

# Electronic Appendices

## Table of Contents

|   |     |
|---|-----|
| <b>Appendix A for Chapter 3</b>   | 1   |
| 1. Ligand synthesis and characterization  | 1   |
| 2. MOF synthesis and characterization   | 4   |
| 3. $^1\text{H}$ NMR analysis of digested MOF samples  | 8   |
| 4. Electron density maps from MUF-7h single crystal X-ray diffraction data                        | 12  |
| 5. Computational details  | 17  |
| <b>Appendix B for Chapter 4</b>   | 24  |
| 1. Ligand synthesis and characterization  | 24  |
| 2. MOF synthesis and characterization   | 38  |
| 3. $^1\text{H}$ NMR analysis of digested MOF samples  | 41  |
| 4. Gas adsorption isotherms   | 46  |
| 5. Aging experiments data   | 50  |
| 6. Water vapor adsorption and desorption isotherms  | 60  |
| 7. The number of theoretical competing phases in multicomponent MOFs                              | 62  |
| <b>Appendix C for Chapter 5</b>   | 64  |
| 1. Ligand synthesis   | 64  |
| 2. $^1\text{H}$ NMR of digested MOFs  | 67  |
| 3. Crystallography of ( <i>S</i> )-Me <sub>2</sub> L2-Boc and ( <i>R</i> )-Me <sub>2</sub> L2-Boc | 72  |
| <b>Appendix D Additional Isotherm Plots</b>   | 74  |
| 1. BET surface area plots   | 74  |
| 2. Isothermic heat of adsorption: plots and fitting parameters                                    | 82  |
| 3. Isotherm fitting plots   | 96  |
| <b>References</b>   | 103 |

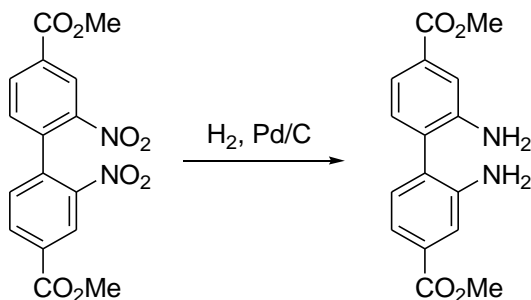


## Appendix A for Chapter 3

### Experimental Details and Supporting Information for Chapter 3

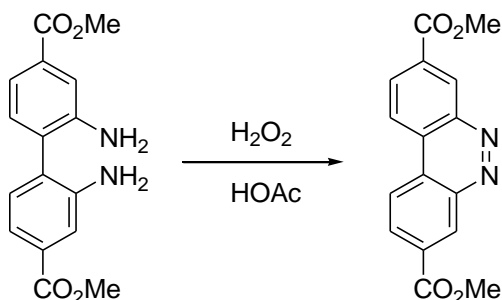
#### 1. Ligand synthesis and characterization

##### (a) Dimethyl 2,2'-diaminobiphenyl-4,4'-dicarboxylate<sup>[1]</sup>



Dimethyl 2,2'-dinitrobiphenyl-4,4'-dicarboxylate<sup>[1]</sup> (1.31 g, 3.63 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and diluted with methanol (20 mL). 10% Pd/C (128 mg) was added, and the reaction mixture was agitated under a hydrogen atmosphere at 45 psi for 15.5 hours on a Parr hydrogenation apparatus. After filtering the reaction mixture through Celite, the filtrate was reduced in volume *in vacuo* to afford the crude product. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH produced an off-white solid. Yield: 915 mg (84%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 3.83 (s, 6H), 4.99 (s, 4H), 7.08 (d, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.44 (m, 2H) ppm.

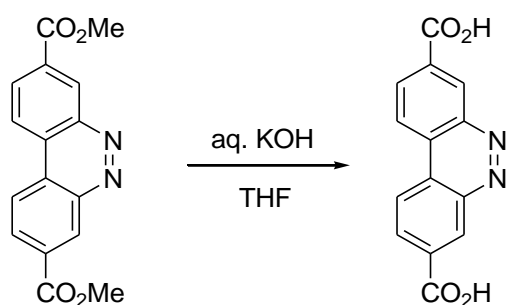
##### (b) Dimethyl benzo[*c*]cinoline-3,8-dicarboxylate<sup>[1]</sup>



30% Aqueous H<sub>2</sub>O<sub>2</sub> (2.85 mL) was added dropwise to a solution of dimethyl 2,2'-diaminobiphenyl-4,4'-dicarboxylate (1.07 g, 3.56 mmol) in acetic acid (32 mL) with stirring. The reaction temperature was kept at 25 °C for 18 hours. After water (65 mL) was added, the crude product was collected through filtration, air dried, taken up by chloroform, and filtered through a plug of neutral alumina. Solvent removal under reduced pressure

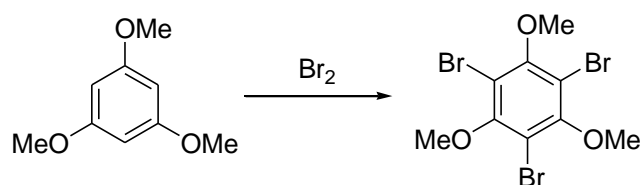
afforded the product as a yellow solid. Yield: 519 mg (49 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.02 (s, 6H), 8.51 (dd,  $J = 8.5$  Hz, 1.7 Hz, 2H), 8.62 (d,  $J = 8.5$  Hz, 2H), 9.40 (d,  $J = 1.5$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  52.82, 122.41, 123.16, 131.69, 131.91, 133.57, 145.08, 165.83 ppm. ES-MS (positive mode,  $\text{CH}_3\text{OH}/\text{CHCl}_3/\text{TFA}$ ):  $m/z = 297.68$  ( $[\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_4]^+$ , calcd. 297.09). FT-IR: 1725 (s), 1524 (w), 1436 (m), 1404 (w), 1300 (s), 1266 (w), 1212 (s), 1148 (m), 1128 (w), 1099 (m), 1082 (w), 971 (m), 908 (w), 833 (s), 784 (w), 754 (s) 724 (w)  $\text{cm}^{-1}$ .

**(c) Benzo[c]cinoline-3,8-dicarboxylic acid<sup>[2]</sup>**



A mixture of dimethyl benzo[c]cinoline-3,8-dicarboxylate (202 mg, 0.68 mmol), THF (3.75 mL) and aq. 1 M KOH (3.75 mL) was refluxed for 6 hours. After cooling to room temperature, the THF was removed *in vacuo* and the solution was acidified with aq. 1 M HCl. The resulting precipitate was separated by filtration, washed with water and air-dried. Yield: 183 mg (100 %).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.53 (dd,  $J = 8.5$  Hz, 1.7 Hz, 2H), 9.08 (d,  $J = 8.6$  Hz, 2H), 9.20 (d,  $J = 1.5$  Hz, 2H), 13.7 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}/\text{KOH}$ ):  $\delta$  121.71, 121.93, 129.91, 132.62, 138.36, 143.48, 173.03 ppm. ES-MS (negative mode,  $\text{H}_2\text{O}/\text{KOH}/\text{CH}_3\text{OH}$ ):  $m/z = 133.22$  ( $[\text{C}_{14}\text{H}_6\text{N}_2\text{O}_4]^{2-}$ , calcd. 133.02). Anal. calcd. for  $(\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4) \cdot 1.25\text{H}_2\text{O}$ : C, 57.83; H, 3.64; N, 9.64; Found: C, 57.84; H, 3.17; N, 9.53. FT-IR: 1699 (s), 1619 (m), 1577 (w), 1543 (w), 1479 (w), 1418 (m), 1363 (w), 1286 (s), 1220 (s), 1152 (w), 1126 (w), 916 (m), 835 (m), 755 (s), 731 (m)  $\text{cm}^{-1}$ .

**(d) 1,3,5-trimethoxy-2,4,6-tribromobenzene**

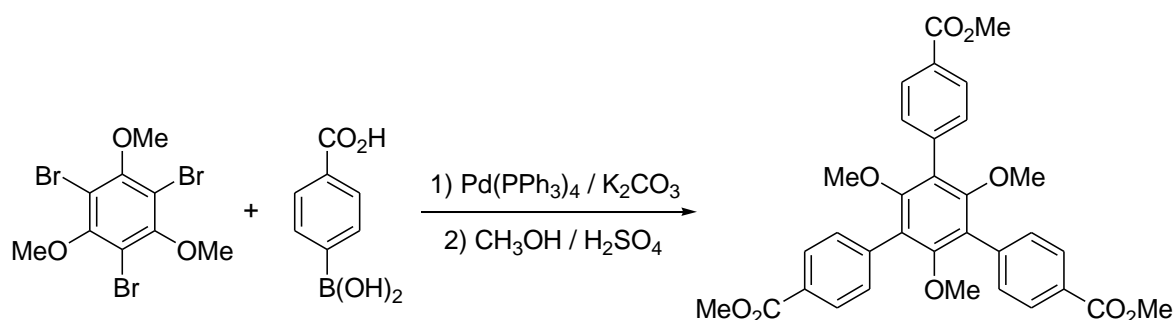


Bromine (9 mL, 349 mmol) was added in two portions to 1,3,5-trimethoxybenzene (1 g, 5.95 mmol) in an open reaction vessel. After the bromine excess was evaporated, the crude

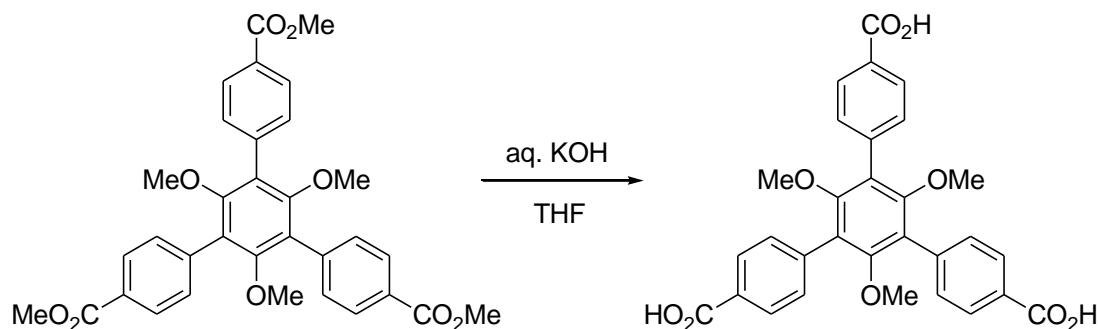


product was dissolved in ether (100 ml) and washed with aq. 5%  $\text{Na}_2\text{SO}_3$  (50 ml  $\times$  2). The organic layer was dried over  $\text{MgSO}_4$  anhydrous and ether was removed from the filtrate *in vacuo* to afford the crude product. Recrystallization from 95% ethanol afforded white needle crystals. Yield: 1.55 g (64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.88 (s, 9H) ppm.

**(e) 1,3,5-trimethoxy-2,4,6-tris(4'-methoxycarbonylphenyl)benzene**



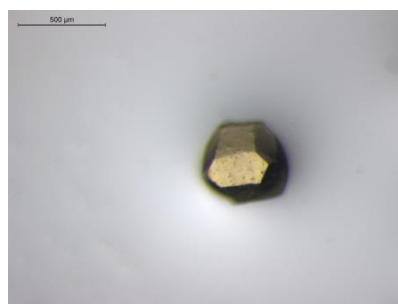
Water (5.5 ml) and 1,4-dioxane (11 ml) were added to a mixture of 1,3,5-trimethoxy-2,4,6-tribromobenzene (220 mg, 0.543 mmol),  $\text{K}_2\text{CO}_3$  (495 mg, 3.58 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (27 mg, 23.4  $\mu\text{mol}$ ) under Ar atmosphere. The reaction was taken place under microwave irradiation at 115  $^\circ\text{C}$  for 90 minutes. The resulting mixture was filtered through a plug of celite and acidified with aq. 1 M  $\text{HCl}$ . The precipitate was separated by filtration and then taken up with methanol (5 ml) and  $\text{H}_2\text{SO}_4$  (0.5 ml). The suspension was refluxed for 24 hours and cooled down to room temperature, affording a white solid. The crude product was separated by filtration, washed with methanol, air-dried and partially purified by silica flash column chromatography (hexane / toluene / methanol then hexane / ethyl acetate). Complete purification was achieved by multiple flash column chromatography. Yield: 171 mg (55%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.03 (s, 9H), 3.94 (s, 9H), 7.61 (d,  $J = 8.2$  Hz, 6H), 8.11 (d,  $J = 8.1$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  52.30, 60.89, 125.40, 129.15, 129.41, 130.76, 139.07, 156.35, 167.20 ppm. ES-MS (positive mode,  $\text{CHCl}_3/\text{CH}_3\text{OH}$ ):  $m/z = 571.59$  ( $[\text{C}_{33}\text{H}_{31}\text{O}_9]^+$ , calcd. 571.20).

**(f) 1,3,5-trimethoxy-2,4,6-tris(4'-carboxyphenyl)benzene (H<sub>3</sub>L2)**

A mixture of 1,3,5-trimethoxy-2,4,6-tris(4'-methoxycarbonylphenyl)benzene (152 mg, 0.27 mmol) in THF (4 ml) and aq. 1M KOH (4 ml) was refluxed for 17 hours. After cooling to room temperature, the insoluble material was removed by filtration. The THF from the filtrate was removed *in vacuo* and the solution was acidified with aq. 1 M HCl. The resulting precipitate was separated by filtration, washed with water and air-dried. Yield: 117 mg (83 %). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 2.97 (s, 9H), 7.55 (d, *J* = 8.0 Hz, 6H), 7.99 (d, *J* = 8.1 Hz, 6H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 60.33, 125.08, 128.79, 130.35, 131.17, 137.67, 155.67, 167.54 ppm. ES-MS (negative mode, H<sub>2</sub>O/KOH/CH<sub>3</sub>OH): *m/z* = 175.18 ([C<sub>30</sub>H<sub>21</sub>O<sub>9</sub>]<sup>3-</sup>, calcd. 175.04). Anal. calcd. for (C<sub>30</sub>H<sub>24</sub>O<sub>9</sub>) H<sub>2</sub>O: C, 65.93; H, 4.80; Found: C, 66.16; H, 4.46.

**2. MOF synthesis and characterization****[Zn<sub>4</sub>O(bt<sub>b</sub>)<sub>4/3</sub>(bcc)<sub>1/2</sub>(bdc)<sub>1/2</sub>] (MUF-7b)**

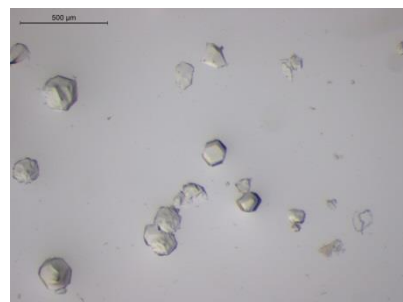
1,3,5-Tris(4-carboxyphenyl)benzene (13.2 mg, 0.030 mmol), benzo[*c*]cinoline-3,8-dicarboxylic acid (13.5 mg, 0.050 mmol) and terephthalic acid (5.0 mg, 0.030 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (55.2 mg, 0.211 mmol) in dry DEF (4.0 mL) in a 20 mL vial and sonicated for 5 minutes before being heated in an 85 °C



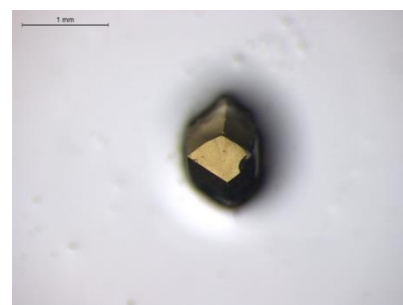
isothermal oven for 16 hours to obtain pale yellow crystals of MUF-7b. Yield: 8.2 mg. FT-IR: 1584 (s), 1536 (s), 1404 (s), 1250 (w), 1186 (w), 1107 (w), 1016 (w), 853 (w), 811 (w), 778 (s), 745 (w), 703 (w). To scale up the synthesis, a parallel synthetic method was adopted (multiple vials using the scale described above).

**Zn<sub>4</sub>O(bt<sub>b</sub>)<sub>4/3</sub>(bpdc)<sub>1/2</sub>(ndc)<sub>1/2</sub> (MUF-7c)**

1,3,5,-Tris(4-carboxyphenyl)benzene (10.8 mg, 0.025 mmol), biphenyl-4,4'-dicarboxylic acid (14.2 mg, 0.059 mmol) and 1,4-naphthalene dicarboxylic acid (10.7 mg, 0.049 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (55.2 mg, 0.211 mmol) in dry DEF (4.0 mL) in a 20 mL vial and sonicated for 5 minutes before being heated in an 85 °C isothermal oven for 16 hours to obtain colorless crystals of MUF-7c. Yield: 7.1 mg. FT-IR: 1644 (m), 1607 (m), 1587 (s), 1545 (m), 1405 (s), 1261 (w), 1178 (w), 1017 (s), 852 (w), 780 (s), 713 (w), 703 (w). To scale up the synthesis, a parallel synthetic method was adopted (multiple vials using the scale described above).

**[Zn<sub>4</sub>O(bt<sub>b</sub>)<sub>4/3</sub>(bcc)<sub>1/2</sub>(ndc)<sub>1/2</sub>] (MUF-7d)**

1,3,5,-Tris(4-carboxyphenyl)benzene (11.0 mg, 0.025 mmol), benzo[c]cinoline-3,8-dicarboxylic acid (13.4 mg, 0.050 mmol) and 1,4-naphthalene dicarboxylic acid (13.2 mg, 0.061 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (55.2 mg, 0.211 mmol) in dry DEF (4.0 mL) in a 20 mL vial and sonicated for 5 minutes. Around 10 freshly prepared MUF-7a crystals with a mean diameter of 0.1 mm were added to the vial as seeds (~ 0.1% w/w) before the mixture was heated in an 85 °C isothermal oven for 16 hours to obtain pale yellow crystals of MUF-7d. Yield: 14.0 mg. FT-IR: 1614 (m), 1586 (s), 1537 (m), 1402 (s), 1366 (m), 1261 (w), 1186 (w), 1107 (w), 1073 (w), 1016 (m), 855 (w), 779 (s), 713 (w), 695 (w).



To scale up the synthesis, crystals prepared as described above were washed with fresh DEF several times and then used (in place of MUF-7a seeds, ~0.1% w/w) to seed a new batch of MUF-7d (Yield: 12-14 mg). The second generation MUF-7d crystals produced in this manner were used as seeds for a third generation of MUF-7d. A parallel synthetic method was then adopted using third-generation MUF-7d seeds (8 vials, 12-14 mg yield per vial).

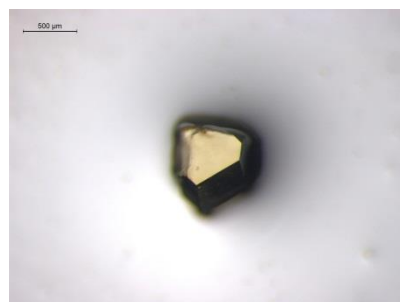
It is noted that the weight ratio of initial MUF-7a seeds to the final yield of MUF-7d is about  $1 \times 10^{-9}$  w/w.

**[Zn<sub>4</sub>O(bt<sub>3</sub>b-OMe)<sub>4/3</sub>(bpdc)<sub>1/2</sub>(bdc)<sub>1/2</sub>] (MUF-7e)**

H<sub>3</sub>btb-OMe (4.0 mg, 0.0076 mmol), biphenyl-4,4'-dicarboxylic acid (3.0 mg, 0.012 mmol) and terephthalic acid (1.3 mg, 0.0078 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (14.2 mg, 0.054 mmol) in dry DEF (1.0 mL) in a 4 mL vial and sonicated for 5 minutes before being heated in an 85 °C isothermal oven for 2 days to obtain colorless crystals of MUF-7e. Yield: 5.0 mg. FT-IR: 1607 (m), 1580 (s), 1535 (w), 1460 (w), 1400 (s), 1375 (m), 1265 (w), 1231 (w), 1210 (w), 1175 (w), 1111 (w), 1024 (W), 834 (m), 821 (m), 791 (m), 771 (w), 722 (w). To scale up the synthesis, a parallel synthetic method was adopted (multiple vials using the scale described above).

**[Zn<sub>4</sub>O(bt<sub>3</sub>b-OMe)<sub>4/3</sub>(bcc)<sub>1/2</sub>(bdc)<sub>1/2</sub>] (MUF-7f)**

H<sub>3</sub>btb-OMe (2.7 mg, 0.0051 mmol), benzo[c]cinoline-3,8-dicarboxylic acid (2.2 mg, 0.0082 mmol) and terephthalic acid (0.8 mg, 0.0048 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (9.6 mg, 0.037 mmol) in dry DEF (1.0 mL) in a 4 mL vial and sonicated for 5 minutes. Around 10 freshly prepared MUF-7a crystals (~0.1% w/w) with a mean diameter of 0.1 mm were added to the vial as seeds before the mixture was heated in an 85 °C isothermal oven for 2 days to obtain pale yellow crystals of MUF-7f. Yield: 8.6 mg. FT-IR: 1614 (s), 1560 (s), 1538 (m), 1410 (s), 1272 (w), 1227 (w), 1205 (w), 1126 (w), 1028 (m), 847 (w), 834 (w), 789 (m), 752 (s), 708 (w). To scale up the synthesis, a parallel synthetic method was adopted (multiple vials using the scale described above).

