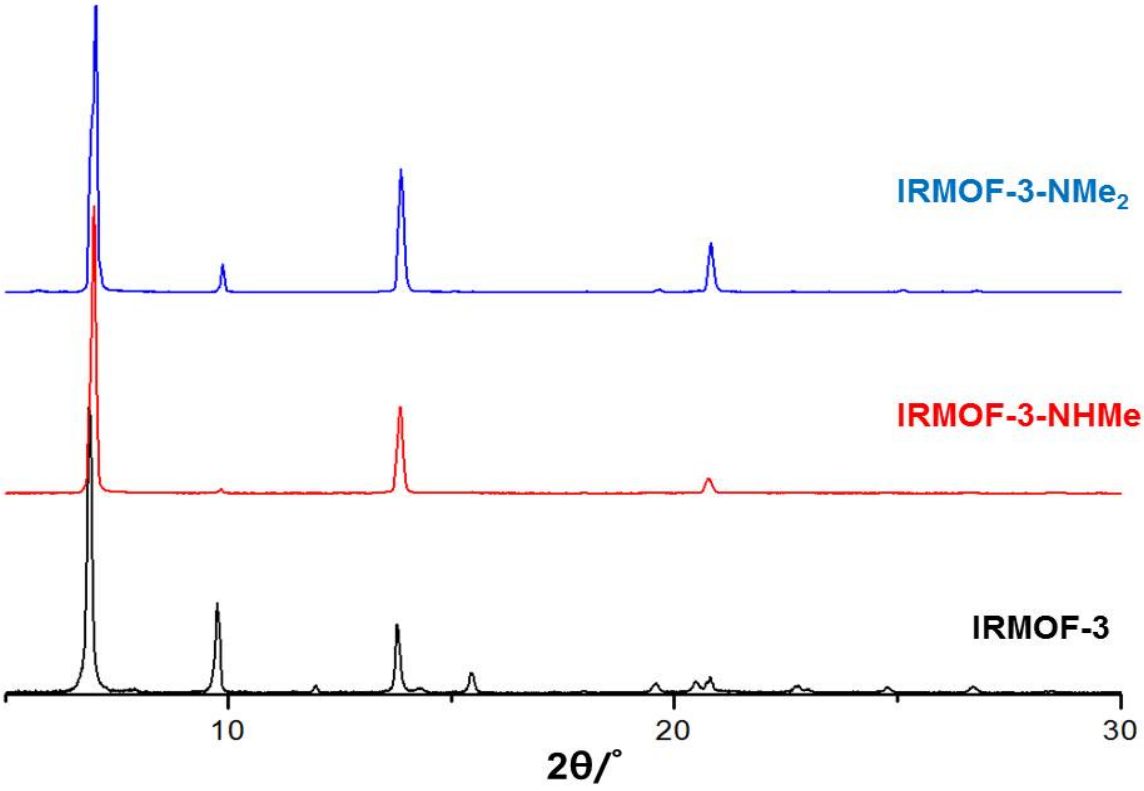


Figure S1. PXRD patterns of IRMOF-3-NH_2, -NHMe and -NMe_2.

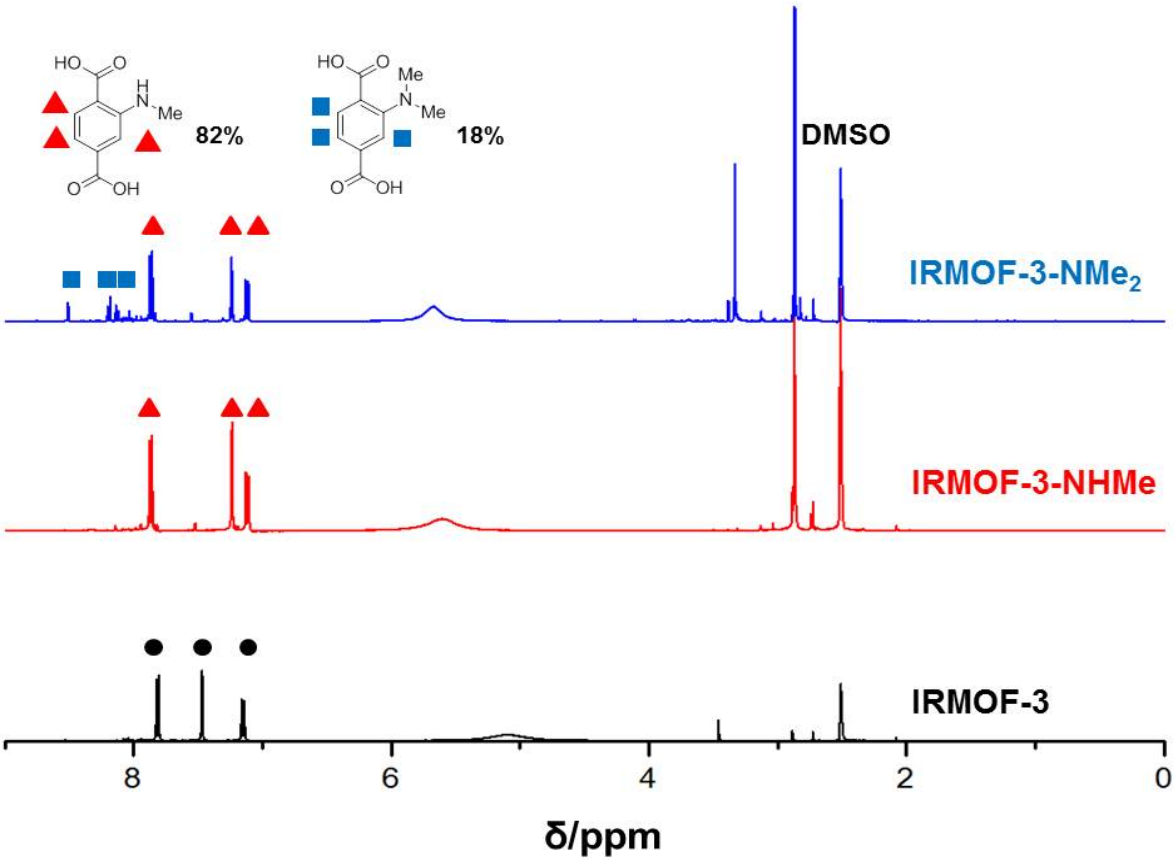


Figure S2. ^{1}H NMR of IRMOF-3, -NHMe and -NMe_2 after digestion.