**[Zn<sub>4</sub>O(bt<sub>3</sub>b-OMe)<sub>4/3</sub>(bpdc)<sub>1/2</sub>(ndc)<sub>1/2</sub>] (MUF-7g)**

H<sub>3</sub>btb-OMe (2.7 mg, 0.0051 mmol), biphenyl-4,4'-dicarboxylic acid (1.2 mg, 0.0050 mmol) and 1,4-naphthalene dicarboxylic acid (1.1 mg, 0.0051 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (9.6 mg, 0.037 mmol) in dry DEF (1.0 mL) in a 4 mL vial and sonicated for 5 minutes. Around 10 freshly prepared MUF-7a crystals (~0.1% w/w) with a mean diameter of 0.1 mm were added to the vial as seeds before the mixture was heated in an 85 °C isothermal oven for 2 days to obtain colorless



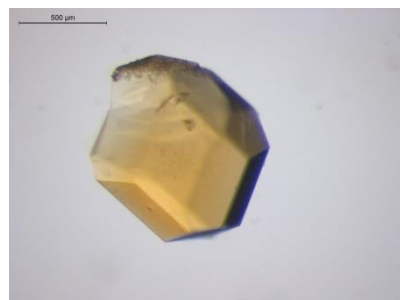
crystals of MUF-7g. Yield: 11.4 mg. FT-IR: 1614 (m), 1581 (s), 1539 (m), 1456 (w), 1410 (s), 1734 (m), 1265 (w), 1227 (w), 1209 (w), 1118 (w), 1028 (m), 839 (m), 790 (m), 752 (m).

To scale up the synthesis, crystals prepared as described above were washed with fresh DEF several times and then used (in place of MUF-7a seeds, ~0.1% w/w) to seed a new batch of MUF-7g (Yield: 10-12 mg). The second generation MUF-7g crystals produced in this manner were used as seeds for a third generation of MUF-7g, which were in turn employed to produce a fourth generation. A parallel synthetic method was then adopted using fourth-generation MUF-7g seeds (8 vials, 10-12 mg yield per vial) to scale up the synthesis.

It is noted that the weight ratio of initial MUF-7a seeds to the final yield of MUF-7g is about  $1 \times 10^{-12}$  w/w.

#### **[Zn<sub>4</sub>O(btb-OMe)<sub>4/3</sub>(bcc)<sub>1/2</sub>(ndc)<sub>1/2</sub>] (MUF-7h)**

H<sub>3</sub>btb-OMe (2.7 mg, 0.0051 mmol), benzo[c]cinoline-3,8-dicarboxylic acid (1.3 mg, 0.0048 mmol) and 1,4-naphthalene dicarboxylic acid (1.1 mg, 0.0051 mmol) were combined with Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (9.6 mg, 0.037 mmol) in dry DEF (1.0 mL) in a 4 mL vial and sonicated for 5 minutes. Around 10 freshly prepared MUF-7a crystals (~0.1% w/w) with a mean diameter of 0.1 mm were added to the vial as seeds before the mixture was heated in an 85 °C isothermal oven for 2 days to obtain pale yellow crystals of MUF-7h. Yield: 8.6 mg. FT-IR: 1607 (m), 1579 (s), 1538 (m), 1468 (w), 1411 (s), 1371 (m), 1265 (w), 1231 (w), 1201 (w), 1122 (w), 1021 (m), 844 (m), 790 (m), 751 (m).

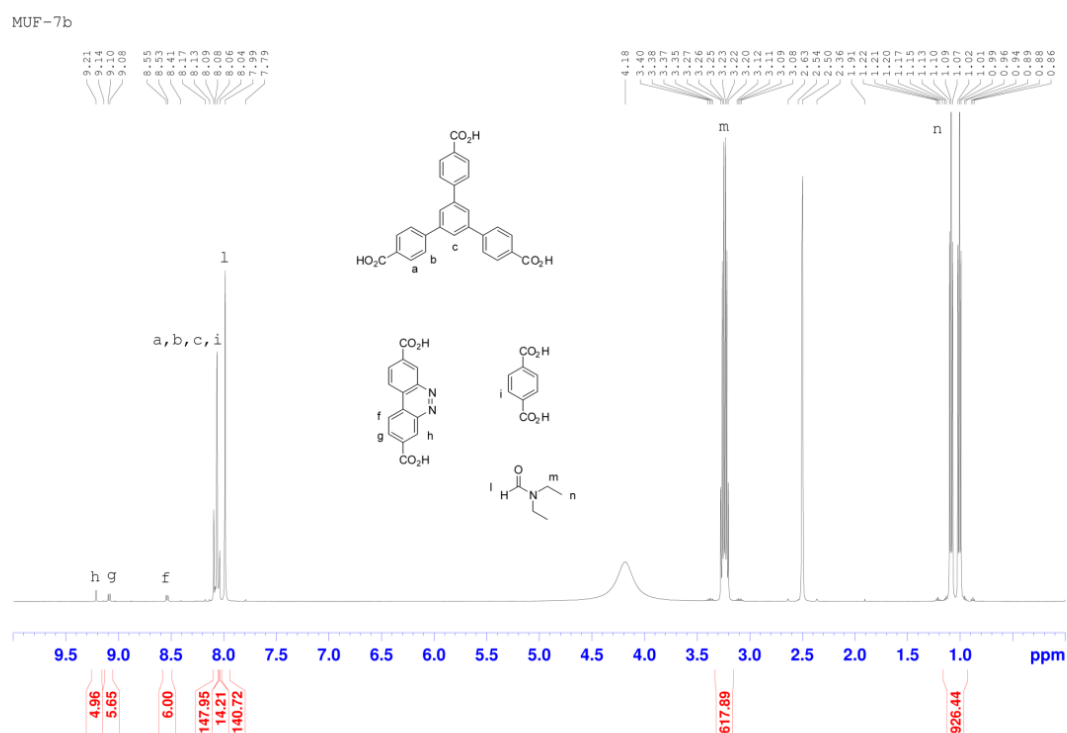


To scale up the synthesis, crystals prepared as described above were washed with fresh DEF several times and then used (in place of MUF-7a seeds, ~0.1% w/w) to seed a new batch of MUF-7h (Yield: 8-10 mg). The second generation MUF-7h crystals produced in this manner were used as seeds for a third generation of MUF-7h, then fourth- fifth- and sixth-generation MUF-7h crystals were prepared. A parallel synthetic method was then adopted using sixth-generation MUF-7h seeds (10 vials, 8-10 mg yield per vial) to scale up the synthesis.

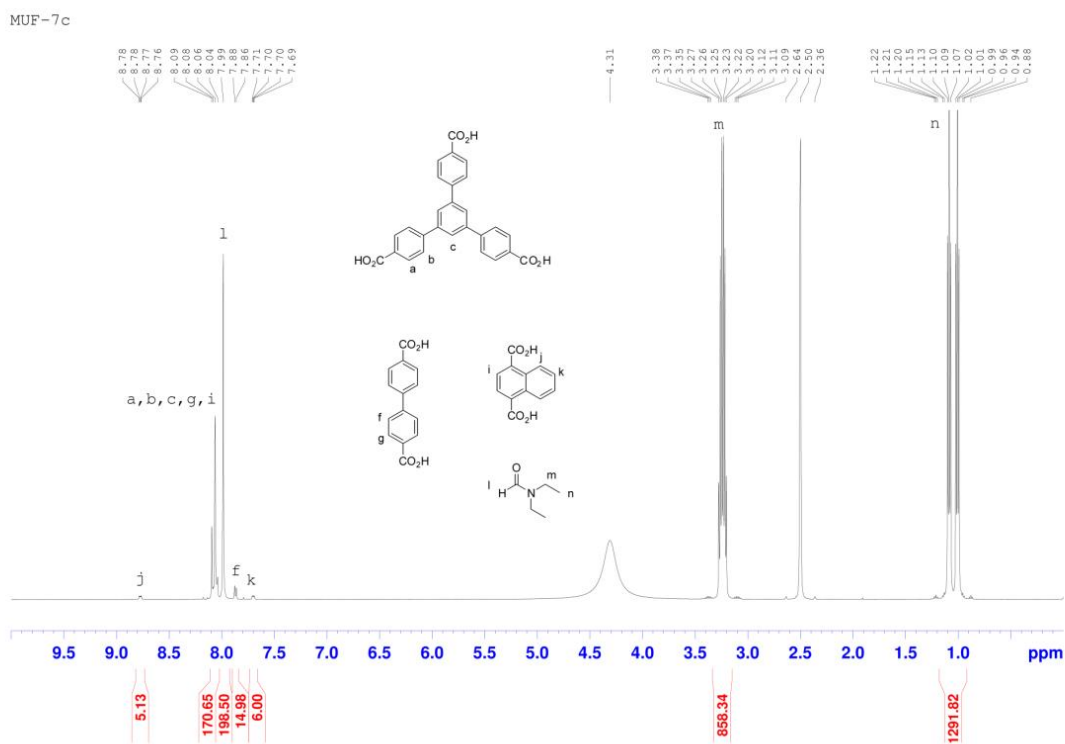
It is noted that the weight ratio of initial MUF-7a seeds to the final yield of MUF-7h is about  $1 \times 10^{-18}$  w/w.

**[Zn<sub>2</sub>L2(OH)]**

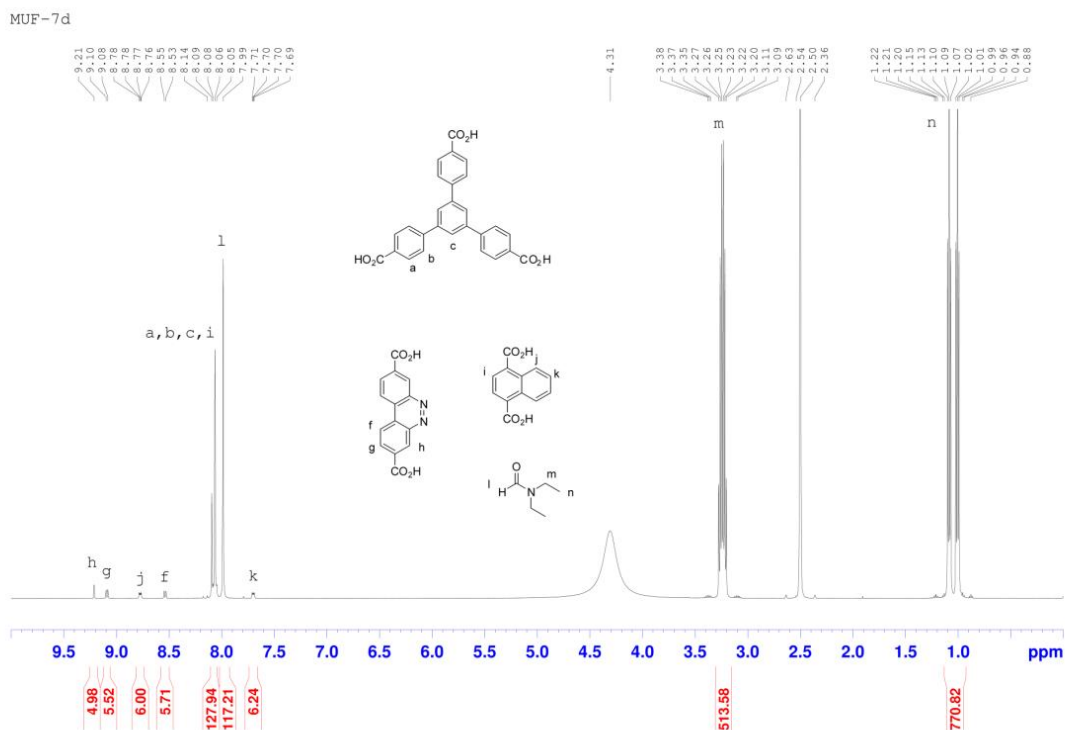
H<sub>3</sub>L2 (5.3 mg, 0.01 mmol), dabco (1.1 mg, 0.01 mmol) and Zn(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O (36.8 mg, 0.152 mmol) in dry DMF (1.3 mL) in a 20 mL scintillation vial which was then placed in an 85 °C isothermal oven for 16 hours. The resulting transparent colourless rod-shaped crystals of [Zn<sub>2</sub>L2(OH)] were washed with dry DMF before single-crystal x-ray analysis.

**3. <sup>1</sup>H NMR analysis of digested MOF samples**

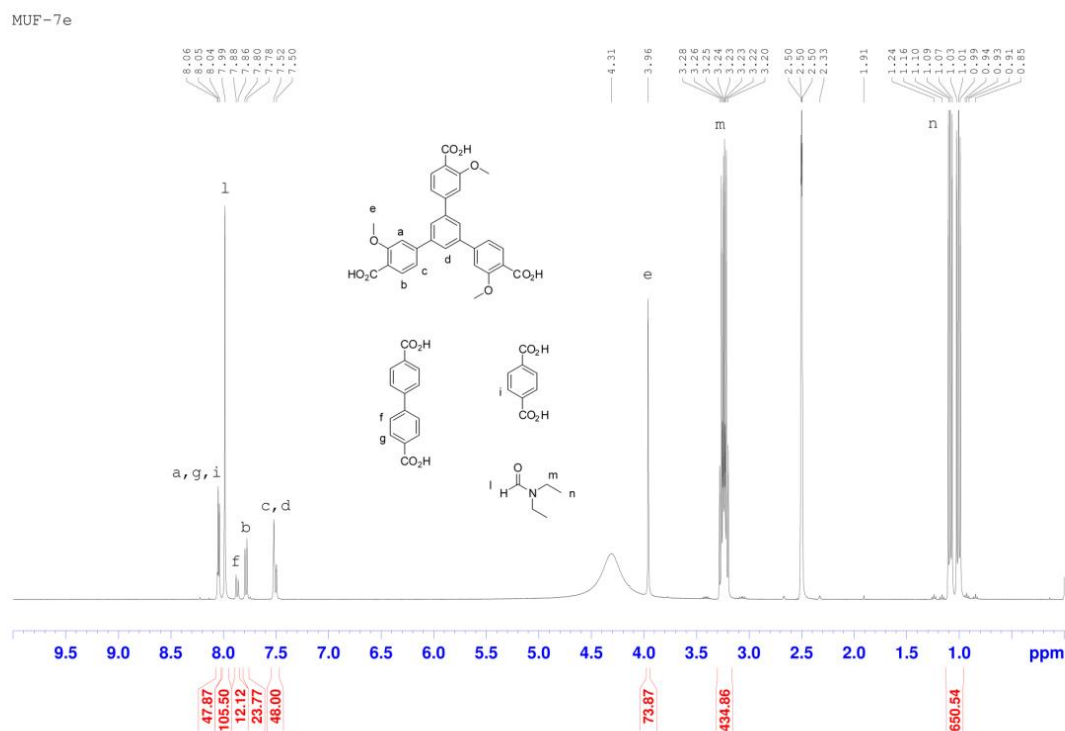
**Figure A.1** <sup>1</sup>H NMR spectra of digested MUF-7b (with occluded DEF solvent molecules) showing the integrals that match with the formula [Zn<sub>4</sub>O(bt<sub>3</sub>)(bcc)<sub>1/2</sub>(bdc)<sub>1/2</sub>].



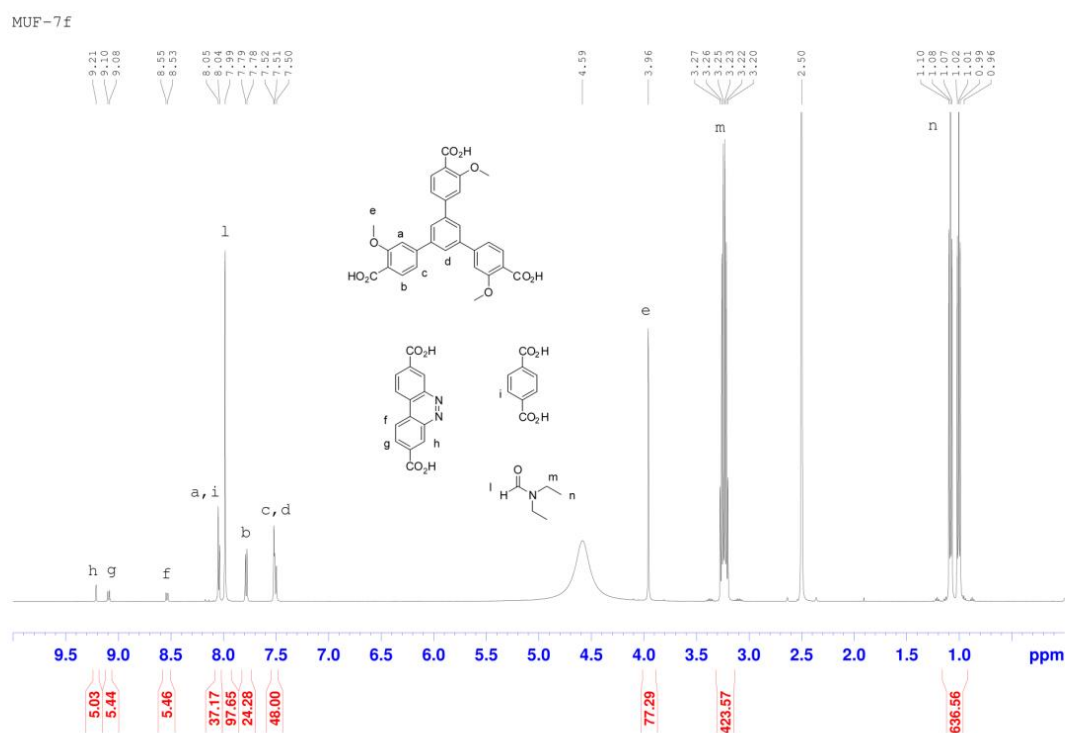
**Figure A.2**  $^1\text{H}$  NMR spectra of digested MUF-7c (with occluded DEF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{btb})_4/3(\text{bpdc})_{1/2}(\text{ndc})_{1/2}]$ .



**Figure A.3**  $^1\text{H}$  NMR spectra of digested MUF-7d (with occluded DEF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{btb})_4/3(\text{bcc})_{1/2}(\text{ndc})_{1/2}]$ .

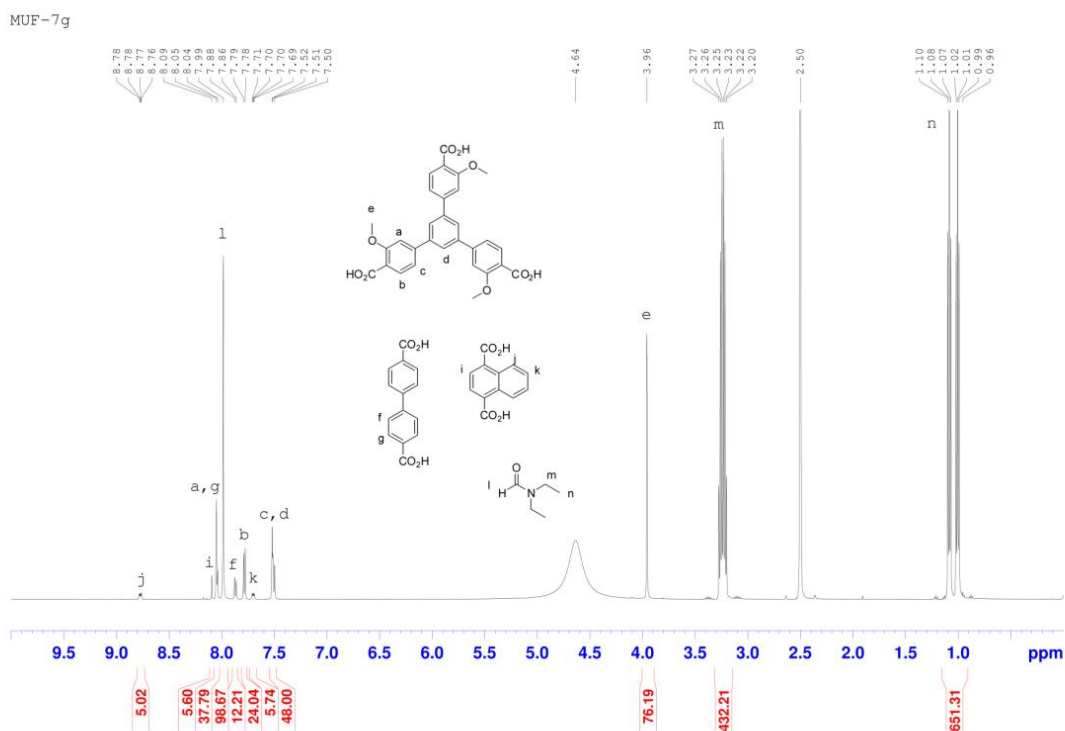


**Figure A.4**  $^1\text{H}$  NMR spectra of digested MUF-7e (with occluded DEF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{btb-OMe})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$ .

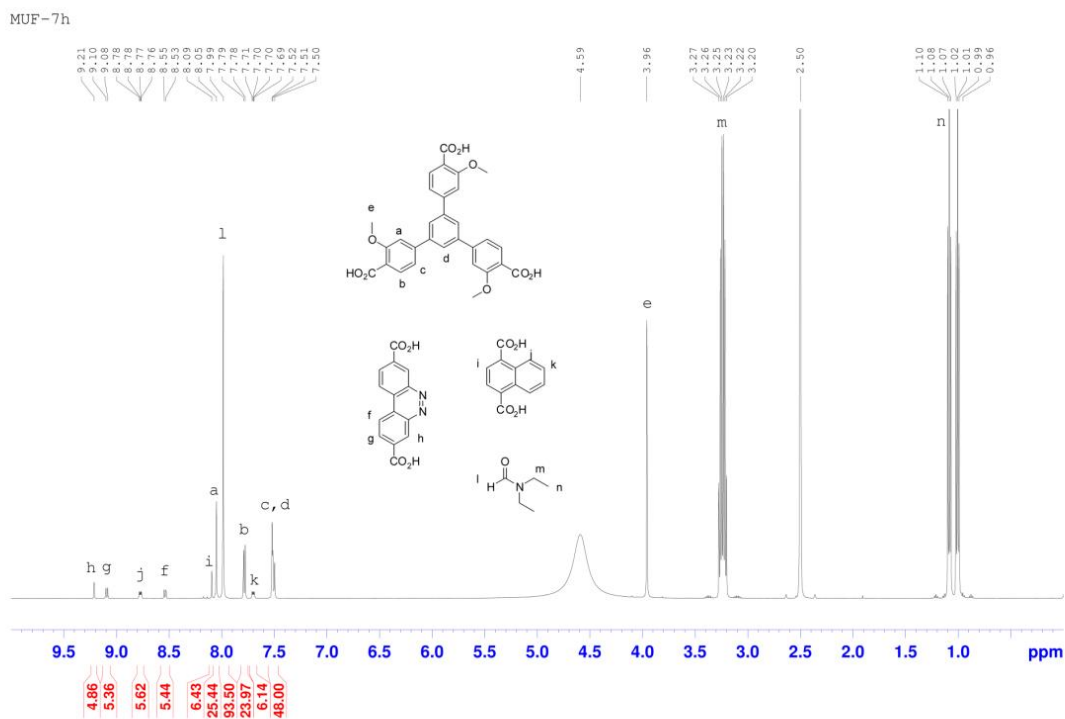


**Figure A.5**  $^1\text{H}$  NMR spectra of digested MUF-7f (with occluded DEF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{btb-OMe})_{4/3}(\text{bcc})_{1/2}(\text{bdc})_{1/2}]$ .





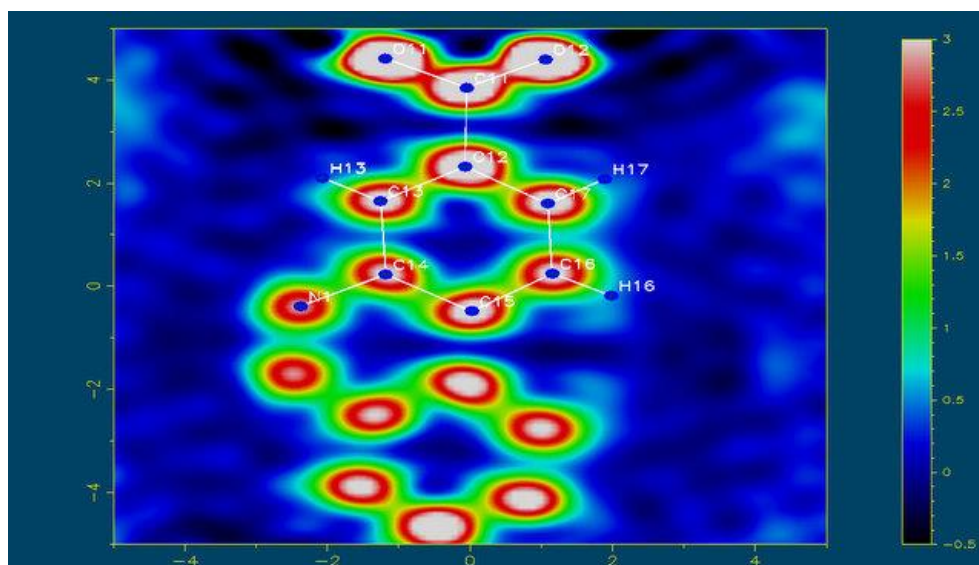
**Figure A.6**  $^1\text{H}$  NMR spectra of digested MUF-7g (with occluded DEF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{btb-OMe})_{4/3}(\text{bpdc})_{1/2}(\text{ndc})_{1/2}]$ .



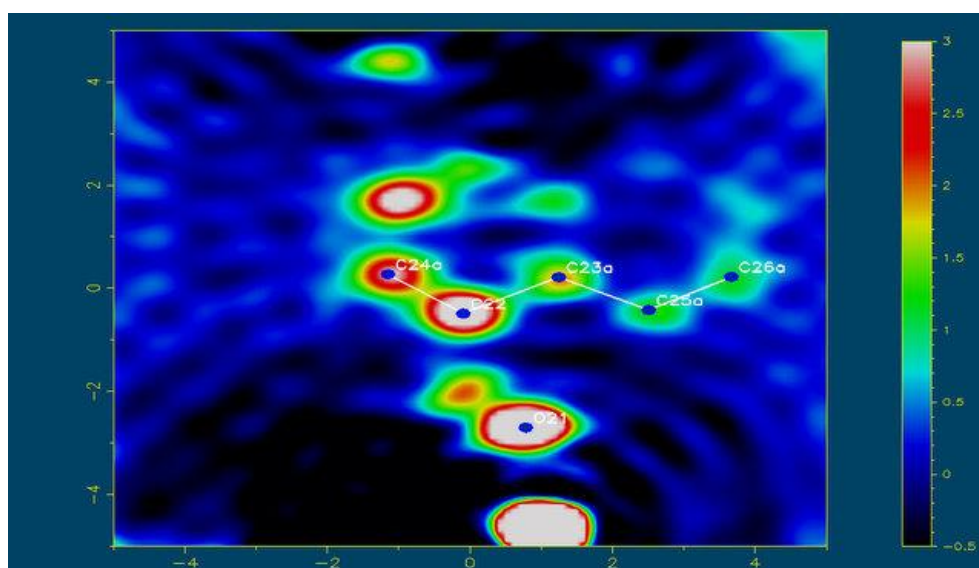
**Figure A.7**  $^1\text{H}$  NMR spectra of digested MUF-7h (with occluded DEF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{btb-OMe})_{4/3}(\text{bcc})_{1/2}(\text{ndc})_{1/2}]$ .

#### 4. Electron density maps from MUF-7h single crystal X-ray diffraction data

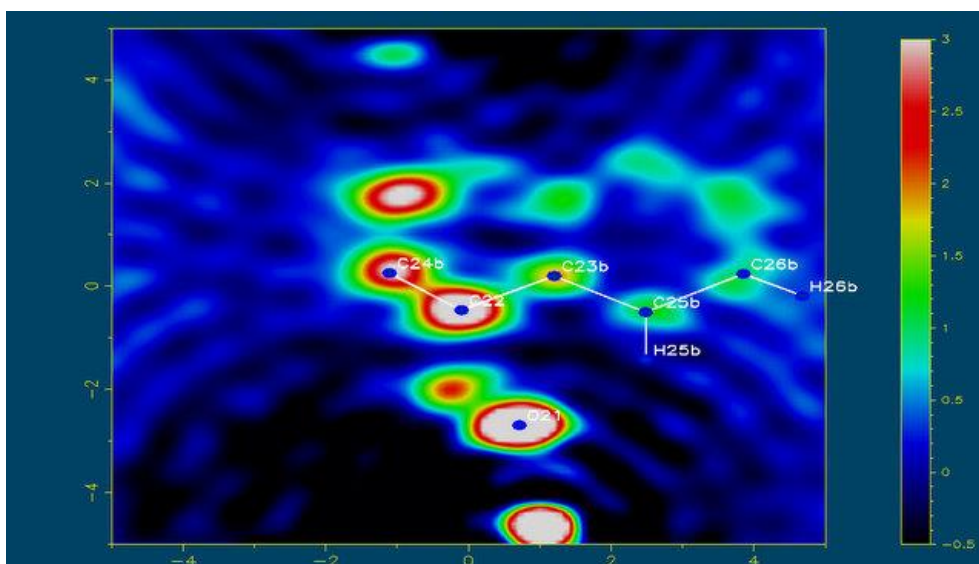
Electron density maps were generated from observed reflections using WinGX v1.80. [3]



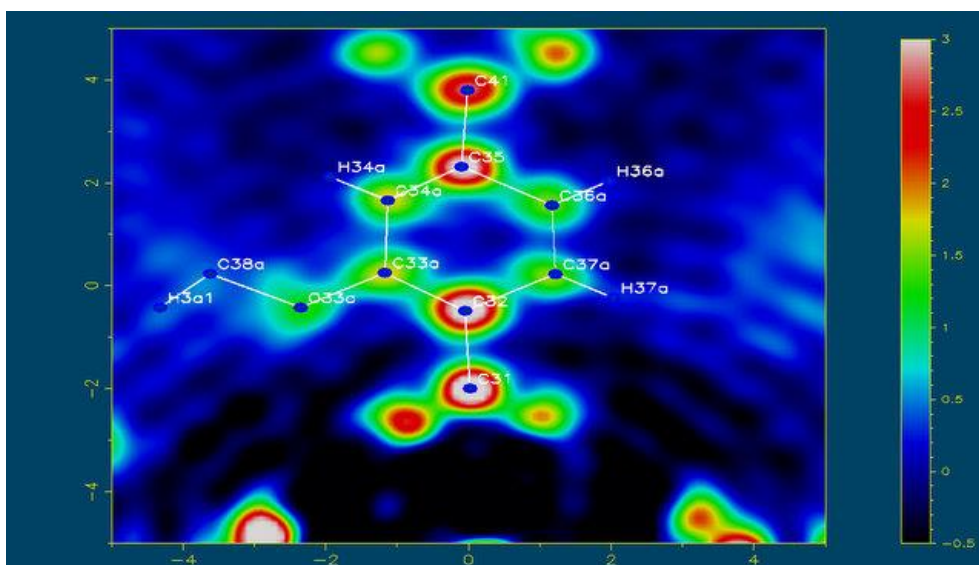
**Figure A.8** Calculated electron density map around the bcc ligand of MUF-7h showing that the pyridazine ring is confined exclusively to one location.



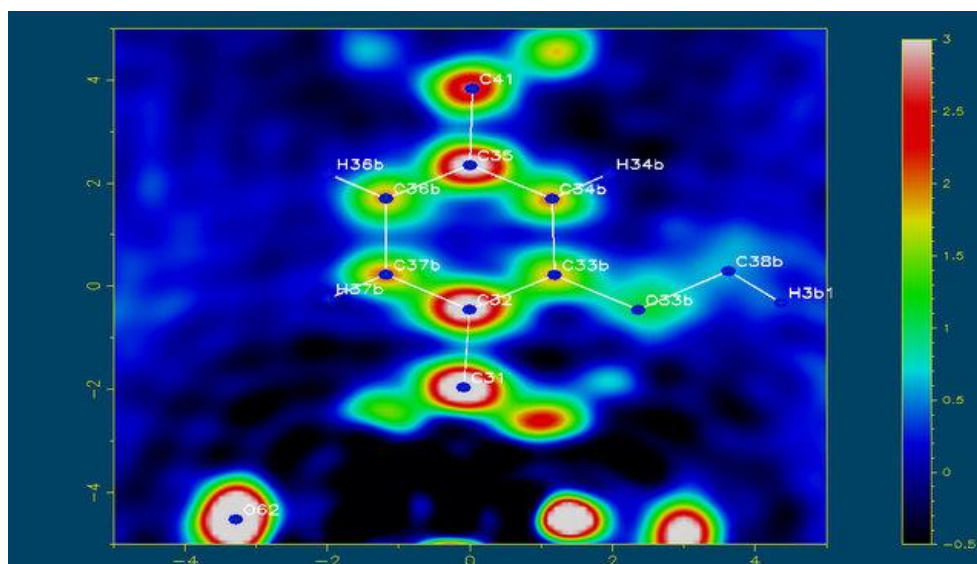
**Figure A.9** Calculated electron density map around conformation A of the ndc ligand of MUF-7h showing that the naphthyl ring is confined exclusively to one location.



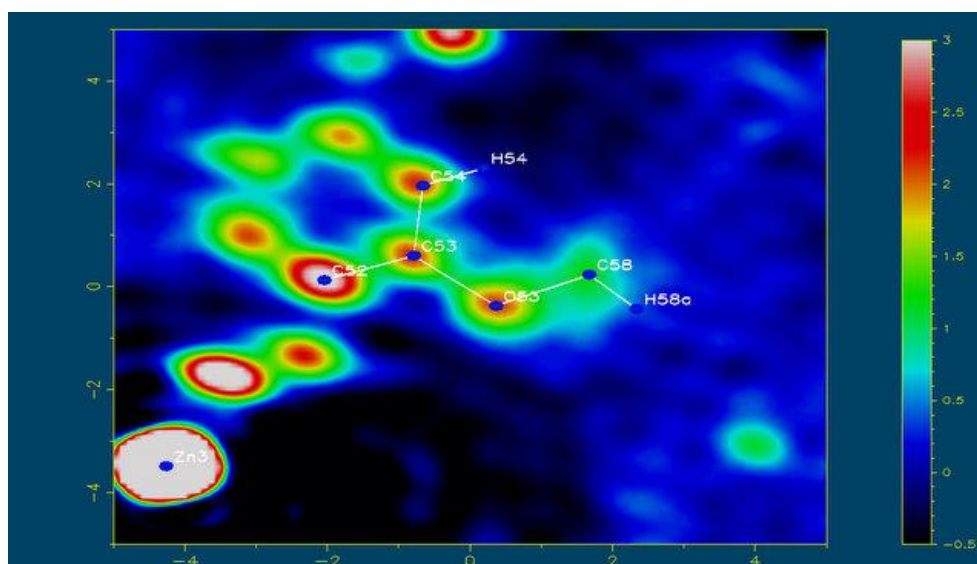
**Figure A.10** Calculated electron density map around conformation B of the ndc ligand of MUF-7h showing that the naphthyl ring is confined exclusively to one location.



**Figure A.11** Calculated electron density map around conformation A of the C32-C37 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.

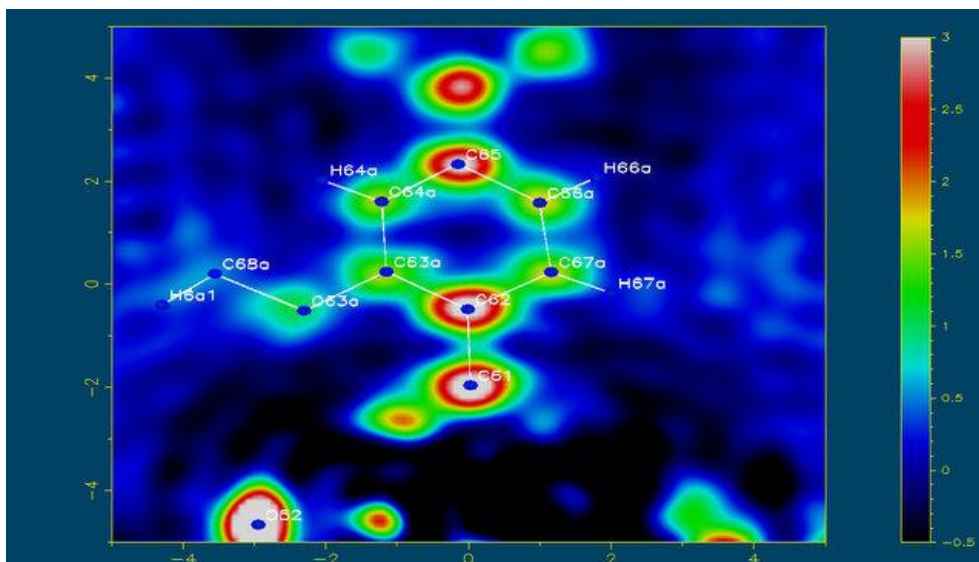


**Figure A.12** Calculated electron density map around conformation B of the C32-C37 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.

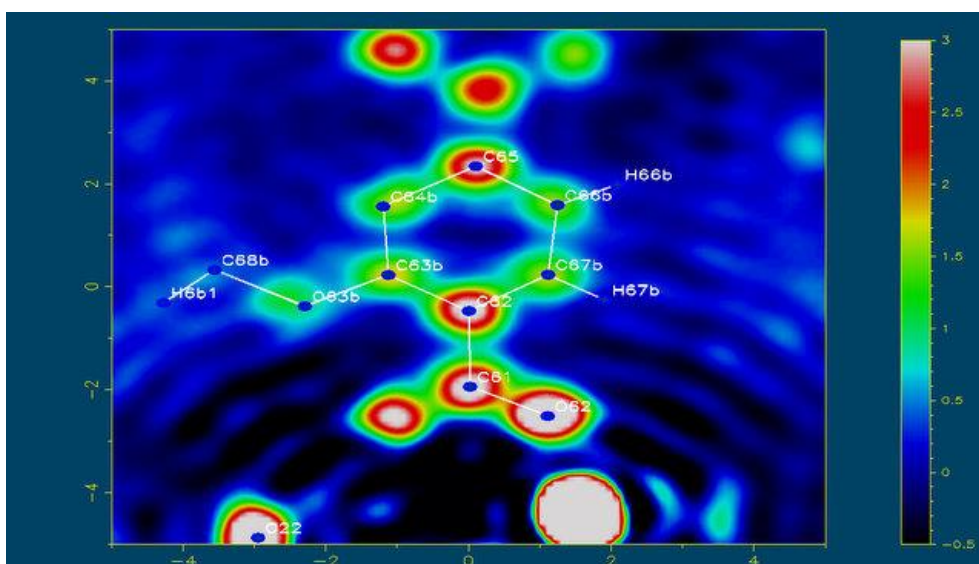


**Figure A.13** Calculated electron density map around the C52-C57 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.

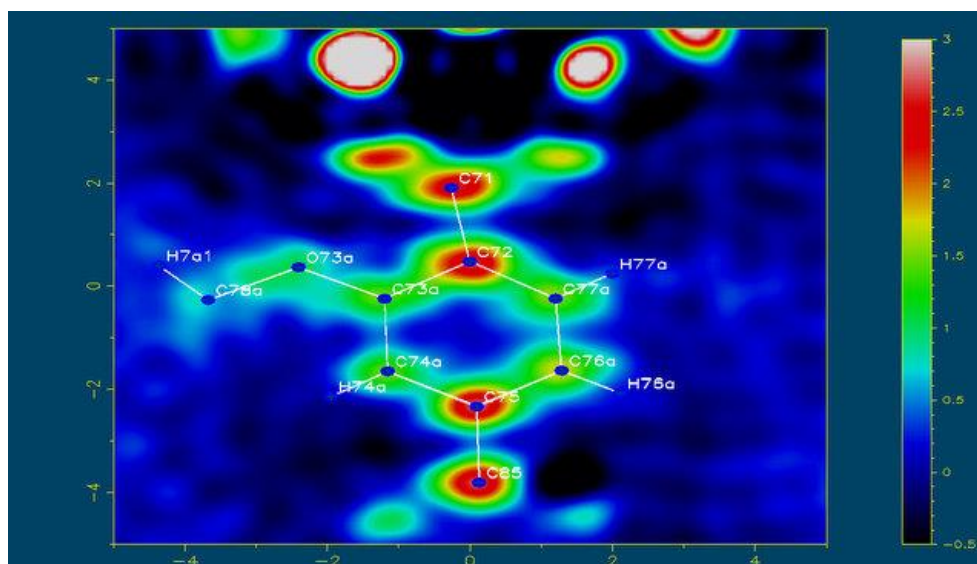




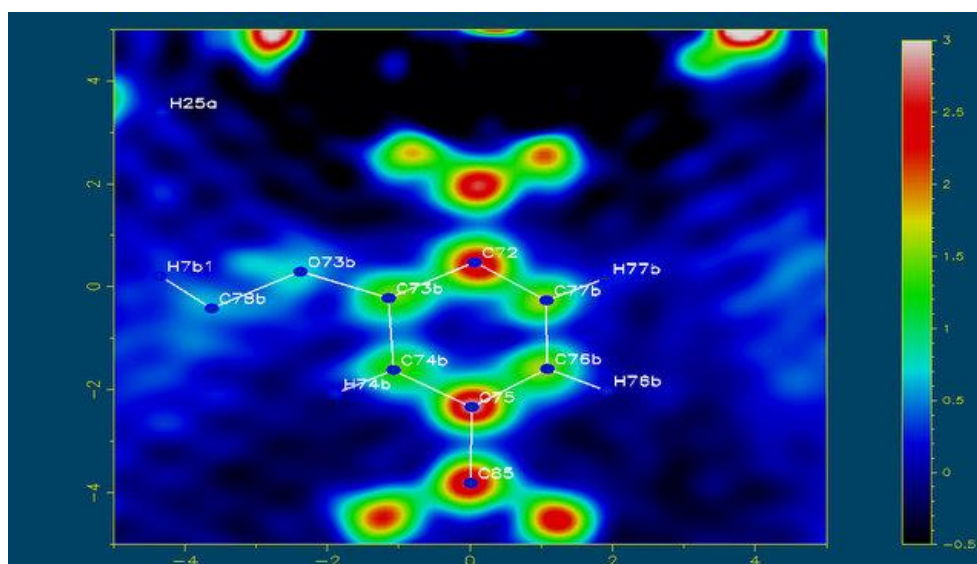
**Figure A.14** Calculated electron density map around conformation A of the C62-C67 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.



**Figure A.15** Calculated electron density map around conformation B of the C62-C67 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.



**Figure A.16** Calculated electron density map around conformation A of the C72-C77 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.



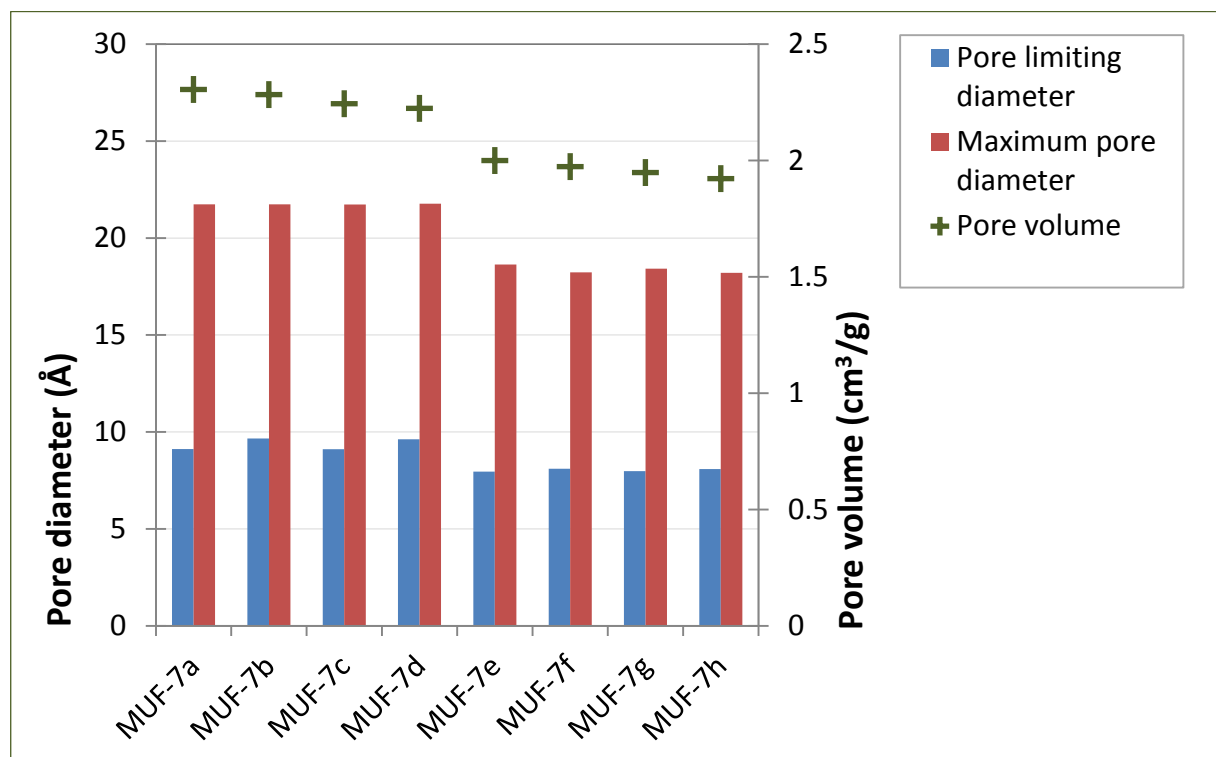
**Figure A.17** Calculated electron density map around conformation B of the C72-C77 phenyl ring of the btb ligand of MUF-7h showing that the methoxy group is confined exclusively to one location.