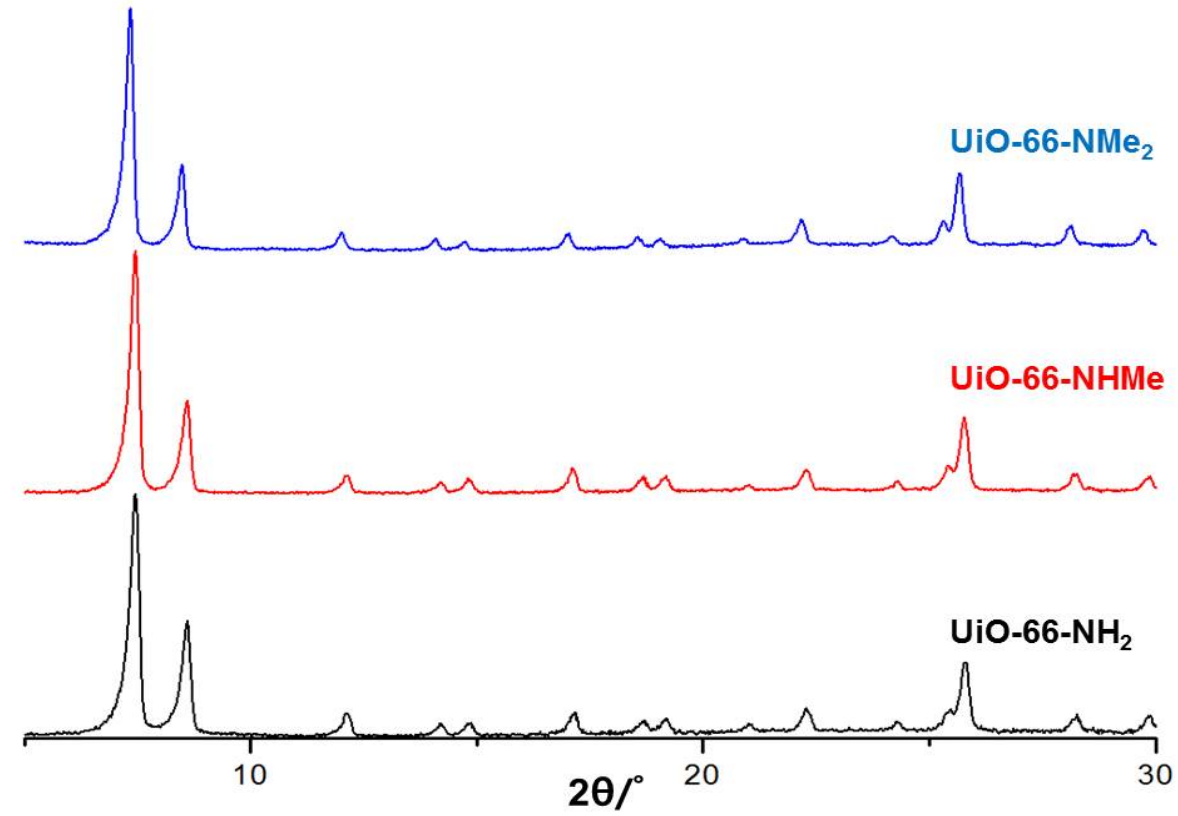


Figure S3. PXRD patterns of UiO-66-NH_2, -NHMe and NMe_2.

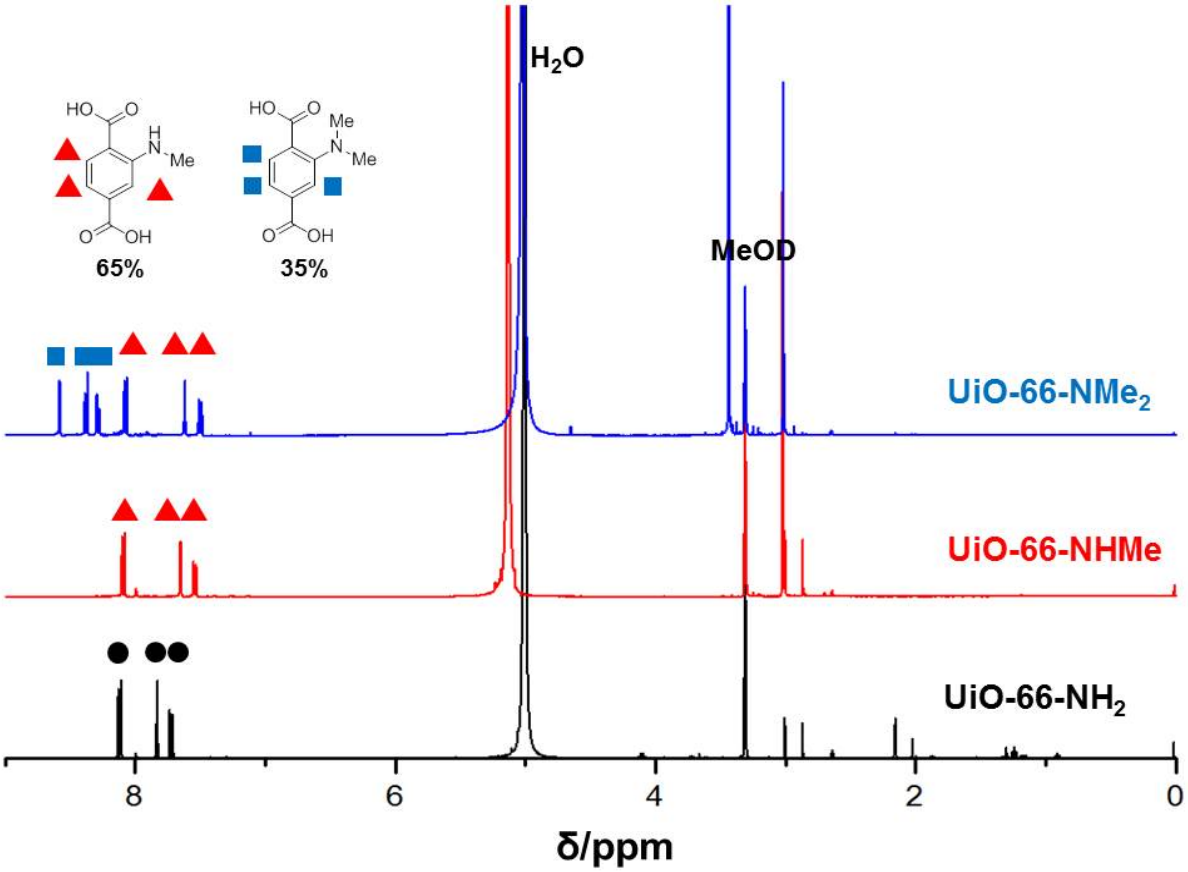


Figure S4. ^{1}H NMR of UiO-66-NH_2, -NHMe and -NMe_2 after digestion.

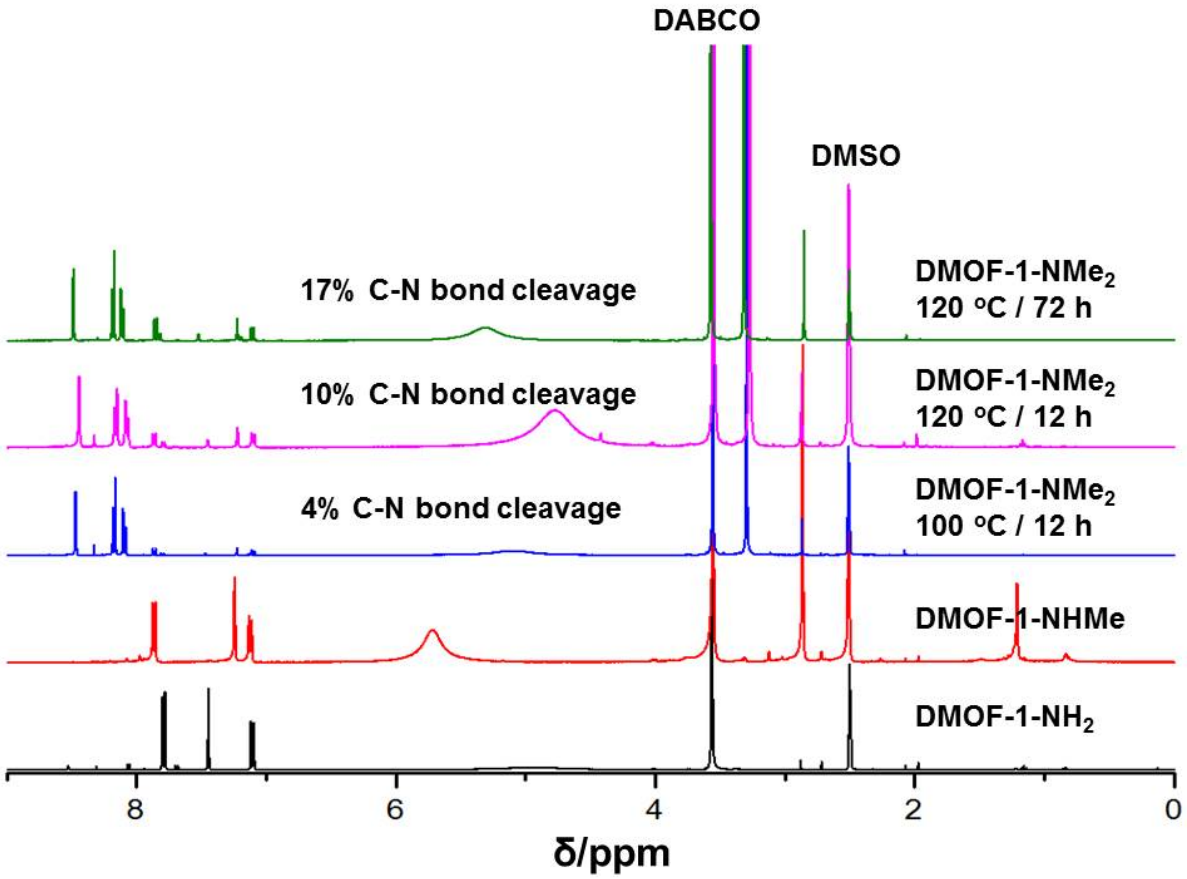


Figure S5. ^{1}H NMR of DMOF-1-NH_2, -NHMe and -NMe_2 after digestion.

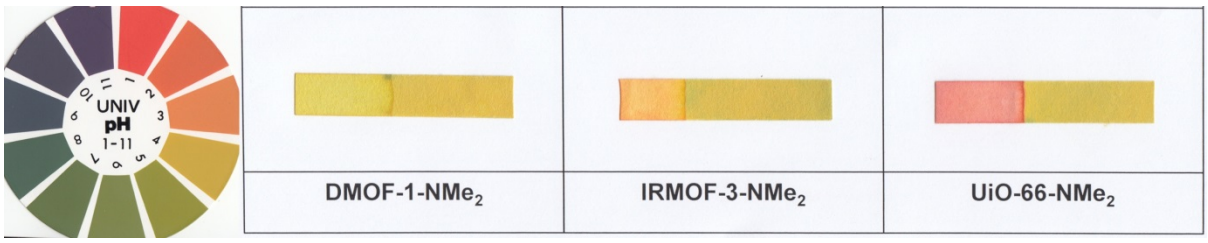


Figure S6. pH paper test of three MOF synthetic solutions.