## 5. Computational details

### Pore diameter and volume calculations

The pore limiting diameters and maximum pore diameters of MUF-7a-h were calculated using Poreblazer v3.0.2.<sup>[4]</sup> on the basis of coordinates obtained from X-ray crystallography. A cubelet size of 0.2 Å was employed. The total pore volumes of these materials that are accessible to helium were calculated by a method detailed in the literature.<sup>[5]</sup>

The free pore diameters of MUF-7a-d, which correspond to the size of a sphere that can freely propagate through a continuous pore, fall in the range 9.1 – 9.6 Å (Figure A.18). On the other hand, the incursion of the methoxy substituents of the btb-OMe ligand into the apertures between the dodecahedral and tetrahedral pores of MUF-7e-h reduces their free pore diameters to around 8.0 Å. The maximum pore diameter of MUF7a-h is the diameter of the major dodecahedral pore of the frameworks. This takes on a fairly uniform of ~21.5 Å for MUF7a-d but drops to ~18 Å for MUF-7e-h due to the presence of the btb-OMe methoxy substituents. The calculated pore volumes are slightly larger than the experimentally-determined values reported in Table 1 due to the smaller size of helium compared to N<sub>2</sub>. Pore volumes steadily decrease across the series MUF-7a – MUF-7h due to increasing bulkiness of the ligands (Figure A.18).



**Figure A.18** Calculated pore limiting diameters and maximum pore diameters of MUF-7a-h as well as the total pore volumes accessible to helium.

## Geometry optimization calculations

Geometry optimization calculations were performed using Gaussian 09.<sup>[6]</sup> Calculations were carried out by using density functional theory (DFT), with Becke's three-parameter exchange functional (B3)<sup>[7]</sup> in combination with the correlation functional of Lee, Yang and Parr (LYP).<sup>[8]</sup> The 6-31(G) basis set was used for all geometry optimization calculations.

**Table A.1** Atomic coordinates for optimized structure of btb.

| Atom | x         | y         | z         | Atom | x         | y         | z         |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| C    | -1.092407 | 0.908323  | 0.019099  | C    | -5.619010 | 4.667205  | 0.139918  |
| C    | -1.308595 | -0.483537 | 0.025536  | C    | -1.233680 | -7.200288 | -0.000740 |
| C    | -0.239573 | -1.400266 | 0.000687  | C    | 6.851869  | 2.532661  | -0.138775 |
| C    | 1.073626  | -0.891685 | -0.024616 | H    | -2.323438 | -0.859332 | 0.099255  |
| C    | 1.333009  | 0.492780  | -0.020217 | H    | 1.905662  | -1.583779 | -0.097360 |
| C    | 0.235950  | 1.375630  | -0.001379 | H    | 0.419020  | 2.444778  | -0.002560 |
| C    | -2.239678 | 1.861497  | 0.053058  | H    | -1.252320 | 3.320816  | 1.304294  |
| C    | -2.160194 | 3.084120  | 0.754880  | H    | -3.530924 | 0.653248  | -1.188343 |
| C    | -3.448262 | 1.575848  | -0.618927 | H    | -3.189468 | 4.913305  | 1.323306  |
| C    | -3.237260 | 3.974712  | 0.780439  | H    | -5.451961 | 2.264403  | -1.108940 |
| C    | -4.521659 | 2.470597  | -0.589366 | H    | 1.215202  | -3.362656 | 1.230590  |
| C    | -4.435389 | 3.684552  | 0.109637  | H    | -2.264845 | -2.765578 | -1.228902 |
| C    | -0.491576 | -2.870437 | 0.000817  | H    | 0.778782  | -5.832847 | 1.200996  |
| C    | 0.367981  | -3.762332 | 0.678514  | H    | -2.675890 | -5.240313 | -1.200292 |
| C    | -1.599094 | -3.424880 | -0.677150 | H    | 2.288637  | 2.707885  | -1.314970 |
| C    | 0.129082  | -5.139519 | 0.676444  | H    | 3.545290  | -0.552962 | 1.196486  |
| C    | -1.832408 | -4.802999 | -0.675669 | H    | 4.645034  | 3.566183  | -1.332798 |
| C    | -0.973696 | -5.683770 | 0.000077  | H    | 5.892930  | 0.327995  | 1.118398  |
| C    | 2.732077  | 1.009825  | -0.054203 | O    | -6.666486 | 4.309794  | -0.513057 |
| C    | 3.065079  | 2.185779  | -0.761188 | O    | -5.440535 | 5.745853  | 0.815179  |
| C    | 3.775424  | 0.341890  | 0.623277  | O    | -2.264314 | -7.596146 | -0.658327 |
| C    | 4.376948  | 2.667715  | -0.786127 | O    | -0.393956 | -7.917674 | 0.656135  |
| C    | 5.085225  | 0.828999  | 0.594414  | O    | 7.719341  | 1.851090  | 0.520257  |
| C    | 5.408947  | 1.999206  | -0.109553 | O    | 7.043683  | 3.605722  | -0.819248 |



**Table A.2** Atomic coordinates for optimized structure of btb-OMe.

| Atom | x         | y         | z         | Atom | x         | y         | z         |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| C    | 1.344135  | -0.420679 | -0.224623 | H    | 0.531747  | -2.418180 | -0.189670 |
| C    | 0.300311  | -1.360731 | -0.122050 | H    | -2.359030 | 0.738429  | 0.165737  |
| C    | -1.045340 | -0.964132 | 0.001455  | H    | 1.804067  | 1.682371  | -0.302423 |
| C    | -1.335264 | 0.413964  | 0.013847  | H    | 3.366556  | 0.734017  | -1.690816 |
| C    | -0.322090 | 1.385460  | -0.100526 | H    | 2.519896  | -2.574612 | 0.904916  |
| C    | 1.011068  | 0.947496  | -0.215955 | H    | 5.732741  | -0.069705 | -1.869399 |
| C    | 2.763451  | -0.858872 | -0.359597 | H    | -3.555787 | -0.820764 | -0.990702 |
| C    | 3.690201  | -0.144027 | -1.139103 | H    | -0.987931 | -3.393251 | 1.285556  |
| C    | 3.221434  | -2.022115 | 0.292002  | H    | -2.864719 | -5.046787 | 1.449666  |
| C    | 5.012773  | -0.583881 | -1.241641 | H    | 1.113627  | 3.399877  | 0.996778  |
| C    | 4.554339  | -2.448829 | 0.184624  | H    | -2.506202 | 2.651892  | -1.178542 |
| C    | 5.497955  | -1.721740 | -0.578827 | H    | -2.996422 | 5.109767  | -1.119988 |
| C    | -2.131124 | -1.979631 | 0.117269  | H    | 4.594707  | -5.261051 | 1.930491  |
| C    | -3.399926 | -1.746458 | -0.450679 | H    | 3.629305  | -3.838678 | 2.418678  |
| C    | -1.939218 | -3.193757 | 0.800198  | H    | 3.194919  | -4.744578 | 0.943206  |
| C    | -4.433698 | -2.691358 | -0.355118 | H    | -5.267375 | -1.054376 | -2.445697 |
| C    | -2.979141 | -4.122451 | 0.893542  | H    | -6.960538 | -1.206082 | -1.893562 |
| C    | -4.241517 | -3.923687 | 0.313318  | H    | -5.768713 | -0.315461 | -0.900181 |
| C    | -0.655689 | 2.838925  | -0.078754 | H    | 2.658432  | 5.066298  | 0.958365  |
| C    | 0.211209  | 3.770978  | 0.526764  | H    | 2.542266  | 6.461646  | 2.071979  |
| C    | -1.832366 | 3.334213  | -0.668016 | H    | 1.851487  | 4.881084  | 2.539526  |
| C    | -0.088683 | 5.142184  | 0.556825  | O    | 4.988301  | -3.626666 | 0.810332  |
| C    | -2.114737 | 4.702400  | -0.636815 | O    | -5.700131 | -2.432245 | -0.899081 |
| C    | -1.280490 | 5.645170  | -0.016467 | O    | 0.797804  | 6.062367  | 1.134920  |
| C    | 4.033887  | -4.399142 | 1.563998  | O    | 7.586506  | -2.669072 | 0.211606  |
| C    | -5.918817 | -1.175182 | -1.568676 | O    | 7.535314  | -1.582220 | -1.818268 |
| C    | 2.027758  | 5.572244  | 1.703214  | O    | -5.068460 | -5.847313 | 1.463196  |
| C    | 7.007260  | -2.042728 | -0.738100 | O    | -6.168816 | -5.186533 | -0.448793 |
| C    | -5.271007 | -5.076354 | 0.451890  | O    | -2.576601 | 7.413181  | -0.965552 |
| C    | -1.764627 | 7.119336  | -0.010358 | O    | -1.369581 | 7.873308  | 0.940920  |

**Table A.3** Atomic coordinates for optimized structure of L2.

| Atom | x         | y         | z         | Atom | x         | y         | z         |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| C    | -0.368286 | -1.370515 | -0.027966 | H    | -1.988464 | -2.710121 | -1.774480 |
| C    | 0.980084  | -0.956573 | 0.043942  | H    | 0.398718  | -3.293442 | 1.751802  |
| C    | 1.377359  | 0.396979  | 0.006438  | H    | -2.586666 | -5.150376 | -1.743199 |
| C    | 0.349588  | 1.366484  | -0.048608 | H    | -0.267005 | -5.715851 | 1.772688  |
| C    | -1.015280 | 1.019851  | -0.092499 | H    | 2.652845  | 1.994739  | -1.793644 |
| C    | -1.340120 | -0.350817 | -0.115234 | H    | 3.359919  | -0.340419 | 1.744802  |
| C    | -0.746263 | -2.819140 | -0.014156 | H    | 5.087313  | 2.621684  | -1.836733 |
| C    | -1.594228 | -3.363557 | -1.003243 | H    | 5.776034  | 0.352315  | 1.689756  |
| C    | -0.267119 | -3.687564 | 0.991004  | H    | -2.732287 | 1.701911  | -2.111178 |
| C    | -1.939893 | -4.718463 | -0.986208 | H    | -1.737819 | 2.659171  | 1.957780  |
| C    | -0.625044 | -5.038968 | 1.003590  | H    | -4.533257 | 3.458218  | -2.056519 |
| C    | -1.464154 | -5.578055 | 0.016097  | H    | -3.555097 | 4.398243  | 1.969995  |
| C    | 2.825353  | 0.779470  | -0.019410 | H    | 3.214768  | -3.231133 | -0.852174 |
| C    | 3.332604  | 1.618533  | -1.035531 | H    | 1.640042  | -2.968892 | -1.661133 |
| C    | 3.726094  | 0.320204  | 0.965737  | H    | 2.913226  | -1.699045 | -1.727632 |
| C    | 4.683355  | 1.980048  | -1.060186 | H    | 1.488764  | 4.384480  | 0.739443  |
| C    | 5.073369  | 0.693361  | 0.936257  | H    | 0.485258  | 3.408196  | 1.851279  |
| C    | 5.574797  | 1.527495  | -0.075038 | H    | 2.131020  | 2.849684  | 1.390495  |
| C    | -2.090316 | 2.065291  | -0.087442 | H    | -4.425665 | -1.206609 | 0.734883  |
| C    | -2.898313 | 2.295720  | -1.216866 | H    | -2.945869 | -1.736249 | 1.590028  |
| C    | -2.338682 | 2.834391  | 1.067660  | H    | -3.432262 | -0.003178 | 1.610486  |
| C    | -3.904688 | 3.266865  | -1.192739 | O    | 1.984796  | -1.941846 | 0.153147  |
| C    | -3.349686 | 3.801028  | 1.087246  | O    | 0.668362  | 2.735525  | -0.139380 |
| C    | -4.147145 | 4.034213  | -0.042800 | O    | -2.698588 | -0.707199 | -0.239706 |
| C    | 2.460862  | -2.488771 | -1.117380 | O    | -1.372133 | -7.765421 | 0.999641  |
| C    | 1.232028  | 3.370604  | 1.049730  | O    | -2.613372 | -7.464475 | -0.922918 |
| C    | -3.410779 | -0.925119 | 1.018838  | O    | 7.787078  | 1.478227  | 0.853616  |
| C    | -1.850763 | -7.067559 | 0.032318  | O    | 7.419332  | 2.692937  | -1.074504 |
| C    | 7.058577  | 1.935415  | -0.101241 | O    | -5.407528 | 5.732965  | 1.091153  |
| C    | -5.260768 | 5.096347  | -0.015998 | O    | -5.932795 | 5.239722  | -1.101626 |

**Table A.4** Atomic coordinates for optimized structure of bcc.

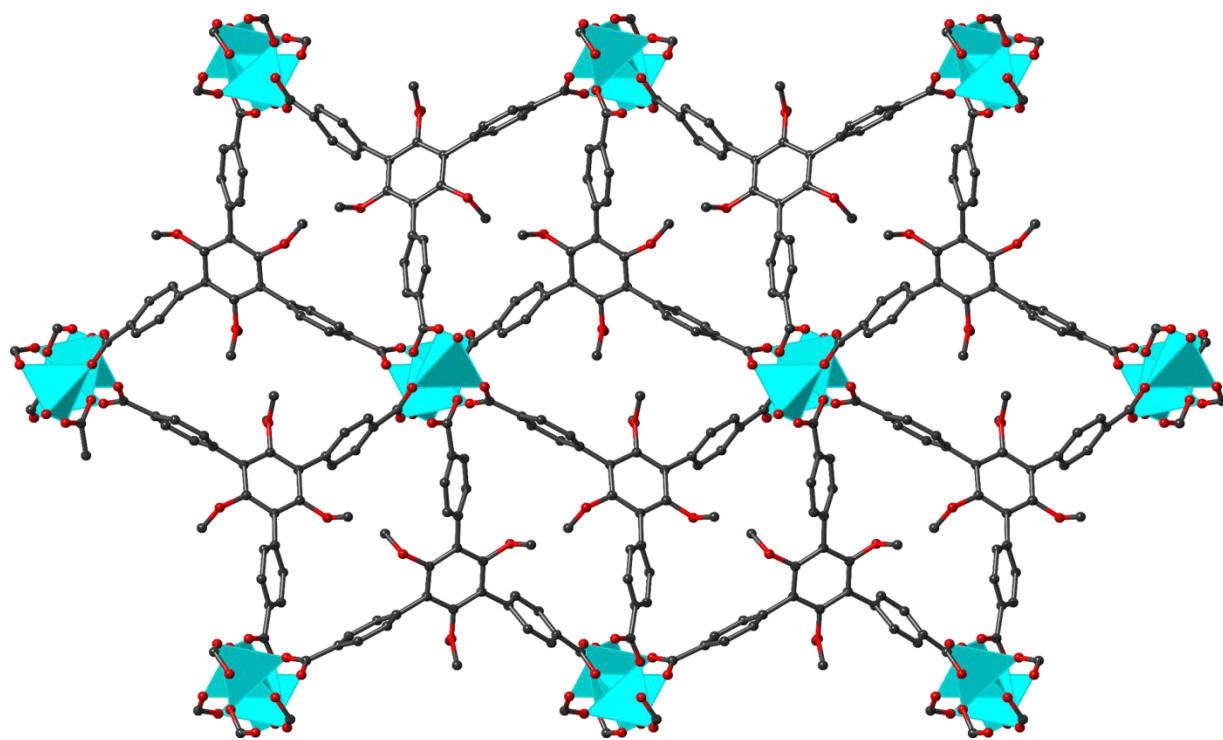
| Atom | x         | y         | z         | Atom | x         | y         | z         |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| C    | -3.567327 | -0.169397 | -0.000012 | C    | -5.105222 | -0.096228 | -0.000030 |
| C    | -2.781469 | 0.974521  | 0.000091  | H    | 3.259058  | 1.947204  | 0.000153  |
| C    | -1.369365 | 0.886583  | 0.000069  | H    | -3.259058 | 1.947204  | 0.000205  |
| C    | -0.722858 | -0.384375 | -0.000026 | H    | -1.077882 | -2.525579 | -0.000203 |
| C    | -1.540573 | -1.542640 | -0.000115 | H    | -3.571148 | -2.301883 | -0.000248 |
| C    | -2.922318 | -1.431934 | -0.000124 | H    | 3.571148  | -2.301883 | -0.000195 |
| C    | 0.722857  | -0.384375 | -0.000031 | H    | 1.077882  | -2.525579 | -0.000203 |
| C    | 1.369365  | 0.886583  | 0.000075  | N    | 0.653916  | 2.094930  | 0.000181  |
| C    | 2.781468  | 0.974521  | 0.000075  | N    | -0.653916 | 2.094930  | 0.000152  |
| C    | 3.567327  | -0.169398 | -0.000022 | O    | 5.713202  | -1.229358 | -0.000102 |
| C    | 2.922318  | -1.431934 | -0.000122 | O    | 5.616003  | 1.078929  | 0.000118  |
| C    | 1.540573  | -1.542640 | -0.000126 | O    | -5.713201 | -1.229358 | 0.000860  |
| C    | 5.105222  | -0.096228 | -0.000024 | O    | -5.616003 | 1.078928  | -0.000865 |

**Table A.5** Atomic coordinates for optimized structure of ndc

| Atom | x         | y         | z         | Atom | x         | y         | z         |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| C    | 0.709229  | 3.010553  | 0.000080  | C    | 2.997283  | -0.851035 | 0.000589  |
| C    | 1.405480  | 1.818173  | 0.000237  | H    | 1.252889  | 3.955964  | 0.000170  |
| C    | 0.727562  | 0.557382  | 0.000126  | H    | 2.489780  | 1.764896  | 0.000446  |
| C    | -0.727550 | 0.557421  | -0.000157 | H    | -2.489688 | 1.765047  | -0.000561 |
| C    | -1.405386 | 1.818258  | -0.000319 | H    | -1.252657 | 3.956040  | -0.000333 |
| C    | -0.709056 | 3.010595  | -0.000201 | H    | -1.266026 | -2.788716 | -0.000167 |
| C    | 1.452640  | -0.690392 | 0.000290  | H    | 1.265894  | -2.788773 | 0.000304  |
| C    | -1.452685 | -0.690329 | -0.000266 | O    | -3.430759 | -2.061204 | -0.000754 |
| C    | -0.704779 | -1.859816 | -0.000096 | O    | -3.737424 | 0.205990  | -0.000536 |
| C    | 0.704687  | -1.859849 | 0.000171  | O    | 3.430725  | -2.061277 | 0.000656  |
| C    | -2.997324 | -0.850957 | -0.000550 | O    | 3.737357  | 0.205931  | 0.000724  |

**Single crystal x-ray structure of Zn<sub>2</sub>L2(OH)****Table A.6** Crystallography data of Zn<sub>2</sub>L2(OH)

| MOF   | Zn <sub>2</sub> L2(OH)  |
|---|---|
| Formula   | C <sub>30</sub> H <sub>22</sub> O <sub>10</sub> Zn <sub>2</sub> |
| Formula weight  | 673.21  |
| Crystal size (mm)                                     | 0.59 × 0.30 × 0.15  |
| Temperature (K)                                       | 293(2)  |
| Wavelength (Å)  | 1.54178   |
| Crystal system  | Orthorhombic  |
| Space group   | <i>Fdd2</i>   |
| Unit cell lengths (Å)                                 | a = 30.7235(6)<br>b = 51.984(4)<br>c = 12.0200(2)               |
| Unit cell volume (Å <sup>3</sup> )                    | 19197.4(15)   |
| Z   | 16  |
| D <sub>calc</sub> (g cm <sup>-3</sup> )               | 0.932   |
| μ (mm <sup>-1</sup> )                                 | 1.528   |
| F(000)  | 5472  |
| Reflns coll./unique, R <sub>int</sub>                 | 34161 / 8592, 0.0331  |
| Data range  | 6.7° < θ < 72 ° or 6.6 Å > d > 0.85 Å                           |
| Index ranges  | -37 ≤ h ≤ 37, -63 ≤ k ≤ 39, -14 ≤ l ≤ 14                        |
| Completeness  | 99.6%   |
| T <sub>min</sub> , T <sub>max</sub>                   | 0.78, 1.00  |
| R indices for data with I > 2σ(I)                     | R <sub>1</sub> = 0.0468; wR <sub>2</sub> = 0.1531               |
| R indices for all data                                | R <sub>1</sub> = 0.0484; wR <sub>2</sub> = 0.1580               |
| Largest difference peak and hole (e Å <sup>-3</sup> ) | 0.80 / -0.34  |



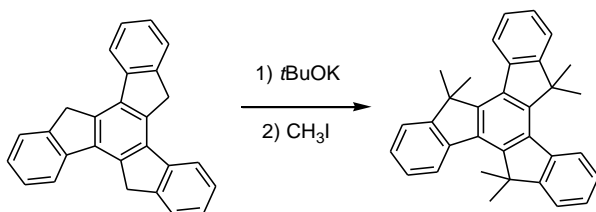
**Figure A.19** A view of the single crystal x-ray structure of  $\text{Zn}_2\text{L}_2(\text{OH})$ .