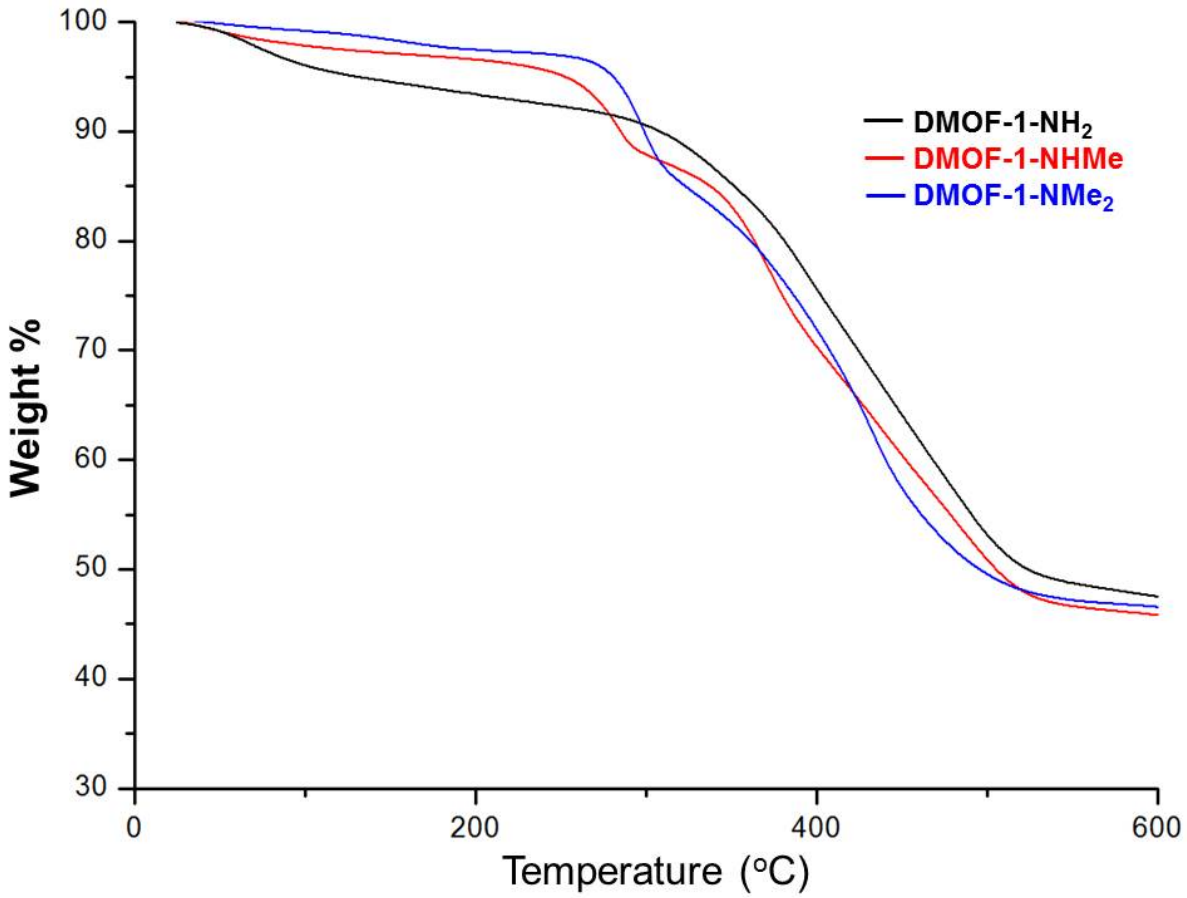


Figure S7. TGA of DMOF-1-NH_2, -NHMe and -NMe_2.

Reference

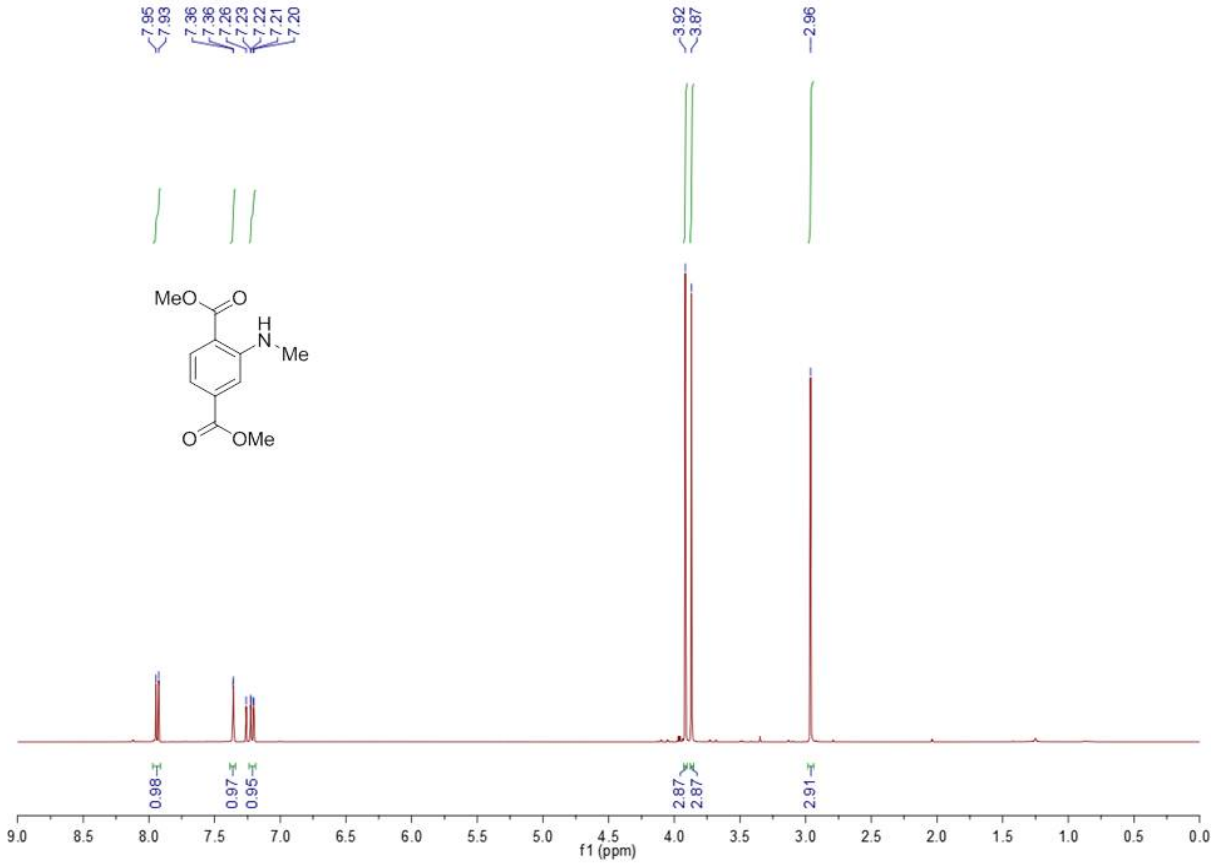
S1 K. K. Tanabe, Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2008**, *130*, 8508.

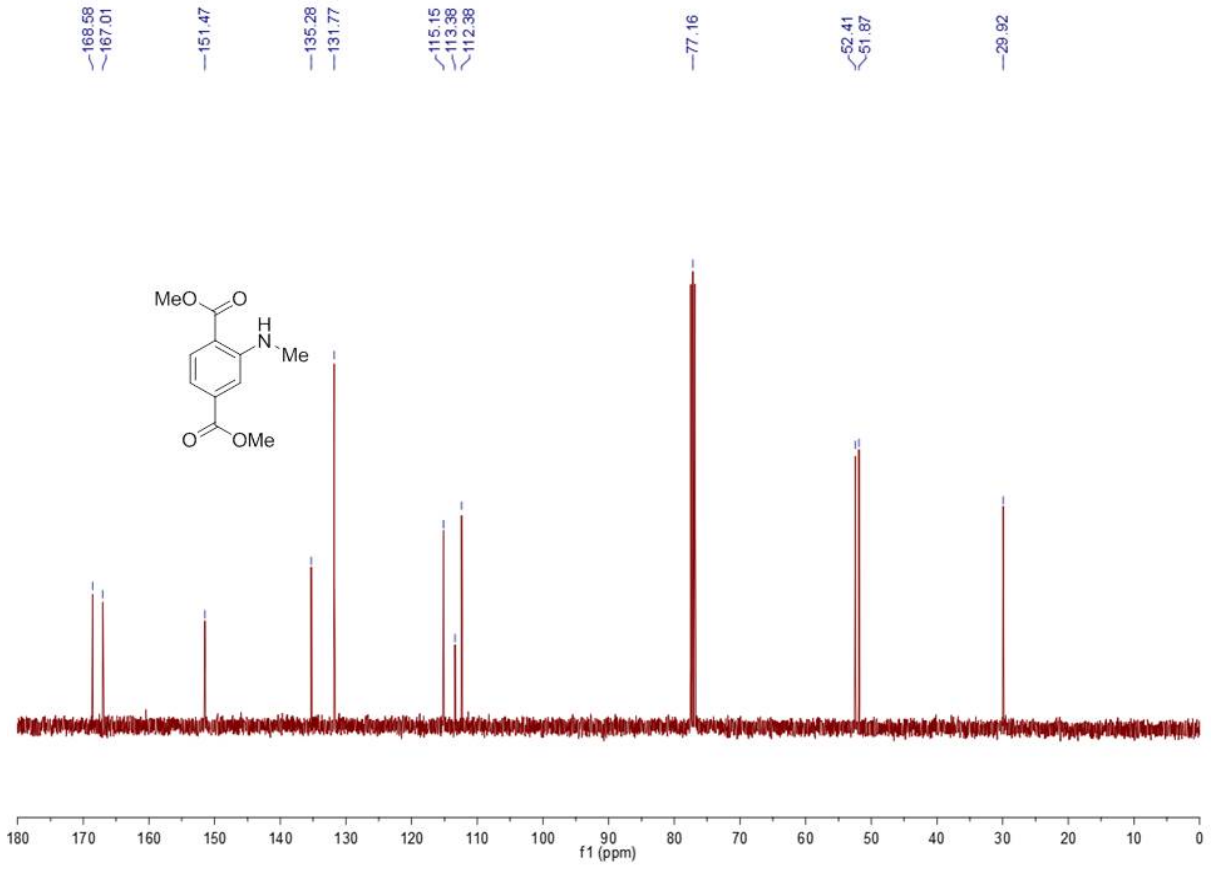
S2 S. J. Garibay, S. M. Cohen, *Chem.Commun.* **2010**, *46*, 7700.

S3 Z. Wang, K. K. Tanabe, S. M. Cohen, *Inorg. Chem.* **2009**, *48*, 296.

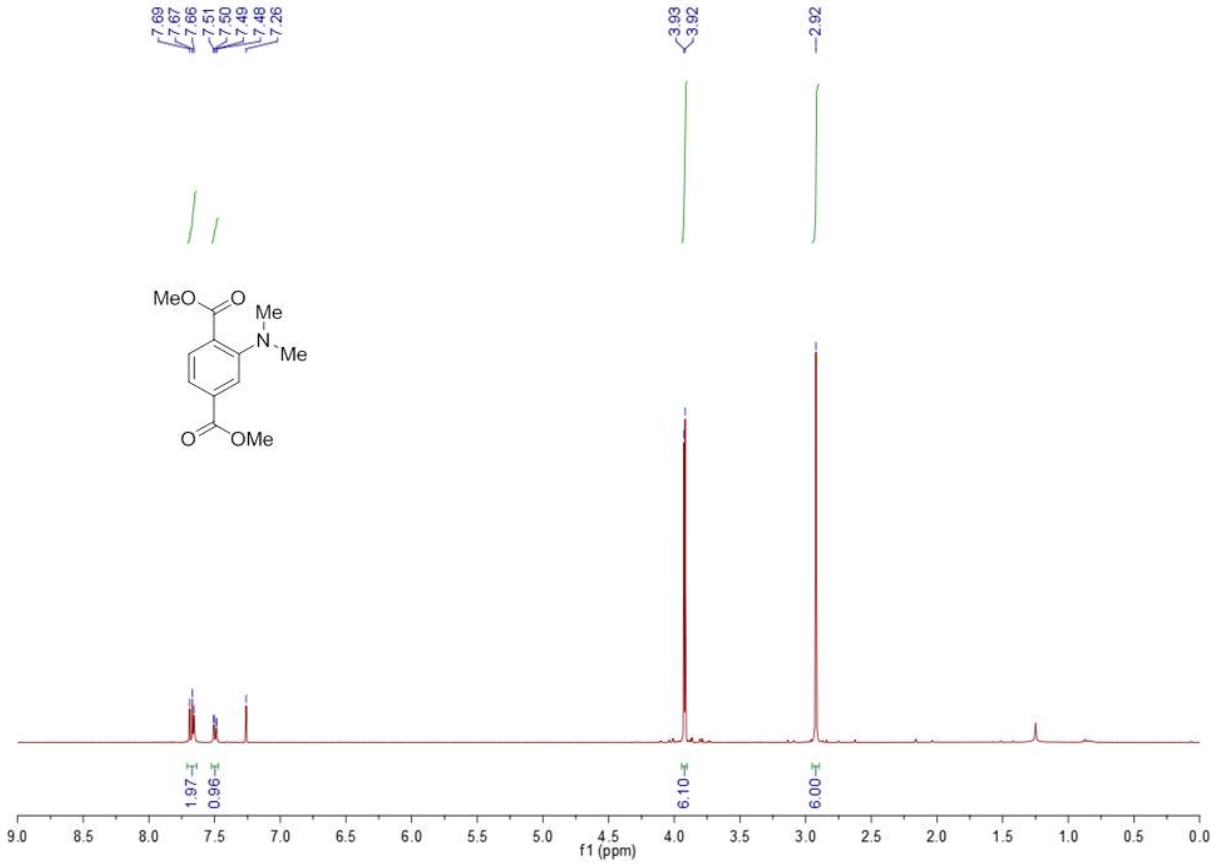
Appendix I. ^{1}H NMR, ^{13}C NMR and IR spectra of ligands