## Appendix B for Chapter 4

### Experimental Details and Supporting Information for Chapter 4

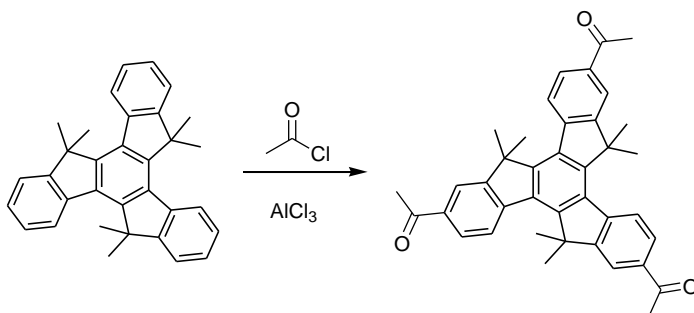
#### 1. Ligand synthesis and characterization

##### 5,5',10,10',15,15'-Hexamethyltruxene



Truxene (2.00 g, 5.84 mmol) and  $t\text{BuOK}$  (13.11 g, 117 mmol) were mixed in dry THF (150 mL) and the resulting crimson coloured solution cooled on ice with stirring under an argon atmosphere.  $\text{CH}_3\text{I}$  (5.45 mL, 87.6 mmol) was added dropwise, and the green reaction mixture was refluxed with stirring overnight under an argon atmosphere. After cooling to room temperature, the green suspension was filtered and washed with THF. The solvent was removed from the collected filtrate under vacuum, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (100 mL) and washed with brine (50 mL). The organic extract was then evaporated under vacuum and the residue was purified by flash chromatography (dry load, silica) eluting with a gradient from hexane to 15%  $\text{CH}_2\text{Cl}_2$ /hexane to afford a white crystalline solid. Yield: 1.71 g (69 %).  $^1\text{H}$  NMR spectrum agrees with literature data<sup>[9]</sup>: (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.90 (s, 18H), 7.38-7.45 (m, 6H), 7.56 (d,  $J = 7.5$  Hz, 3H), 8.32 (d,  $J = 7.5$  Hz, 3H) ppm.

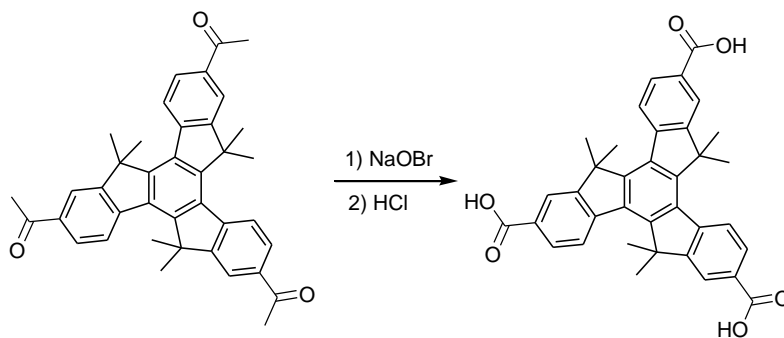
##### 2,7,12-Triacetyl-5,5',10,10',15,15'-hexamethyltruxene



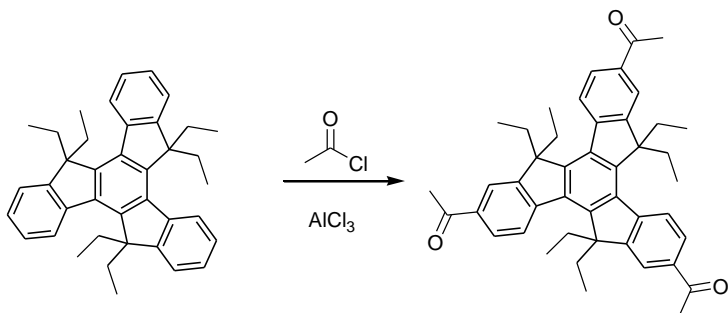
Anhydrous  $\text{AlCl}_3$  (4.78 g, 359 mmol) was weighed into a 2-necked round bottom flask and acetyl chloride (25.5 mL, 359 mmol) was added with stirring. After cooling on ice

under argon, a solution of 5,5',10,10',15,15'-hexamethyltruxene (1.69 g, 3.96 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (40 mL) was added drop-wise, and the resulting green/yellow suspension was stirred for 10 min on ice, and then 2.5 hours at room temperature. The reaction was quenched by pouring onto an ice/water slurry, and the solid was collected by filtration and washed with  $\text{H}_2\text{O}$ . The material was further dried under high vacuum to afford a white solid (Yield: 2.17 g, 99 %) which was then recrystallized from  $\text{CHCl}_3/\text{CH}_3\text{OH}$  to afford pure material as white crystals.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.93 (s, 18H), 2.73 (s, 9H), 8.07 (dd,  $J = 8.3$  Hz, 1.7 Hz, 3H), 8.17 (d,  $J = 1.6$  Hz, 3H), 8.39 (d,  $J = 8.3$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.88, 26.81, 47.19, 122.01, 125.46, 127.56, 135.08, 135.73, 140.94, 151.48, 157.59, 197.81 ppm. ES-MS (positive mode):  $m/z = 553.09$  ( $[\text{C}_{39}\text{H}_{37}\text{O}_3]^+$ , calcd. 553.27).

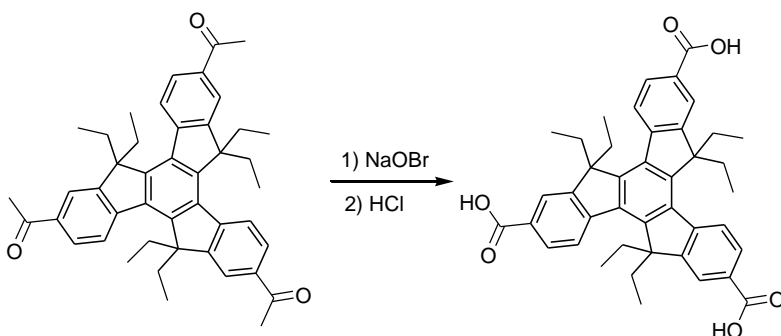
### 5,5',10,10',15,15'-Hexamethyltruxene-2,7,12-tricarboxylic acid ( $\text{H}_3\text{hmtt}$ )<sup>[9]</sup>



$\text{NaOH}$  (3.48 g, 86.9 mmol) was dissolved in  $\text{H}_2\text{O}$  (60 mL) and cooled on ice with stirring before  $\text{Br}_2$  (1.59 mL, 30.9 mmol) was added and stirring continued for a further 20 min. This  $\text{NaOBr}$  solution was then slowly added to a suspension of 2,7,12-triacetyl-5,5',10,10',15,15'-hexamethyltruxene (1.26 g, 2.29 mmol) in 1,4-dioxane (90 mL). The yellow solution was stirred at  $60^\circ\text{C}$  for 2 hours. After cooling to room temperature, the reaction was quenched by the addition of aq.  $\text{NH}_2\text{OH HCl}$  (2.62 g, 50 mL  $\text{H}_2\text{O}$ ) and the 1,4-dioxane was removed under vacuum. The resulting yellow suspension was cooled on ice and acidified with 3 M  $\text{HCl}$  and stirred overnight at room temperature. The solid was collected by filtration and washed with  $\text{H}_2\text{O}$  and dried under high vacuum to produce the crude product as a pale yellow powder (Yield: 1.22 g, 95%), which was then recrystallized from  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  to afford pure material as a white powder.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ): 1.86 (s, 18H), 2.73 (s, 9H), 8.11 (dd,  $J = 7.3$  Hz, 1.6 Hz, 3H), 8.25 (d,  $J = 1.6$  Hz, 3H), 8.40 (d,  $J = 8.3$  Hz, 3H) ppm.

**2,7,12-Triacetyl-5,5',10,10',15,15'-hexaethyltruxene**

5,5',10,10',15,15'-Hexaethyltruxene<sup>[10]</sup> (102 mg, 0.200 mmol) was dissolved in dichloromethane (1.5 mL). This solution was gradually added to a  $\text{AlCl}_3$ /acetyl chloride solution at 0 °C which was prepared by dissolving  $\text{AlCl}_3$  (224 mg, 1.68 mmol) in acetyl chloride (1.2 mL) at 0 °C under argon atmosphere. The red reaction mixture was stirred for 10 min at 0 °C, and further stirred at room temperature for 25 minutes. The mixture was poured gradually on ice while it was stirred. The resulting mixture was then stirred at room temperature for 15 minutes. The aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$ , which was washed with saturated aq.  $\text{NaHCO}_3$  and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed from the filtrate under reduced pressure to afford the crude product as a yellow solid. Yield: 121 mg (96 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.20 (t,  $J = 7.3$  Hz, 18H), 2.23-2.32 (m, 6H), 2.72 (s, 9H), 2.97-3.06 (m, 6H), 8.05 (dd,  $J = 8.3$  Hz, 1.5 Hz, 3H), 8.10 (d,  $J = 1.3$  Hz, 3H), 8.45 (d,  $J = 8.3$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54, 26.84, 29.40, 57.29, 121.69, 124.45, 127.67, 135.50, 138.36, 144.76, 147.38, 153.08, 197.96 ppm.

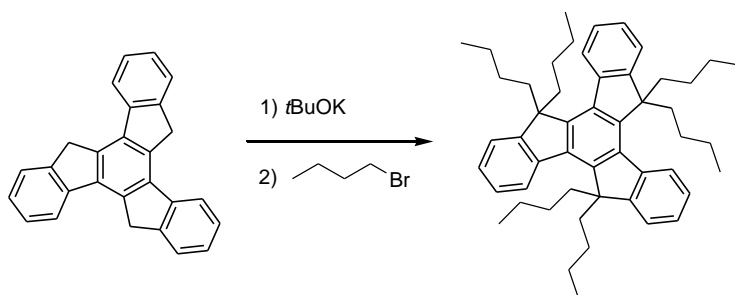
**5,5',10,10',15,15'-Hexaethyltruxene-2,7,12-tricarboxylic acid ( $\text{H}_3\text{hett}$ )<sup>[10]</sup>**

$\text{NaOH}$  (5.95 g, 149 mmol) was dissolved in  $\text{H}_2\text{O}$  (640 mL) and cooled on ice with stirring before  $\text{Br}_2$  (2.70 mL, 105 mmol) was added and stirring continued for a further 20 min. This  $\text{NaOBr}$  solution was then slowly added to a suspension of 2,7,12-triacetyl-5,5',10,10',15,15'-hexaethyltruxene (2.77 g, 4.35 mmol) in 1,4-dioxane (80 mL). The yellow solution was stirred at 60 °C for 2 hours. After cooling to room temperature, the reaction was quenched by addition of aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (325 mg in 3.25 mL  $\text{H}_2\text{O}$ ) and the 1,4-



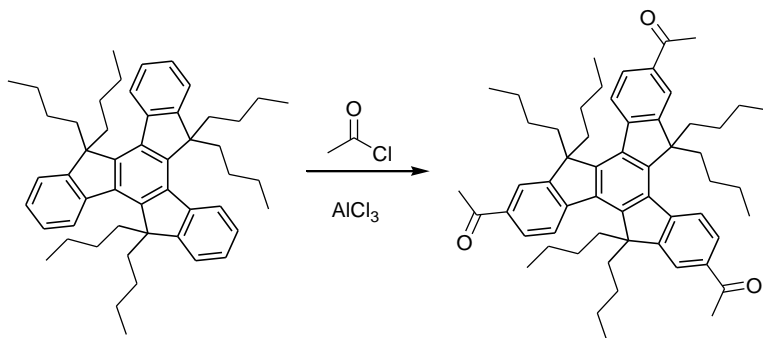
dioxane was removed under vacuum. The resulting yellow suspension was cooled on ice and acidified with 3 M HCl and stirred overnight at room temperature. The solid was collected by filtration and washed with H<sub>2</sub>O and dried under high vacuum to afford the product as a pale yellow powder. Yield: 2.79 g (100 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 0.11 (t, *J* = 7.2 Hz, 18H), 2.21-2.26 (m, 6H), 2.97-3.02 (m, 6H), 8.06 (d, *J* = 8.1 Hz, 3H), 8.09 (s, 3H), 8.41 (d, *J* = 8.3 Hz, 3H) ppm.

### 5,5',10,10',15,15'-Hexabutyltruxene



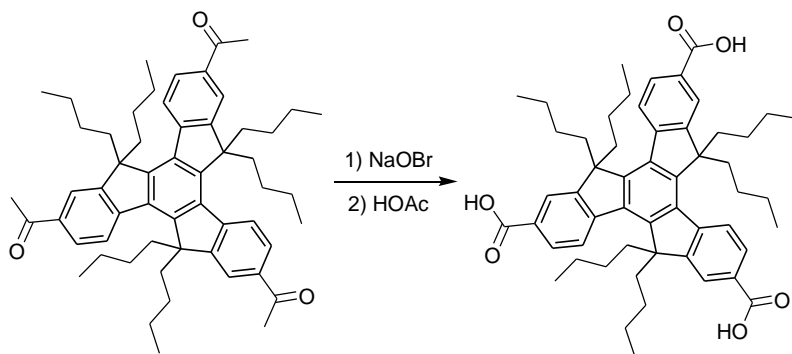
To a suspension of truxene (995 mg, 2.91 mmol) and *t*BuOK (11 g, 98 mmol) in dry THF (100 mL) under argon atmosphere, distilled 1-bromobutane (4.70 mL, 43.5 mmol) was added at room temperature. The resulting suspension was refluxed for 17 hours. The solvent was evaporated after the reaction and the residue was partitioned between dichloromethane and brine. The organic layer was dried over MgSO<sub>4</sub> and then filtered through Celite. The filtrate was concentrated *in vacuo* then chromatographed on a long silica column, eluting with hexane, to afford the product as a crystalline yellow solid. Yield: 1.72 g (87 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.42 – 0.54 (m, 30H), 0.89 (m, 12H), 2.10 (m, 6H), 2.98 (m, 6H), 7.38 (m, 6H), 7.46 (dd, *J* = 6.7 Hz, 1.4 Hz, 3H), 8.38 (d, *J* = 7.4 Hz, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.96, 23.00, 26.65, 36.78, 55.70, 122.41, 124.85, 126.10, 126.49, 138.58, 140.50, 145.09, 153.81 ppm.

### 2,7,12-Triacetyl-5,5',10,10',15,15'-hexabutyltruxene



5,5',10,10',15,15'-Hexabutyltruxene (1.95 g, 2.87 mmol) was dissolved in dichloromethane (15 mL). This solution was gradually added to the  $\text{AlCl}_3$ /acetyl chloride solution at 0 °C which was prepared by dissolving  $\text{AlCl}_3$  (3.69 g, 27.7 mmol) in acetyl chloride (17.5 mL) at 0 °C under argon atmosphere. The red reaction mixture was stirred for 10 min at 0 °C, and further stirred at room temperature for 2 hours. The mixture was poured gradually on ice (~150 mL) while it was stirred. The resulting mixture was stirred at room temperature overnight. The aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  and washed with a saturated  $\text{Na}_2\text{CO}_3$  aqueous solution. The resulting solution was dried over  $\text{MgSO}_4$  and filtered. The solvent was removed under reduced pressure to afford the product as a yellow solid. Yield: 2.31 g (100%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.41 – 0.54 (m, 30H), 0.89 (m, 12H), 2.22 (m, 6H), 2.73 (s, 9H) 2.94 (m, 6H), 8.05 (d,  $J$  = 8.1 Hz, 3H), 8.10 (s, 3H), 8.48 (d,  $J$  = 8.4 Hz, 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.86, 22.84, 26.64, 26.93, 36.62, 56.19, 121.80, 124.62, 127.66, 135.58, 138.03, 144.57, 148.52, 153.96, 198.10 ppm.

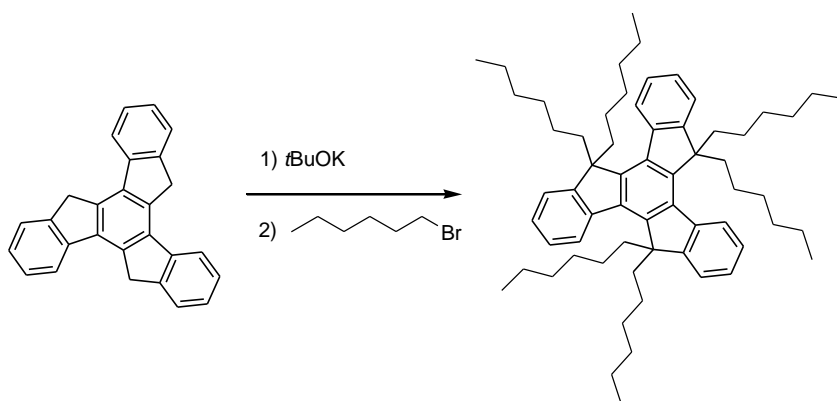
#### 5,5',10,10',15,15'-Hexabutyltruxene-2,7,12-tricarboxylic acid ( $\text{H}_3\text{hbtt}$ )



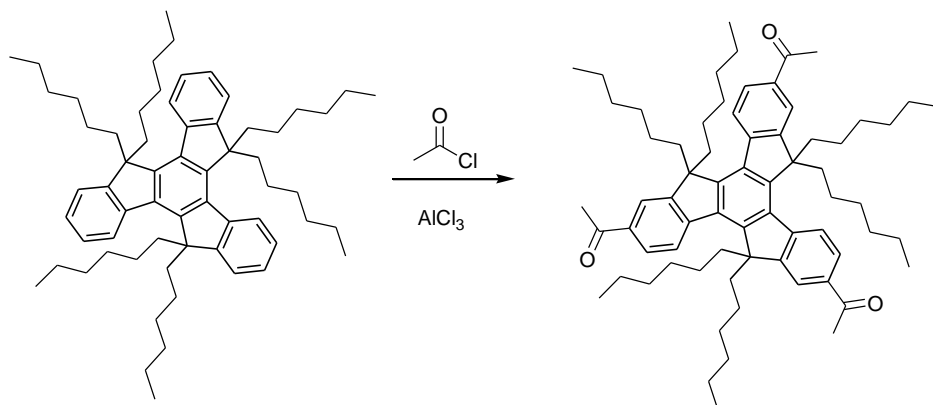
2,7,12-Triacetyl-5,5',10,10',15,15'-hexabutyltruxene (2.31 g, 2.87 mmol) was suspended and stirred in 1,4-dioxane (60 mL).  $\text{NaOH}$  (4.35 g, 109 mmol) was dissolved in 30 mL of water. At 0 °C, bromine (2.00 mL) was added to the  $\text{NaOH}$  solution, which was stirred for 15 minutes. The  $\text{NaOBr}$  solution was added to the above suspension at room temperature. The resulting mixture was then stirred at 60 °C for 2 hours and cooled to room temperature. An aqueous solution of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (2.62 g, 37.7 mmol) was added to the reaction mixture to quench  $\text{NaOBr}$ . Dioxane was removed under reduced pressure and the resulting aqueous suspension was acidified with 3 M  $\text{HCl}$  until  $\text{pH} < 1$ . The resulting solid was filtered, washed with water, and dried under vacuum to afford the product as a yellow solid (Yield: 2.37 g, 100%) which was then recrystallized from glacial acetic acid / water to afford pure material as a crystalline yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.33 – 0.48 (m, 30H), 0.80 (m, 12H), 2.20 (m, 6H), 3.00 (m, 6H), 8.04 (d,  $J$  = 8.3 Hz,

3H), 8.08 (s, 3H), 8.44 (d,  $J = 8.3$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  13.63, 22.15, 26.30, 35.56, 55.49, 123.10, 124.43, 128.25, 129.22, 137.67, 143.36, 147.15, 153.11, 167.41 ppm. ES-MS (positive mode):  $m/z = 811.49$  ( $[\text{C}_{54}\text{H}_{67}\text{O}_6]^+$ , calcd. 811.49). Anal. calcd. for  $[\text{C}_{54}\text{H}_{66}\text{O}_6]$ : C, 79.96; H, 8.20; Found: C, 79.72; H, 8.23.