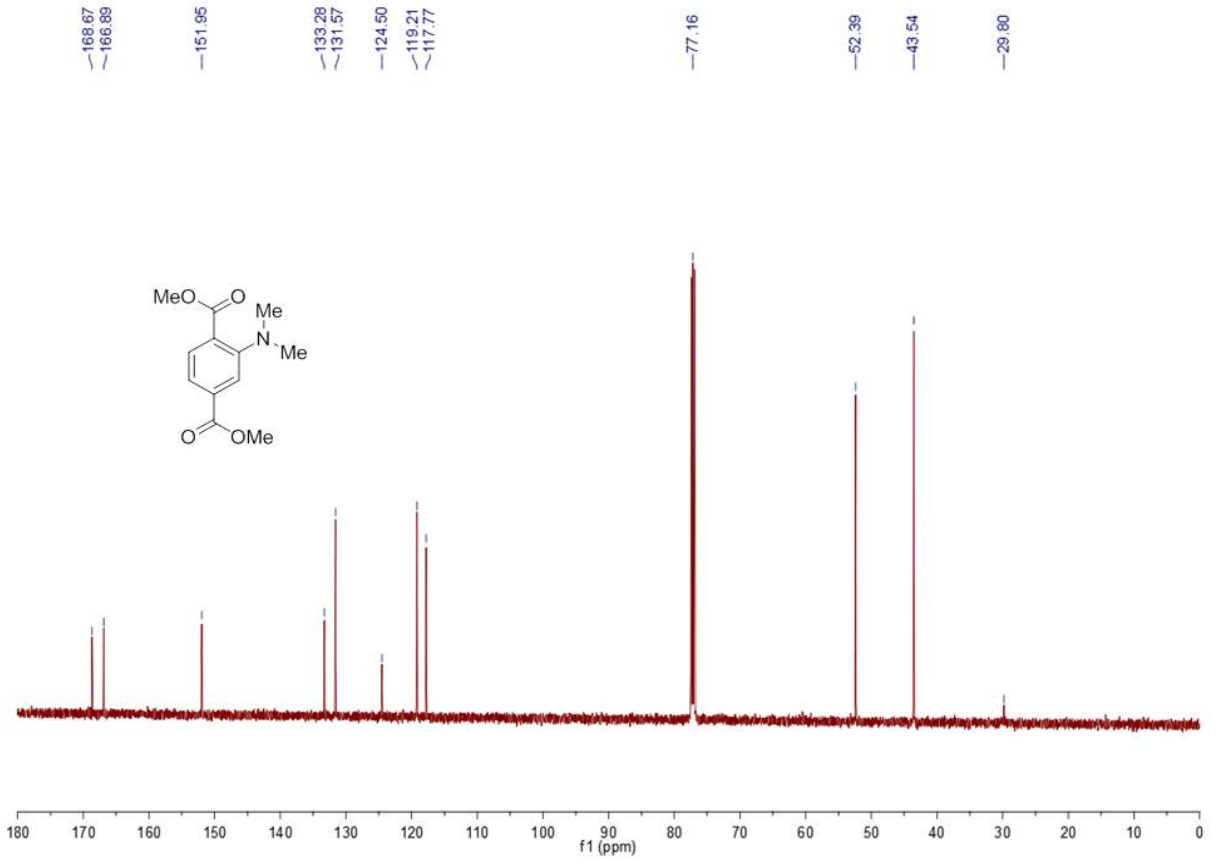
Dimethyl-2-(methylamino)terephthalate (**2**).



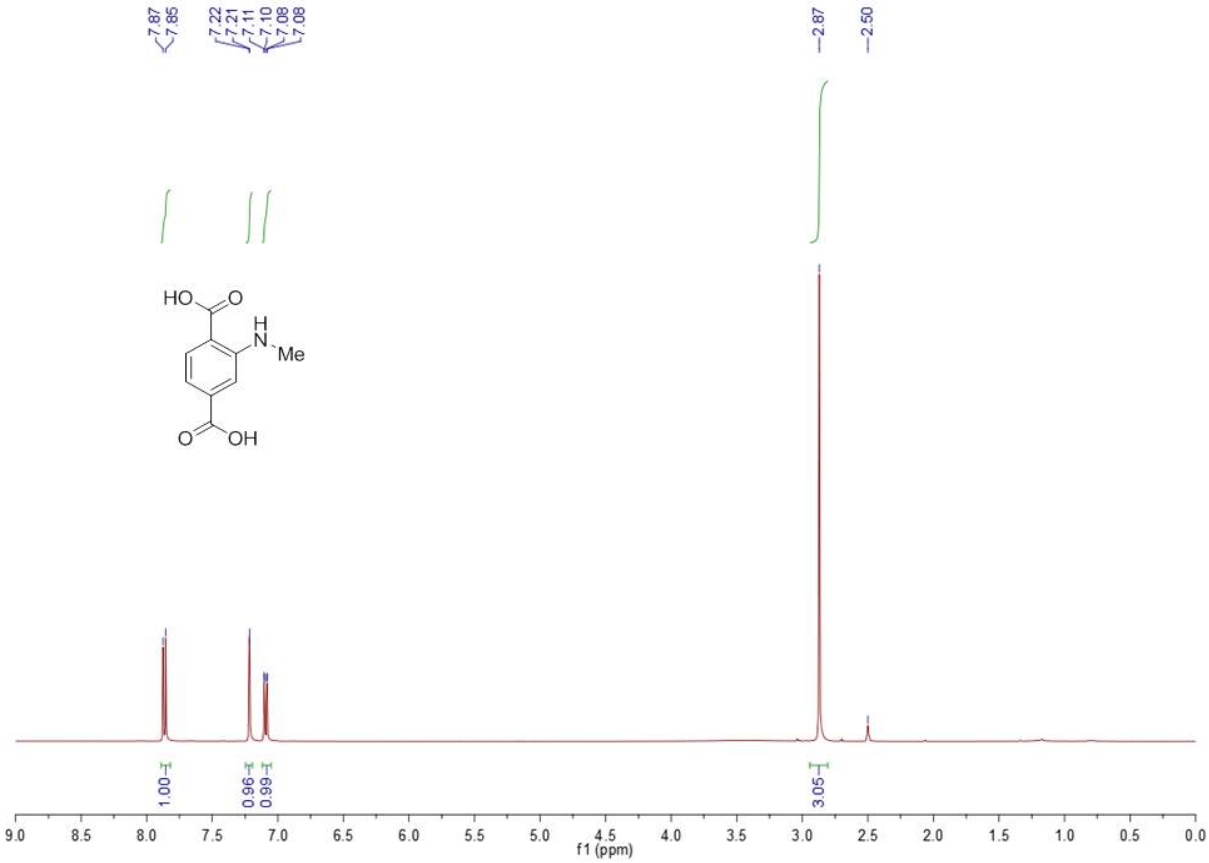


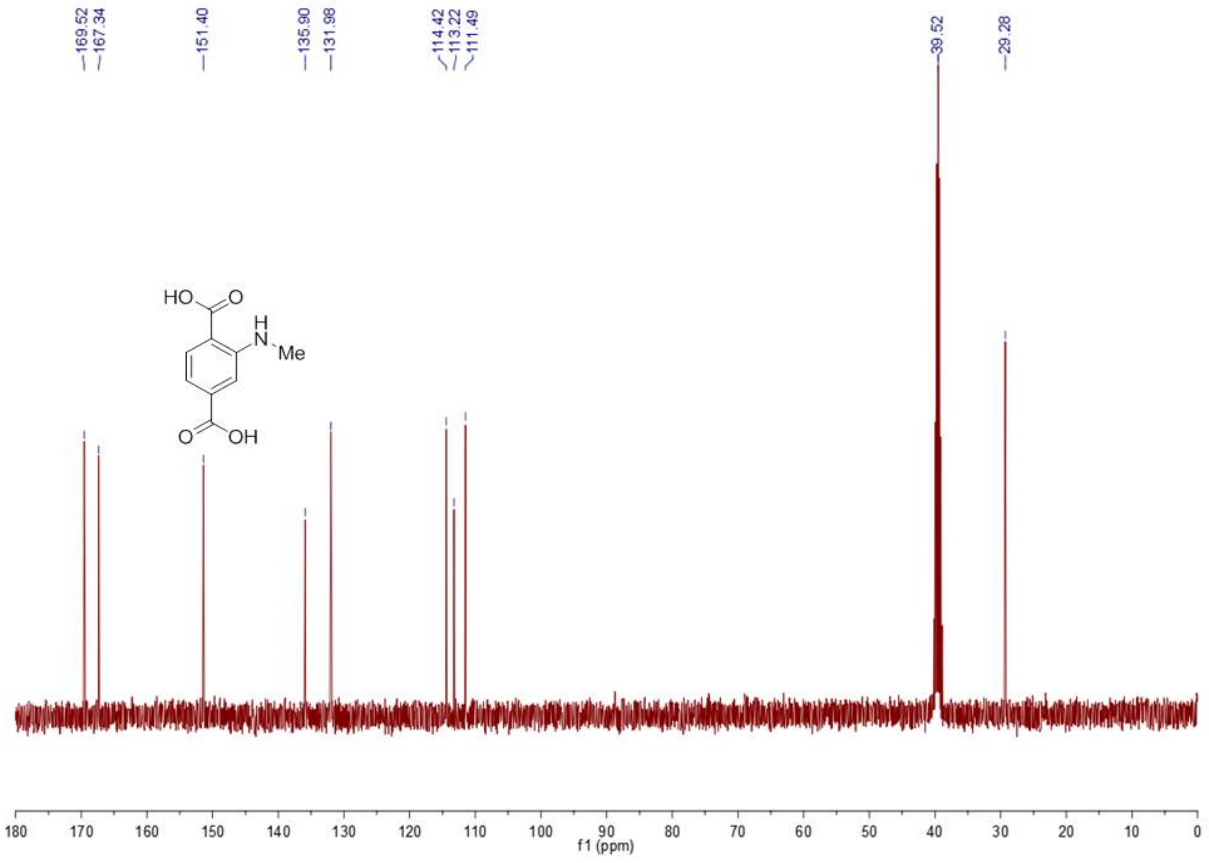
Dimethyl-2-(dimethylamino)terephthalate (**3**).