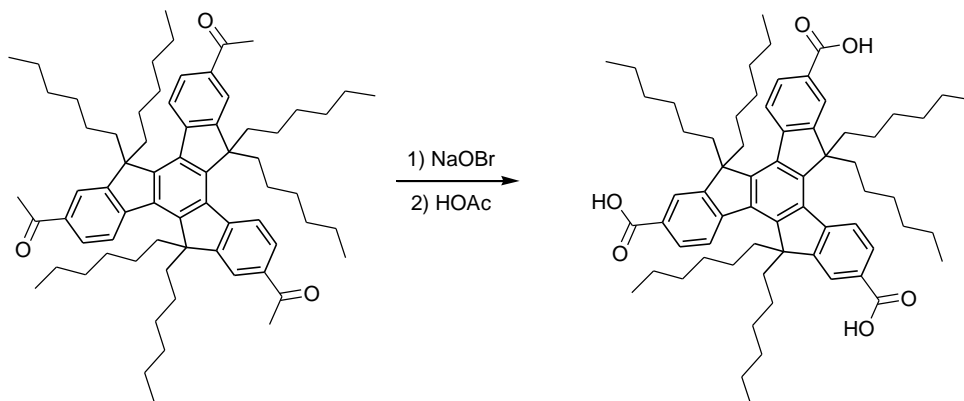
### 5,5',10,10',15,15'-Hexabutyltruxene



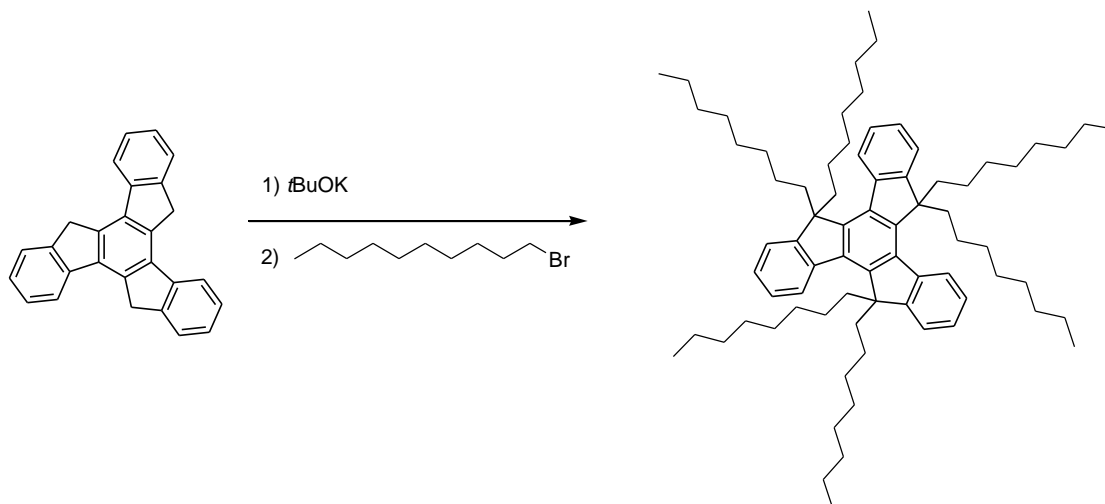
To a suspension of truxene (1.001 mg, 2.92 mmol) and  $t\text{BuOK}$  (11 g, 98 mmol) in dry THF (100 mL) under argon atmosphere, distilled 1-bromohexane (6.1 mL, 43.5 mmol) was added at room temperature. The resulting suspension was refluxed for 17 hours. The solid material in the reaction mixture was removed through filtration and the filtrate was concentrated under reduced pressure. The resulting oil was dissolved in hexane and washed with 0.2 M HCl and then saturated  $\text{NaHCO}_3$ . The organic layer was dried over  $\text{MgSO}_4$  and the filtrate was concentrated under reduced pressure. The resulting oil was heated under high vacuum to afford a solid which was then chromatographed on a long silica column, eluting with hexane, to afford the product as a crystalline yellow solid. Yield: 2.23 g (90 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.49 (m, 12H), 0.59 (m, 18H), 0.79-0.93 (m, 36H), 2.07 (m, 6H), 2.95 (m, 6H), 7.46 (m, 6H), 7.46 (dd,  $J = 7.1$  Hz, 1.2 Hz, 3H), 8.36 (d,  $J = 7.6$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.02, 22.42, 24.03, 29.64, 31.63, 37.10, 55.75, 122.31, 124.77, 126.08, 126.45, 138.51, 140.49, 144.96, 153.79 ppm.

**2,7,12-Triacetyl-5,5',10,10',15,15'-hexahexyltruxene**

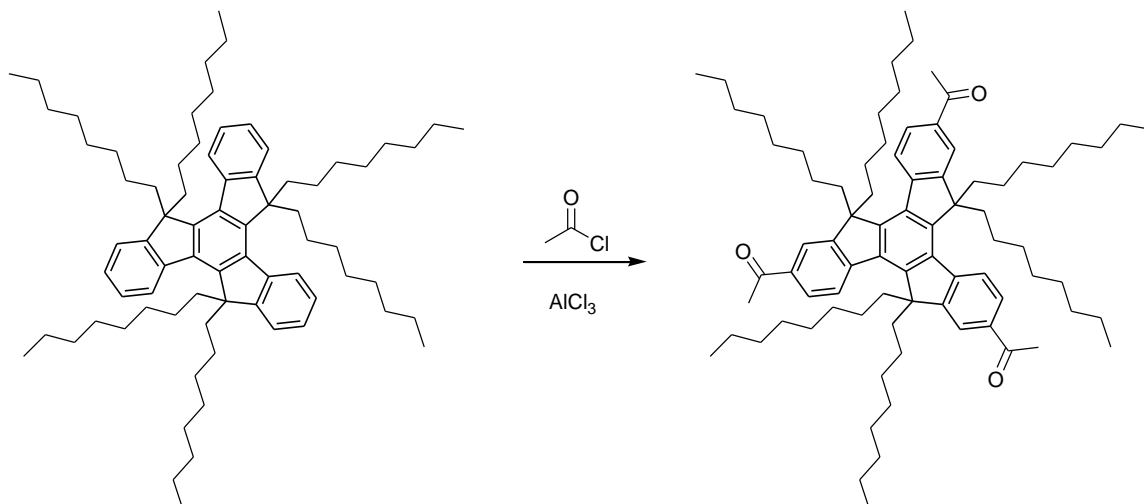
5,5',10,10',15,15'-Hexahexyltruxene (2.21 g, 2.61 mmol) was dissolved in dichloromethane (15 mL). This solution was gradually added to the AlCl<sub>3</sub>/acetyl chloride solution at 0 °C which was prepared by dissolving AlCl<sub>3</sub> (3.2 g, 24.0 mmol) in acetyl chloride (15.0 mL) at 0 °C under argon atmosphere. The red reaction mixture was stirred for 10 min at 0 °C, and further stirred at room temperature for 1.5 hours. The mixture was poured gradually on ice (~150 mL) while it was stirred. The resulting mixture was then stirred at room temperature for 15 minutes. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated NaHCO<sub>3</sub> aqueous solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed from the filtrate under reduced pressure to afford the crude product as a yellow solid which was then recrystallized in EtOH/EtOAc/H<sub>2</sub>O to afford pure material as yellow crystals. Yield: 2.32 g (91 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.45 (m, 12H), 0.58 (m, 18H), 0.78-0.93 (m, 36H), 2.19 (m, 6H), 2.73 (s, 9H), 2.95 (m, 6H), 8.05 (dd, *J* = 8.3 Hz, 1.5 Hz, 3H), 8.10 (d, *J* = 1.4 Hz, 3H), 8.46 (d, *J* = 8.4 Hz, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.84, 22.21, 23.95, 26.86, 29.34, 31.42, 36.82, 56.15, 121.61, 124.44, 127.56, 135.41, 137.84, 144.47, 148.30, 153.84 ppm.

**5,5',10,10',15,15'-Hexahexyltruxene-2,7,12-tricarboxylic acid (H<sub>3</sub>hhtt)**

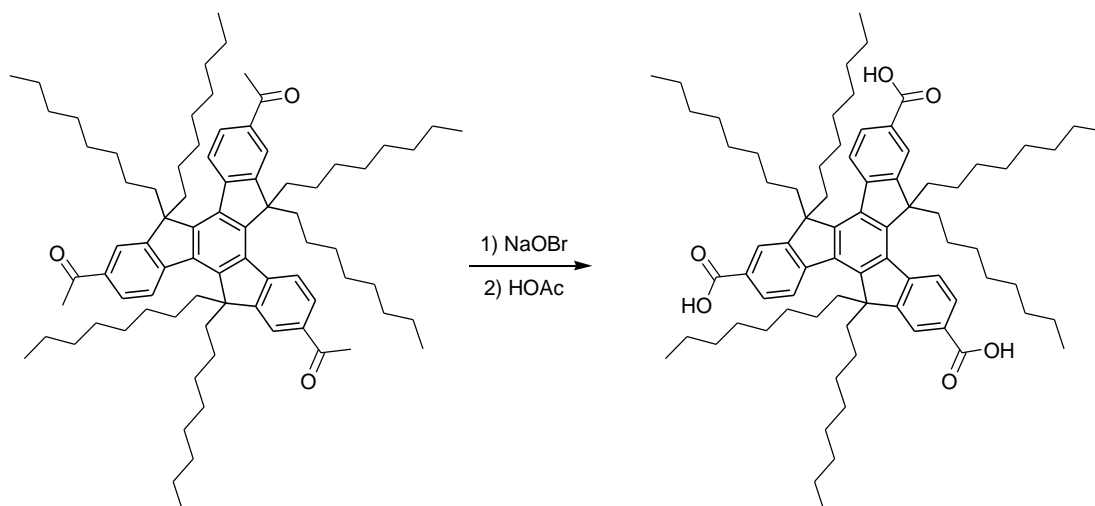
2,7,12-Triacetyl-5,5',10,10',15,15'-hexahexyltruxene (2.32 g, 2.38 mmol) was dissolved in 1,4-dioxane (45 mL). NaOH (5.43 g, 136 mmol) was dissolved in 35 mL of water. At 0 °C, bromine (2.50 mL) was added to the NaOH solution, which was stirred for 15 minutes. The NaOBr solution was added to the above dioxane solution at room temperature. The resulting mixture was then stirred at 60 °C for 2 hours and cooled to room temperature. An aqueous solution of NH<sub>2</sub>OH HCl (5.12 g, 73.7 mmol) was added to the reaction mixture to quench NaOBr. Dioxane was removed under reduced pressure and the resulting aqueous suspension was acidified with 3 M HCl until pH < 1. The resulting solid was filtered, washed with water, and dried under vacuum to afford crude Na<sub>3</sub>hhtt as a pale pink solid (Yield: 2.43 g, 98 %), which was then recrystallized from acetic acid to afford the final product as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 0.37 (m, 12H), 0.50 (t, *J* = 6.6 Hz, 18H), 0.70-0.91 (m, 36H), 2.18 (m, 6H), 2.98 (m, 6H), 8.08 (d, *J* = 8.3 Hz, 3H), 8.11 (s, 3H), 8.48 (d, *J* = 8.3 Hz, 3H), 13.04 (m, br, 3H) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 13.59, 21.49, 23.44, 28.64, 30.89, 35.90, 55.57, 122.99, 124.33, 128.22, 129.19, 137.62, 143.37, 146.97, 153.06, 167.48 ppm. ES-MS (positive mode): *m/z* = 979.68 ([C<sub>66</sub>H<sub>91</sub>O<sub>6</sub>]<sup>+</sup>, calcd. 979.68). Anal. calcd. for [C<sub>66</sub>H<sub>90</sub>O<sub>6</sub>] 0.5 H<sub>2</sub>O: C, 80.20; H, 9.28; Found: C, 80.07; H, 9.38.

**5,5',10,10',15,15'-Hexaoctyltruxene**

To a suspension of truxene (994 mg, 2.90 mmol) and *t*BuOK (10 g, 89 mmol) in dry THF (100 mL) under argon atmosphere, distilled 1-bromooctane (7.50 mL, 43.4 mmol) was added at room temperature. The resulting suspension was refluxed for 16 hours. The solid material in the reaction mixture was removed through filtration and the filtrate was concentrated under reduced pressure. The resulting oil was dissolved in hexane and washed with 0.2 M HCl and then saturated NaHCO<sub>3</sub>. The organic layer was dried over MgSO<sub>4</sub> and the filtrate was concentrated down under reduced pressure. The resulting oil was heated under high vacuum to afford a solid was then chromatographed on a long silica column, eluting with hexane, to afford the product as a crystalline yellow solid. Yield: 2.502 g (85 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.46-0.53 (m, 12H), 0.73 (t, *J* = 7.1 Hz, 18H), 0.82-1.09 (m, 60H), 2.03-2.10 (m, 6H), 2.91-2.98 (m, 6H), 7.33-7.40 (m, 6H), 7.45 (dd, *J* = 6.9 Hz, 1.7 Hz, 3H), 8.35 (d, *J* = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.16, 22.66, 24.11, 29.22, 29.39, 30.00, 31.94, 37.03, 55.71, 76.91, 77.16, 77.41, 122.32, 124.77, 126.08, 126.44, 138.49, 140.50, 144.98, 153.80 ppm.

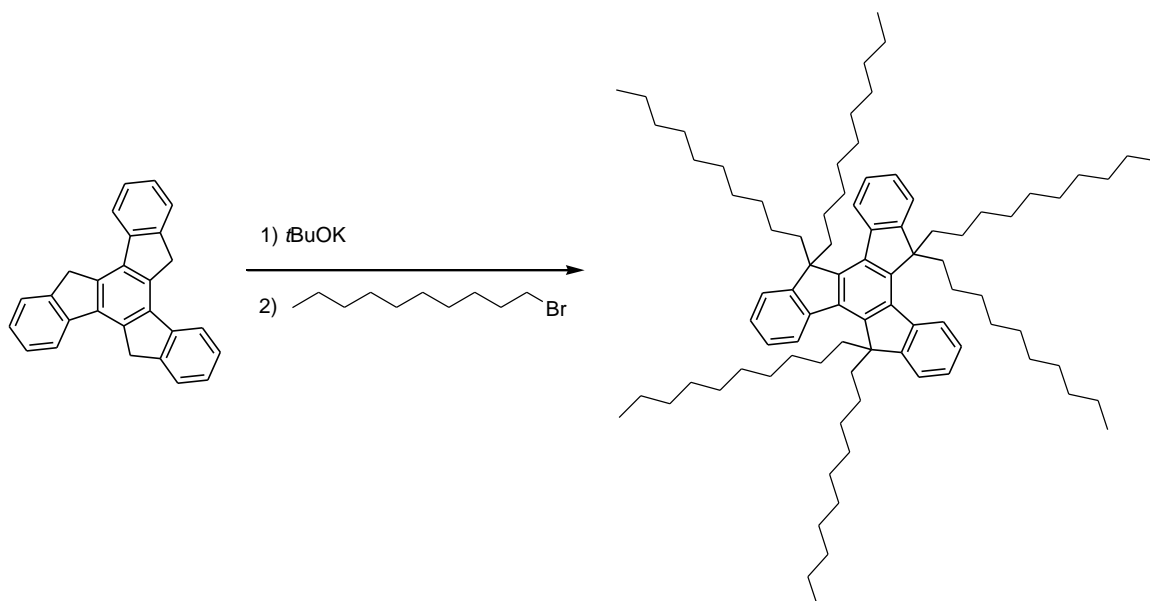
**2,7,12-Triacetyl-5,5',10,10',15,15'-hexaoctyltruxene**

5,5',10,10',15,15'-Hexaoctyltruxene (2.52 g, 2.48 mmol) was dissolved in dichloromethane (15 mL). This solution was gradually added to the AlCl<sub>3</sub>/acetyl chloride solution at 0 °C which was prepared by dissolving AlCl<sub>3</sub> (3.00 g, 22.5 mmol) in acetyl chloride (16.0 mL) at 0 °C under argon atmosphere. The red reaction mixture was stirred for 10 min at 0 °C, and further stirred at room temperature for 2 hours. The mixture was poured gradually on ice (~150 mL) while it was stirred. The resulting mixture was stirred at room temperature overnight. The organic portion was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with NaHCO<sub>3</sub> aqueous solution. The resulting solution was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure to afford the a yellow solid which was then recrystallized from ethanol to afford the product as yellow crystals. Yield: 2.60 g (91 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.45 (m, 12H), 0.70 (t, *J* = 7.0 Hz, 18H), 0.80-1.06 (m, 60H), 2.15-2.22 (m, 6H), 2.73 (s, 9H), 2.90-2.97 (m, 6H), 8.04 (dd, *J* = 8.2 Hz, 1.3 Hz, 3H), 8.09 (s, 3H), 8.46 (d, *J* = 8.4 Hz, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.12, 22.61, 24.14, 26.94, 29.12, 29.30, 29.79, 31.87, 26.87, 56.25, 121.75, 124.56, 127.69, 135.53, 137.96, 144.62, 148.45, 154.00, 198.10 ppm. This compound was further characterised by single crystal X-ray diffraction (Table B.2).

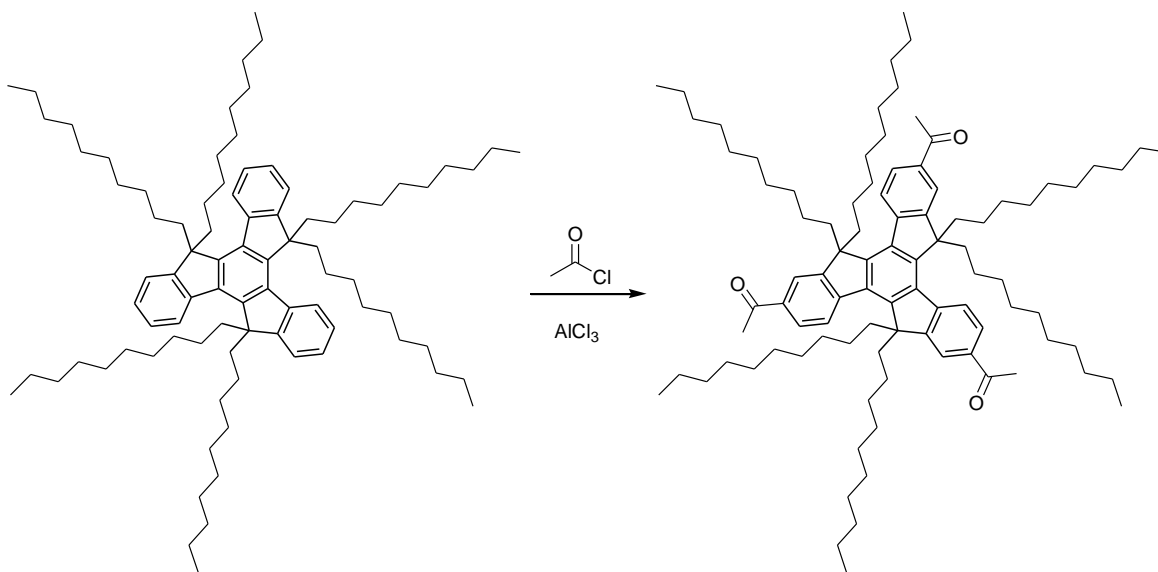
**5,5',10,10',15,15'-Hexaacyltruxene-2,7,12-tricarboxylic acid (H<sub>3</sub>hott)**

2,7,12-Triacetyl-5,5',10,10',15,15'-hexaacyltruxene (2.36 g, 2.06 mmol) was dissolved in 1,4-dioxane (42 mL). NaOH (4.21 g, 105 mmol) was dissolved in 27 mL of water. At 0 °C, bromine (1.95 mL) was added to the NaOH solution, which was stirred for 15 minutes. This NaOBr solution was added to the above dioxane solution at room temperature. The resulting mixture was then stirred at 60 °C for 2 hours and cooled to room temperature. An aqueous solution of NH<sub>2</sub>OH HCl (2.65 g, 38.1 mmol) was added to the reaction mixture to quench NaOBr. Dioxane was removed under reduced pressure and the resulting aqueous suspension was acidified with 3 M HCl until pH < 1. The resulting solid was filtered off, washed with water, and dried under vacuum to afford Na<sub>3</sub>hott as a yellow solid. Yield: 2.27 g (91 %). This sodium salt was refluxed in acetic acid overnight to give H<sub>3</sub>hott. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 40 °C): δ 0.39 (m, 12H), 0.63 (t, *J* = 6.9 Hz, 18H), 0.76-0.96 (m, 60H), 2.17 (m, 6H), 2.98 (m, 6H), 8.07 (d, *J* = 8.2 Hz, 3H), 8.10 (s, 3H), 8.48 (d, *J* = 8.2 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 40 °C): δ 13.53, 21.66, 23.27, 28.03, 28.37, 28.77, 31.02, 35.76, 55.42, 122.87, 124.11, 128.02, 129.16, 137.54, 143.25, 146.83, 152.93, 167.27 ppm. Anal. calcd. for [C<sub>78</sub>H<sub>114</sub>O<sub>6</sub>] 0.5 H<sub>2</sub>O: C, 80.99; H, 10.02; Found: C, 81.02; H, 10.16.

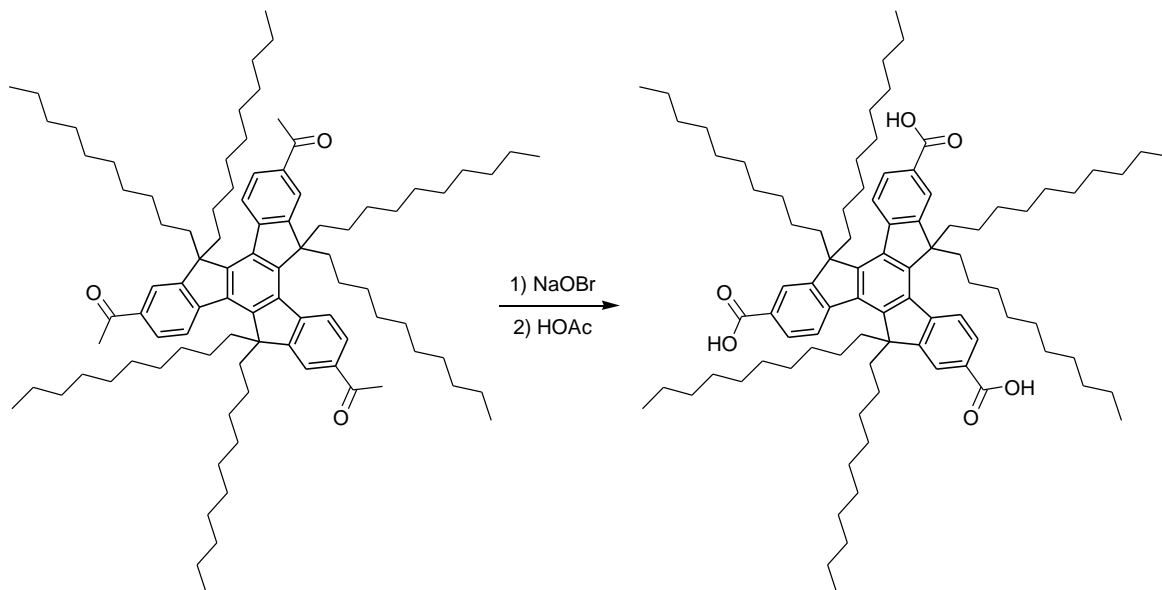


**5,5',10,10',15,15'-Hexadecyltruxene**

To a suspension of truxene (1.000 g, 2.92 mmol) and *t*BuOK (12.320 g, 109.8 mmol) in dry THF (100 mL) under an argon atmosphere, distilled 1-bromodecane (9.00 mL, 43.4 mmol) was added at room temperature. The resulting suspension was refluxed for 3.5 hours. The solvent was evaporated *in vacuo* after the reaction and the residue was taken up with dichloromethane and filtered through celite. The filtrate was washed with brine and the organic layer was concentrated under reduced pressure. The residue solvent was further removed by vacuum distillation. The resulting solid was chromatographed on a long silica column, eluting with hexane, to afford the crude product as a green solid without further purification (the green impurity was not NMR active). Yield: 2.51 g (73 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.50 (m, 12H), 0.80-1.21 (m, 102H), 2.07 (m, 6H), 2.95 (m, 6H), 7.37 (m, 6H), 7.46 (dd,  $J = 7.2$  Hz, 1.1 Hz, 3H), 8.36 (d,  $J = 7.6$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.21, 22.78, 24.10, 29.41, 29.45, 29.58, 29.73, 29.98, 32.05, 37.01, 55.71, 122.32, 124.77, 126.08, 126.46, 138.49, 140.50, 145.00, 153.81 ppm.

**2,7,12-Triacetyl-5,5',10,10',15,15'-hexadecyltruxene**

Crude 5,5',10,10',15,15'-hexadecyltruxene (2.47 g, 2.91 mmol) was dissolved in dichloromethane (15 mL). This solution was gradually added to the AlCl<sub>3</sub>/acetyl chloride solution at 0 °C which was prepared by dissolving AlCl<sub>3</sub> (3.191 g, 23.9 mmol) in acetyl chloride (17.0 mL) at 0 °C under an argon atmosphere. The red reaction mixture was stirred for 10 min at 0 °C, and further stirred at room temperature for 80 minutes. The mixture was poured gradually on ice (~150 mL) while it was stirred. The resulting mixture was stirred at room temperature overnight. The organic portion was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with a Na<sub>2</sub>CO<sub>3</sub> aqueous solution. The resulting solution was dried over MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure to afford a green solid which was then recrystallized in ethanol to afford pure product as yellow crystals. Yield: 2.32 g (85%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.46 (m, 12H), 0.77-1.18 (m, 102H), 2.19 (m, 6H), 2.72 (s, 9H), 2.93 (m, 6H), 8.04 (dd, *J* = 8.2 Hz, 1.3 Hz, 3H), 8.10 (d, *J* = 1.4 Hz, 3H), 8.46 (d, *J* = 8.4 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.18, 22.75, 24.17, 26.93, 29.39, 29.51, 29.68, 29.81, 29.85, 32.00, 36.89, 56.27, 121.79, 124.59, 127.67, 135.57, 137.99, 144.64, 148.50, 154.03, 198.04 ppm.

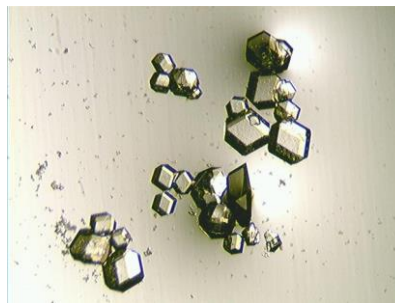
**5,5',10,10',15,15'-Hexadecyltruxene-2,7,12-tricarboxylic acid (H<sub>3</sub>hdtt)**

2,7,12-Triacetyl-5,5',10,10',15,15'-hexahexyltruxene (2.32 g, 1.77 mmol) was suspended and stirred in 1,4-dioxane (40 mL). NaOH (5.46 g, 136 mmol) was dissolved in 36 mL of water. At 0 °C, bromine (2.50 mL) was added to the NaOH solution, which was stirred for 15 minutes. The NaOBr solution was added to the above suspension at room temperature. The resulting mixture was then stirred at 60 °C for 2 hours and cooled to room temperature. An aqueous solution of NH<sub>2</sub>OH HCl (3.30 g, 47.5 mmol) was added to the reaction mixture to quench NaOBr. Dioxane was removed under reduced pressure and the resulting aqueous suspension was acidified with 3 M HCl until pH < 1. The resulting solid was filtered, washed with water, and dried under vacuum to afford Na<sub>3</sub>hdtt as a yellow solid (Yield: 2.32 g, 95 %), which was then refluxed in acetic acid overnight to afford H<sub>3</sub>hdtt as a yellow solid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 80 °C): δ 0.45 (m, 12H), 0.73-1.14 (m, 102H), 2.20 (m, 6H), 2.97 (m, 6H), 8.06 (d, *J* = 8.2 Hz, 3H), 8.10 (s, 3H), 8.46 (d, *J* = 8.3 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 80 °C): δ 13.15, 21.41, 23.05, 27.97, 28.08, 28.38, 28.50, 30.71, 35.69, 55.23, 122.65, 123.74, 127.61, 129.06, 137.35, 142.97, 146.62, 152.70, 166.87 ppm. Anal. calcd. for [C<sub>90</sub>H<sub>138</sub>O<sub>6</sub>]: C, 82.14; H, 10.57; Found: C, 82.08; H, 10.77.

## 2. MOF synthesis and characterization

### (a) $[\text{Zn}_4\text{O}(\text{hmtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$ (MUF-77-methyl)

$\text{H}_3\text{hmtt}$  (4.3 mg, 7.7  $\mu\text{mol}$ ), biphenyl-4,4'-dicarboxylic acid (2.1 mg, 8.7  $\mu\text{mol}$ ) and terephthalic acid (1.4 mg, 8.4  $\mu\text{mol}$ ) were combined with  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13.8 mg, 52.8  $\mu\text{mol}$ ) in dry DEF (1.0 mL) and water (30  $\mu\text{L}$ ) in a 4 mL vial which had been treated with Sigmacote. The mixture was sonicated for 5 minutes before being

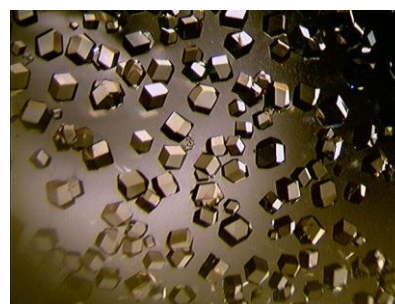


heated in an 85  $^{\circ}\text{C}$  isothermal oven for 12 hours to obtain pale yellow crystals of MUF-77-methyl. For yield calculation, TGA and NMR analysis, the mother liquor was decanted and replaced with anhydrous DMF. The DMF was then replaced with fresh anhydrous DMF and this process was repeated for 5 times. The crystals were isolated by filtration and allowed to dry on a filter paper. Yield: 11.0 mg (51 %, based on the formula  $[\text{Zn}_4\text{O}(\text{hmtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}(\text{DMF})_{21.8}]$  determined by  $^1\text{H}$  NMR of a digested sample). Anal. calcd. for  $[\text{C}_{59}\text{H}_{42}\text{O}_{13}\text{Zn}_4] \cdot 0.25 \text{H}_2\text{O}$ : C, 57.85; H, 3.50; Found: C, 57.79; H, 3.42.

To scale up the synthesis, 20 mL DEF was used and all reagents were scaled up accordingly (0.15 mmol  $\text{H}_3\text{hmtt}$ , 0.15 mmol  $\text{H}_2\text{bpdc}$ , 0.15 mmol  $\text{H}_2\text{bdc}$ , 1.056 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.6 mL water). The reaction was carried out in a Sigmacote-treated 100 mL Schott bottle at 85  $^{\circ}\text{C}$ .

### (b) $[\text{Zn}_4\text{O}(\text{hett})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$ (MUF-77-ethyl)

$\text{H}_3\text{hett}$  (4.9 mg, 7.6  $\mu\text{mol}$ ), biphenyl-4,4'-dicarboxylic acid (3.0 mg, 12  $\mu\text{mol}$ ) and terephthalic acid (1.3 mg, 7.8  $\mu\text{mol}$ ) were combined with  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13.8 mg, 52.8  $\mu\text{mol}$ ) in dry DEF (1.0 mL) and water (50  $\mu\text{L}$ ) in a 4 mL vial which had been treated with Sigmacote. The reaction mixture was sonicated for 5 minutes before being



heated in an 85  $^{\circ}\text{C}$  isothermal oven for 19 hours to obtain pale yellow crystals of MUF-77-ethyl. For yield calculation, TGA and NMR analysis, the mother liquor was decanted and replaced with anhydrous DMF. The DMF was then replaced with fresh anhydrous DMF and this process was repeated for 5 times. The crystals were isolated by filtration and allowed to dry on a filter paper. Yield: 12.3 mg (53 %, based on the formula  $[\text{Zn}_4\text{O}(\text{hett})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}(\text{DMF})_{22.8}(\text{DEF})_{0.6}]$  determined by  $^1\text{H}$  NMR of a digested

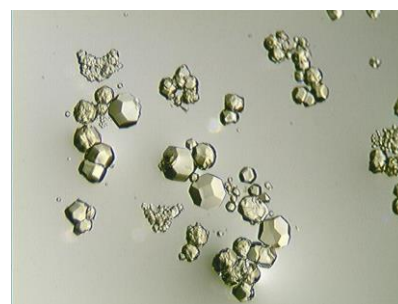
sample). Anal. calcd. for  $[\text{C}_{67}\text{H}_{58}\text{O}_{13}\text{Zn}_4] \cdot 1.5 \text{ H}_2\text{O}$ : C, 59.18; H, 4.52; Found: C, 59.21; H, 4.45.

To scale up the synthesis, 20 mL DEF was used and all reagents were scaled up accordingly (0.15 mmol  $\text{H}_3\text{hett}$ , 0.25 mmol  $\text{H}_2\text{bpdc}$ , 0.15 mmol  $\text{H}_2\text{bdc}$ , 1.056 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.6 mL water). The reaction was carried out in a Sigmacote-treated 100 mL Schott bottle at 85 °C.

It was found that a rod shaped MOF based on zinc(II) and hett could form occasionally as a competing phase in small quantities during the synthesis when the water content was lower than 3 %. This phase can be completely eliminated by adding around 10 seeding crystals of MUF-77-ethyl to the reaction mixture prior to solvothermal reactions. This competing phase was not observed when synthesizing other members of MUF-77 series with different alkyl substituents.

**(c)  $[\text{Zn}_4\text{O}(\text{hbtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$  (MUF-77-butyl)**

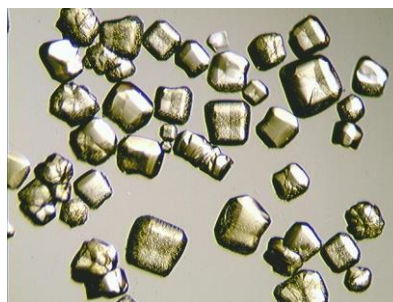
$\text{H}_3\text{hbtt}$  (6.2 mg, 7.6  $\mu\text{mol}$ ), biphenyl-4,4'-dicarboxylic acid (1.7 mg, 7.0  $\mu\text{mol}$ ) and terephthalic acid (1.1 mg, 6.6  $\mu\text{mol}$ ) were combined with  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13.8 mg, 52.8  $\mu\text{mol}$ ) in dry DEF (1.0 mL) and water (30  $\mu\text{L}$ ) in a 4 mL vial which had been treated with Sigmacote. The reaction mixture was sonicated for 5 minutes before being heated in an 85 °C isothermal oven for 4.5 hours to obtain pale yellow crystals of MUF-77-butyl. For yield calculation, TGA and NMR analysis, the mother liquor was decanted and replaced with anhydrous DMF. The DMF was then replaced with fresh anhydrous DMF and this process was repeated for 5 times. The crystals were isolated by filtration and allowed to dry on a filter paper. Yield: 9.2 mg (55 %, based on the formula  $[\text{Zn}_4\text{O}(\text{hbtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}(\text{DMF})_{18.7}]$  determined by  $^1\text{H}$  NMR of a digested sample). Anal. calcd. for  $[\text{C}_{83}\text{H}_{90}\text{O}_{13}\text{Zn}_4]$ : C, 64.02; H, 5.83; Found: C, 63.98; H, 5.88.



To scale up the synthesis, 20 mL DEF was used and all reagents were scaled up accordingly (0.15 mmol  $\text{H}_3\text{hbtt}$ , 0.15 mmol  $\text{H}_2\text{bpdc}$ , 0.15 mmol  $\text{H}_2\text{bdc}$ , 1.056 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.6 mL water). The reaction was carried out in a Sigmacote-treated 100 mL Schott bottle at 85 °C.

**(d)  $[\text{Zn}_4\text{O}(\text{hhtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$  (MUF-77-hexyl)**

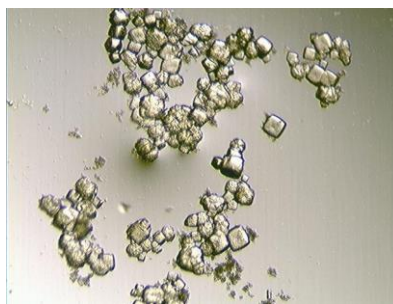
$\text{H}_3\text{hhtt}$  (7.4 mg, 7.6  $\mu\text{mol}$ ), biphenyl-4,4'-dicarboxylic acid (2.2 mg, 9.1  $\mu\text{mol}$ ) and terephthalic acid (1.2 mg, 7.2  $\mu\text{mol}$ ) were combined with  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13.8 mg, 52.8  $\mu\text{mol}$ ) in dry DEF (1.0 mL) and water (30  $\mu\text{L}$ ) in a 4 mL vial which was treated with Sigmacote and sonicated for 5 minutes before being heated in an 85  $^\circ\text{C}$  isothermal oven for 5.5 hours to obtain pale yellow crystals of MUF-77-hexyl. For yield calculation, TGA and NMR analysis, the mother liquor was decanted and replaced with anhydrous DMF. The DMF was then replaced with fresh anhydrous DMF and this process was repeated for 5 times. The crystals were isolated by filtration and allowed to dry on a filter paper. Yield: 5.1 mg (34 %, based on the formula  $[\text{Zn}_4\text{O}(\text{hhtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}(\text{DMF})_{12.3}]$  determined by  $^1\text{H}$  NMR of a digested sample). Anal. calcd. for  $[\text{C}_{99}\text{H}_{122}\text{O}_{13}\text{Zn}_4] \cdot 0.5 \text{H}_2\text{O}$ : C, 66.41; H, 6.92; Found: C, 66.26; H, 6.90.



To scale up the synthesis, 20 mL DEF was used and all reagents were scaled up accordingly (0.15 mmol  $\text{H}_3\text{hhtt}$ , 0.15 mmol  $\text{H}_2\text{bpdc}$ , 0.15 mmol  $\text{H}_2\text{bdc}$ , 1.056 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.6 mL water). The reaction was carried out in a Sigmacote-treated 100 mL Schott bottle at 85  $^\circ\text{C}$ .

**(e)  $[\text{Zn}_4\text{O}(\text{hott})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$  (MUF-77-octyl)**

$\text{H}_3\text{hott}$  (8.8 mg, 7.7  $\mu\text{mol}$ ), biphenyl-4,4'-dicarboxylic acid (1.9 mg, 7.8  $\mu\text{mol}$ ) and terephthalic acid (2.7 mg, 16  $\mu\text{mol}$ ) were combined with  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13.8 mg, 52.8  $\mu\text{mol}$ ) in dry DEF (1.0 mL) and water (30  $\mu\text{L}$ ) in a 4 mL vial which was treated with Sigmacote and sonicated for 5 minutes before being heated in an 85  $^\circ\text{C}$  isothermal oven for 12 hours to obtain pale yellow crystals of MUF-77-methyl. For yield calculation, TGA and NMR analysis, the mother liquor was decanted and replaced with anhydrous DMF. The DMF was then replaced with fresh anhydrous DMF and this process was repeated for 5 times. The crystals were isolated by filtration and allowed to dry on a filter paper. Yield: 10.1 mg (45 %, based on the formula  $[\text{Zn}_4\text{O}(\text{hott})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}(\text{DMF})_{12.4}]$  determined by  $^1\text{H}$  NMR of a digested sample). Anal. calcd. for  $[\text{C}_{115}\text{H}_{154}\text{O}_{13}\text{Zn}_4]$ : C, 68.85; H, 7.74; Found: C, 68.91; H, 7.73.



To scale up the synthesis, 20 mL DEF was used and all reagents were scaled up accordingly (0.15 mmol  $\text{H}_3\text{hdt}$ , 0.15 mmol  $\text{H}_2\text{bpdc}$ , 0.15 mmol  $\text{H}_2\text{bdc}$ , 1.056 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.6 mL water). The reaction was carried out in a Sigmacote-treated 100 mL Schott bottle at 85 °C.

**(f)  $[\text{Zn}_4\text{O}(\text{hdt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$  (MUF-77-decyl)**

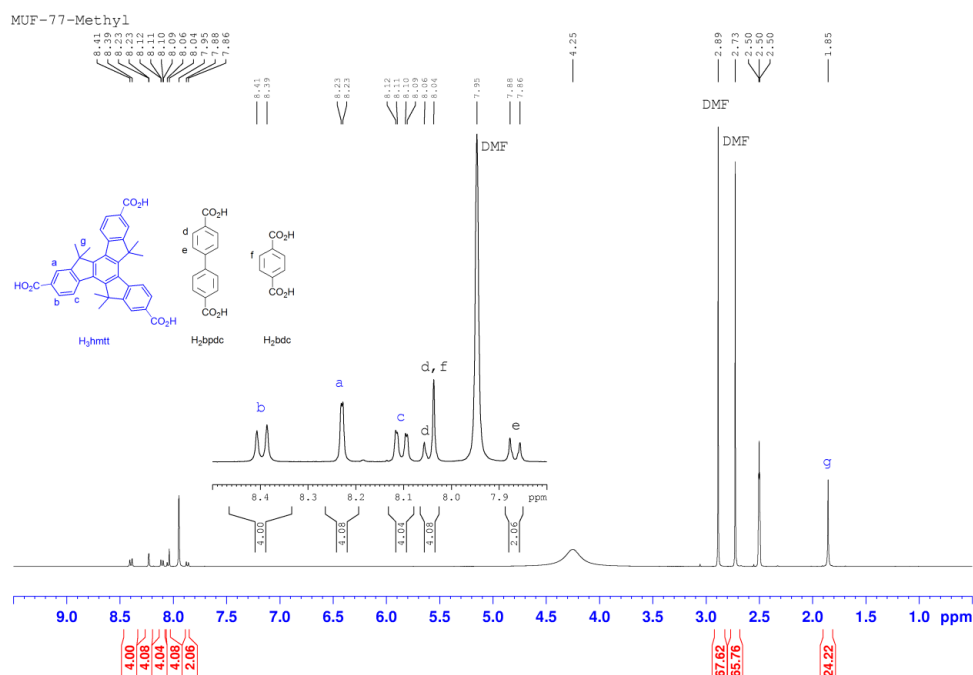
$\text{H}_3\text{hdt}$  (9.9 mg, 7.5  $\mu\text{mol}$ ), biphenyl-4,4'-dicarboxylic acid (1.8 mg, 7.4  $\mu\text{mol}$ ) and terephthalic acid (1.2 mg, 7.2  $\mu\text{mol}$ ) were combined with  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13.8 mg, 52.8  $\mu\text{mol}$ ) in dry DEF (1.0 mL) and water (30  $\mu\text{L}$ ) in a 4 mL vial which was treated with Sigmacote and sonicated for 5 minutes before being heated in an 85 °C isothermal oven for 6.5 hours to obtain pale yellow crystals of MUF-77-decyl. For yield calculation, TGA and NMR analysis, the mother liquor was decanted and replaced with anhydrous DMF. The DMF was then replaced with fresh anhydrous DMF and this process was repeated for 5 times. The crystals were isolated by filtration and allowed to dry on a filter paper. Yield: 7.2 mg (44 %, based on the formula  $[\text{Zn}_4\text{O}(\text{hdt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}(\text{DMF})_{9.3}]$  determined by  $^1\text{H}$  NMR of a digested sample). Anal. calcd. for  $[\text{C}_{131}\text{H}_{186}\text{O}_{13}\text{Zn}_4]$ : C, 70.54; H, 8.41; Found: C, 70.48; H, 8.41.



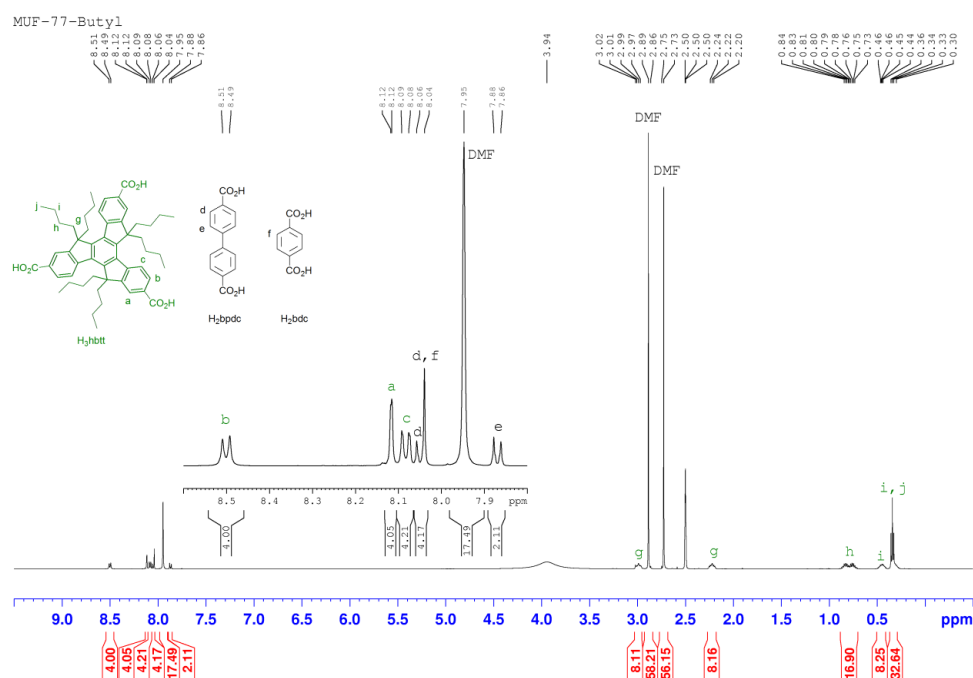
To scale up the synthesis, 20 mL DEF was used and all reagents were scaled up accordingly (0.15 mmol  $\text{H}_3\text{hdt}$ , 0.15 mmol  $\text{H}_2\text{bpdc}$ , 0.15 mmol  $\text{H}_2\text{bdc}$ , 1.056 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.6 mL water). The reaction was carried out in a Sigmacote-treated 100 mL Schott bottle at 85 °C.