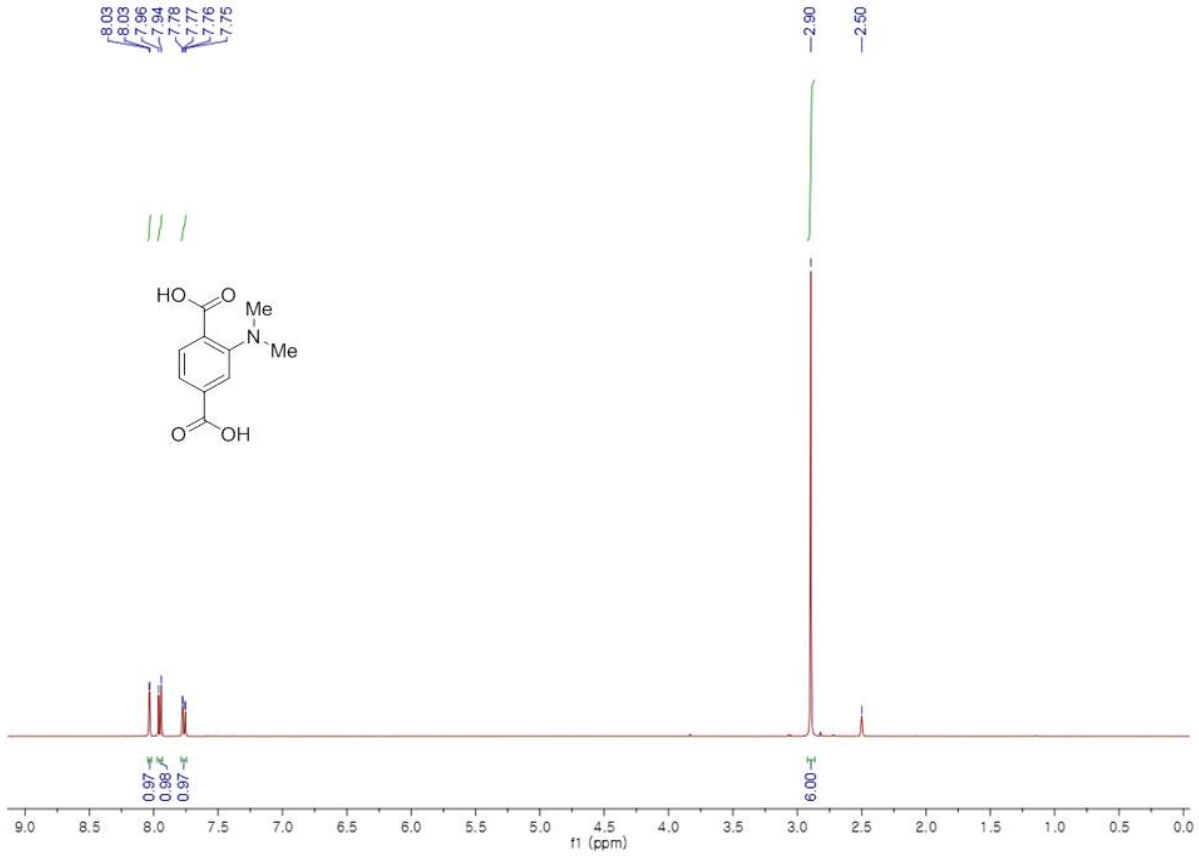


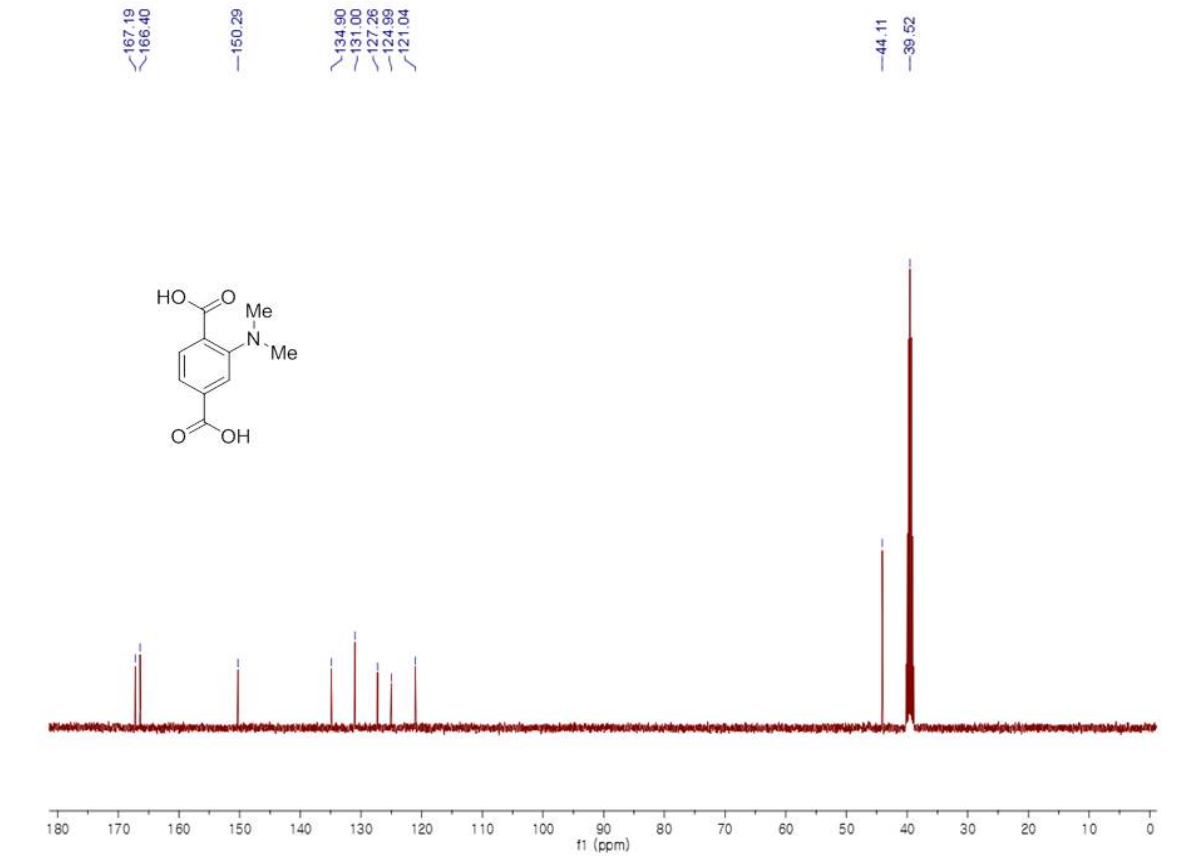
2-(Methylamino)terephthalic acid (**4**).

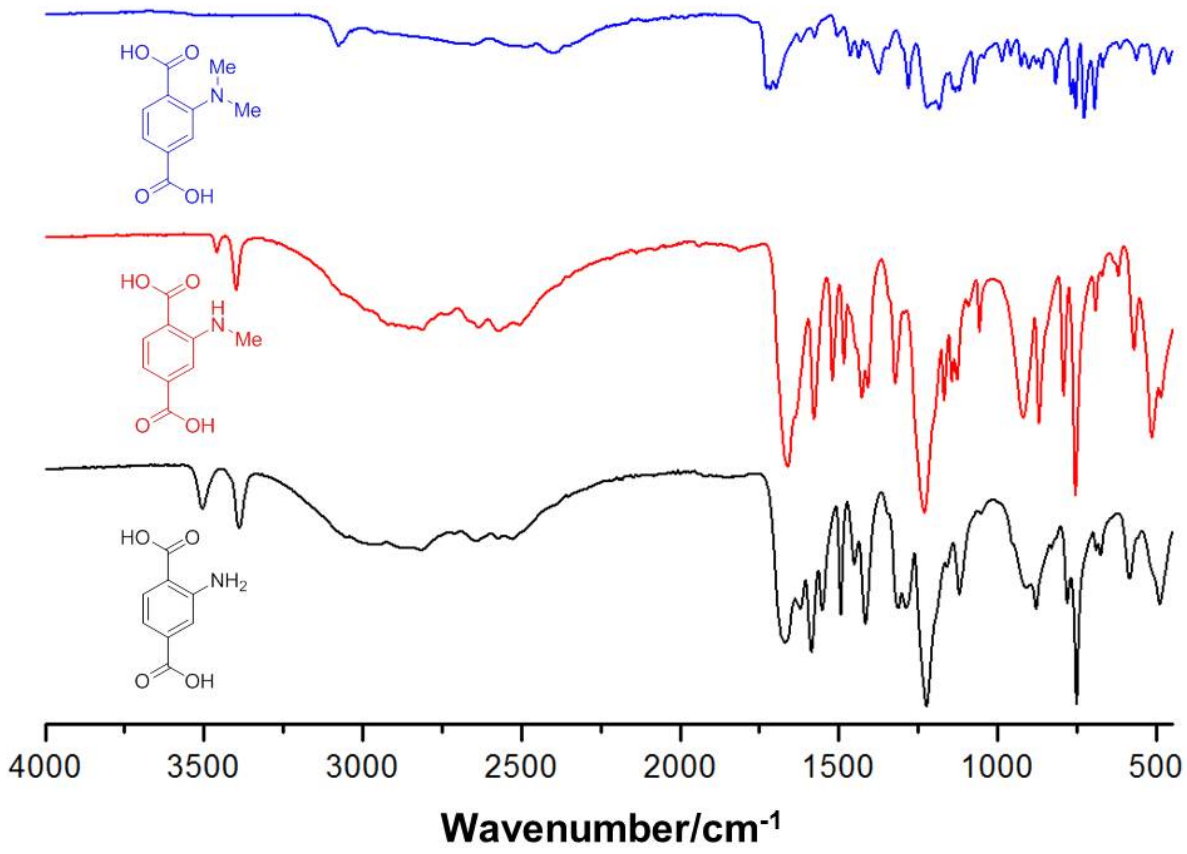




2-(Dimethylamino)terephthalic acid (**5**).



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