### 3. $^1\text{H}$ NMR analysis of digested MOF samples



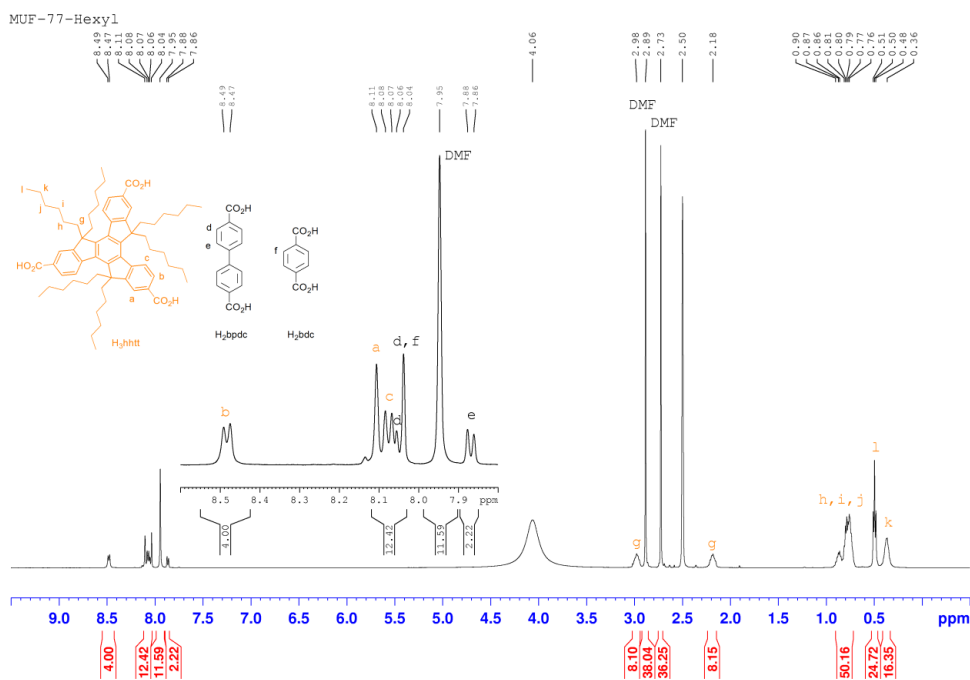


**Figure B.1**  $^1\text{H}$  NMR spectra of digested (see experimental section for procedure) MUF-77-methyl (with occluded DMF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{hmtt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$ .

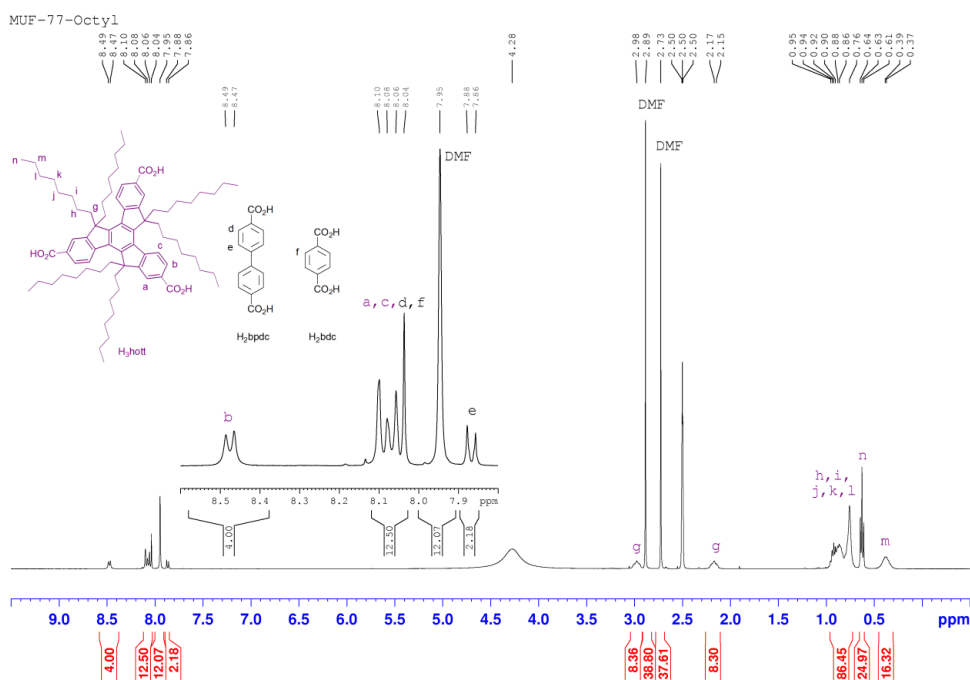


**Figure B.2**  $^1\text{H}$  NMR spectra of digested (see experimental section for procedure) MUF-77-butyl (with occluded DMF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{hbt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$ .

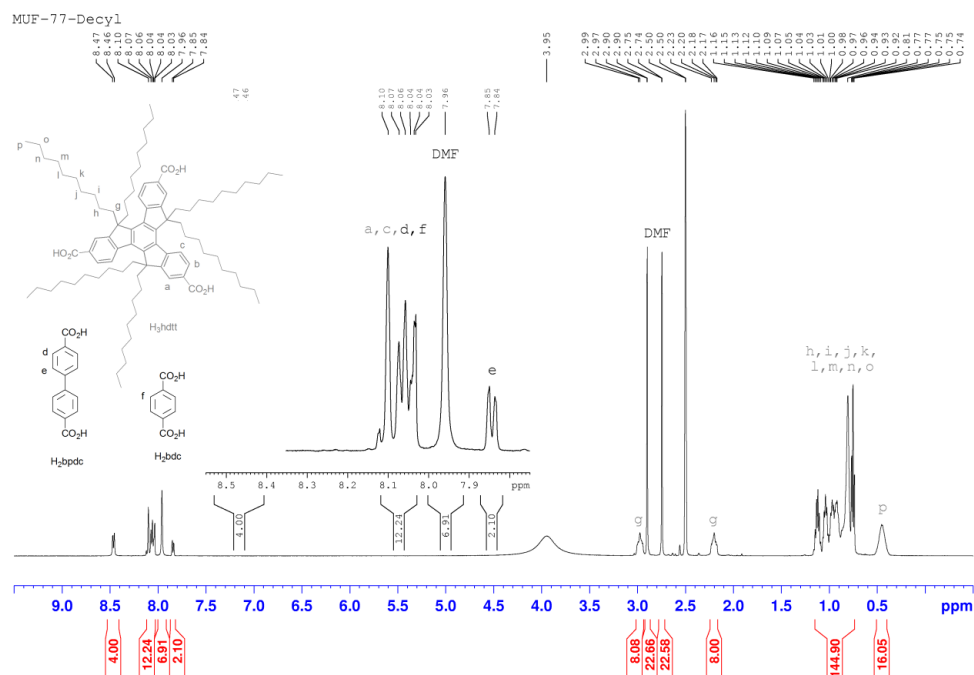




**Figure B.3**  $^1H$  NMR spectra of digested (see experimental section for procedure) MUF-77-hexyl (with occluded DMF solvent molecules) showing the integrals that match with the formula  $[Zn_4O(hhtt)_{4/3}(bpdc)_1(bdc)_1]_2$ .



**Figure B.4**  $^1H$  NMR spectra of digested (see experimental section for procedure) MUF-77-octyl (with occluded DMF solvent molecules) showing the integrals that match with the formula  $[Zn_4O(hott)_{4/3}(bpdc)_1(bdc)_1]_2$ .



**Figure B.5**  $^1\text{H}$  NMR spectra of digested (see experimental section for procedure) MUF-77-decyl (with occluded DMF solvent molecules) showing the integrals that match with the formula  $[\text{Zn}_4\text{O}(\text{hdt})_{4/3}(\text{bpdc})_{1/2}(\text{bdc})_{1/2}]$ .

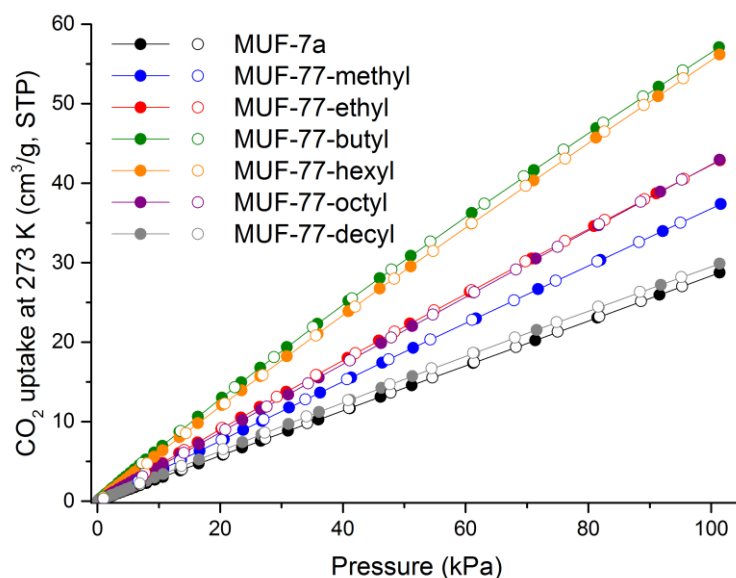
#### 4. Crystallography of 2,7,12-triacetyl-5,5',10,10',15,15'-hexaoctyltruxene

Data were collected at 143 K. All non-hydrogen atoms were found on the electron density map and refined anisotropically. Ideal positions for all hydrogen atoms were calculated and refined as a riding model. Three of the carbon atoms of an octyl chain were found to be disordered over two positions. The occupancies of these two positions were refined freely and equal atomic displacement parameters were used for these positions.

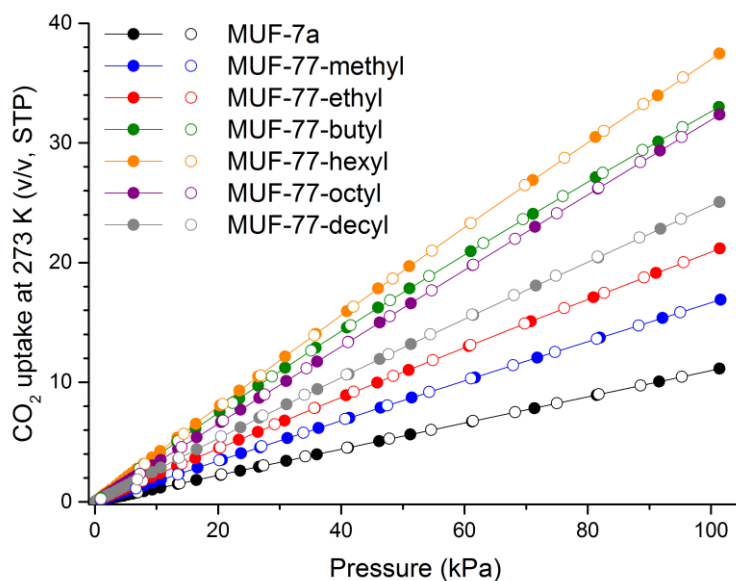
**Table B.2** Crystal data and structure refinement for 2,7,12-triacetyl-5,5',10,10'-15,15'-hexaoctyltruxene

|   |   |   |
|---|---|---|
| Identification code                                   | 2,7,12-triacetyl-5,5',10,10'-15,15'-hexaoctyltruxene                                    |   |
| Formula   | $C_{81}H_{120}O_3$  |   |
| Formula weight  | 1141.76   |   |
| Crystal size (mm)                                     | 1.102 x 0.355 x 0.230   |   |
| Temperature (K)                                       | 143(2)  |   |
| Wavelength (Å)  | 1.54178   |   |
| Crystal system  | Triclinic   |   |
| Space group   | <i>P</i> -1   |   |
| Unit cell dimensions                                  | $a = 11.1927(2) \text{ Å}$<br>$b = 15.0300(3) \text{ Å}$<br>$c = 22.5983(16) \text{ Å}$ | $\alpha = 100.200(7)^\circ$<br>$\beta = 101.975(7)^\circ$<br>$\gamma = 96.601(7)^\circ$ |
| Unit cell volume (Å <sup>3</sup> )                    | 3614.4(3)   |   |
| Z   | 2   |   |
| $D_{\text{calc}}$ (g cm <sup>-3</sup> )               | 1.049   |   |
| $\mu$ (mm <sup>-1</sup> )                             | 0.458   |   |
| F(000)  | 1260  |   |
| Reflections collected / unique                        | 48841 / 13521   |   |
| $R_{\text{int}}$                                      | 0.0513  |   |
| Data range (Å)  | $0.81 < d < 6.7$  |   |
| Index ranges  | $-12 \leq h \leq 9$<br>$-18 \leq k \leq 18$<br>$-27 \leq l \leq 27$                     |   |
| Completeness  | 97.8%   |   |
| $T_{\text{min}}, T_{\text{max}}$                      | 0.77, 1.00  |   |
| R indices for data with $I > 2\sigma(I)$              | $R_1 = 0.0856$ , $wR_2 = 0.2505$  |   |
| R indices for all data                                | $R_1 = 0.1093$ , $wR_2 = 0.3020$  |   |
| Largest difference peak and hole (e Å <sup>-3</sup> ) | 0.537 / -0.405  |   |

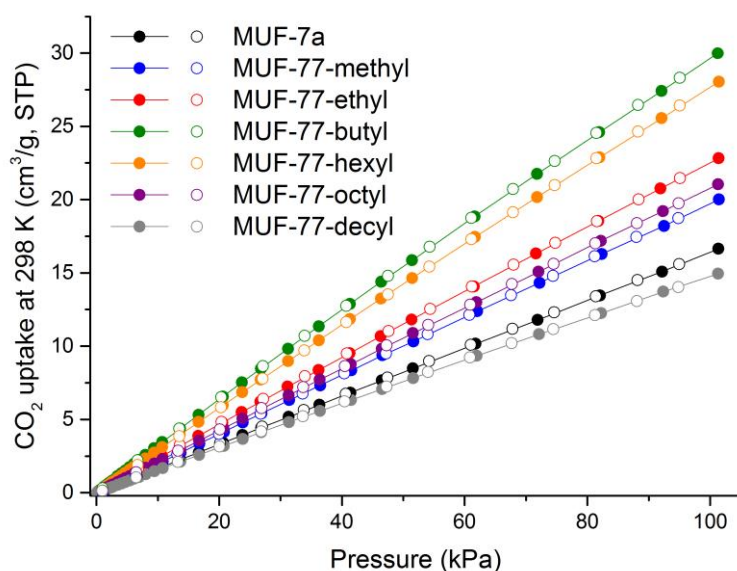
## 4. Gas adsorption isotherms



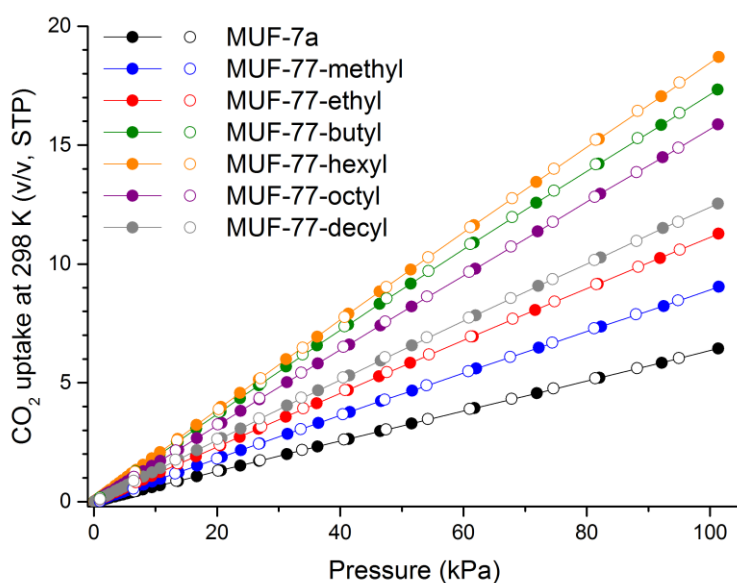
**Figure B.6** Gravimetric CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for MUF-7a and MUF-77s.



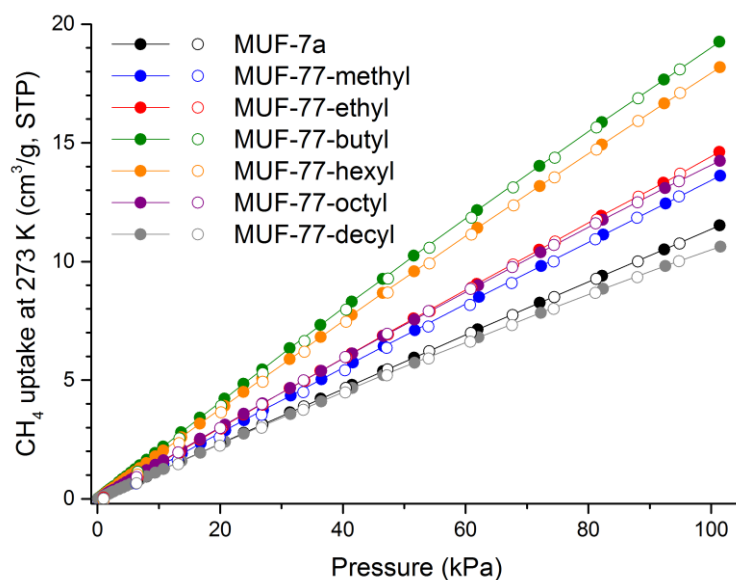
**Figure B.7** Volumetric CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for MUF-7a and MUF-77s.



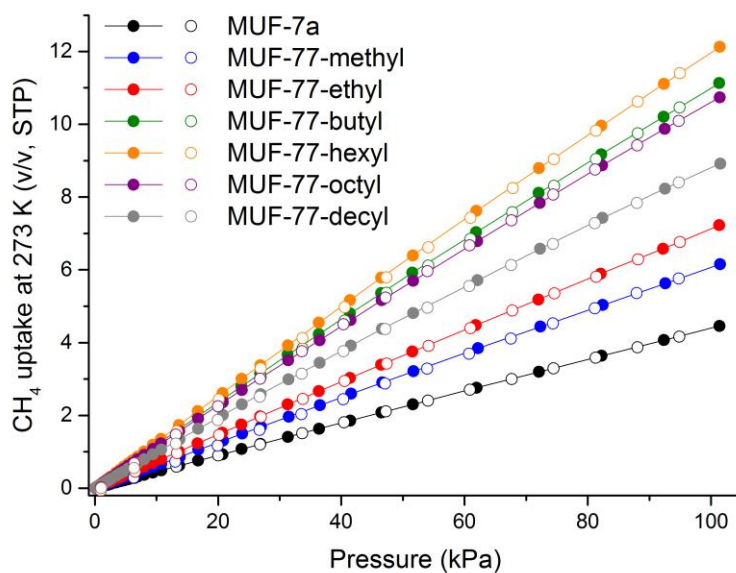
**Figure B.8** Gravimetric CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 298 K for MUF-7a and MUF-77s.



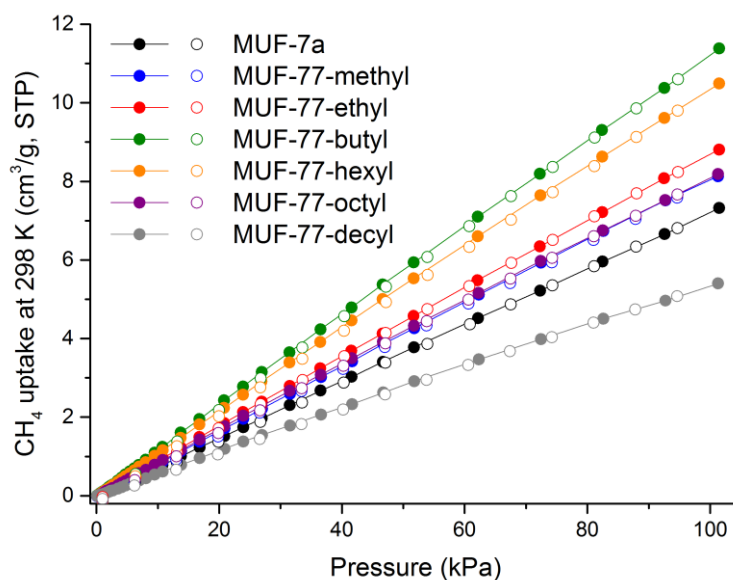
**Figure B.9** Volumetric CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 298 K for MUF-7a and MUF-77s.



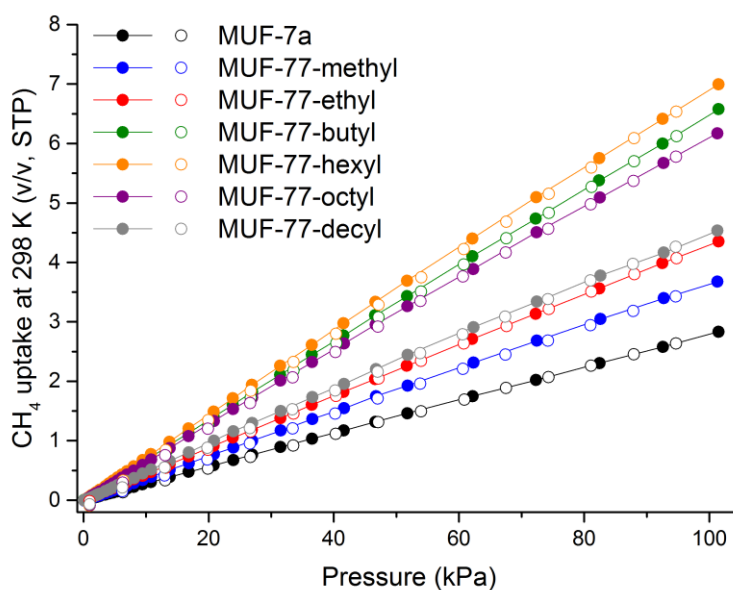
**Figure B.10** Gravimetric  $\text{CH}_4$  adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for MUF-7a and MUF-77s.



**Figure B.11** Volumetric  $\text{CH}_4$  adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for MUF-7a and MUF-77s.

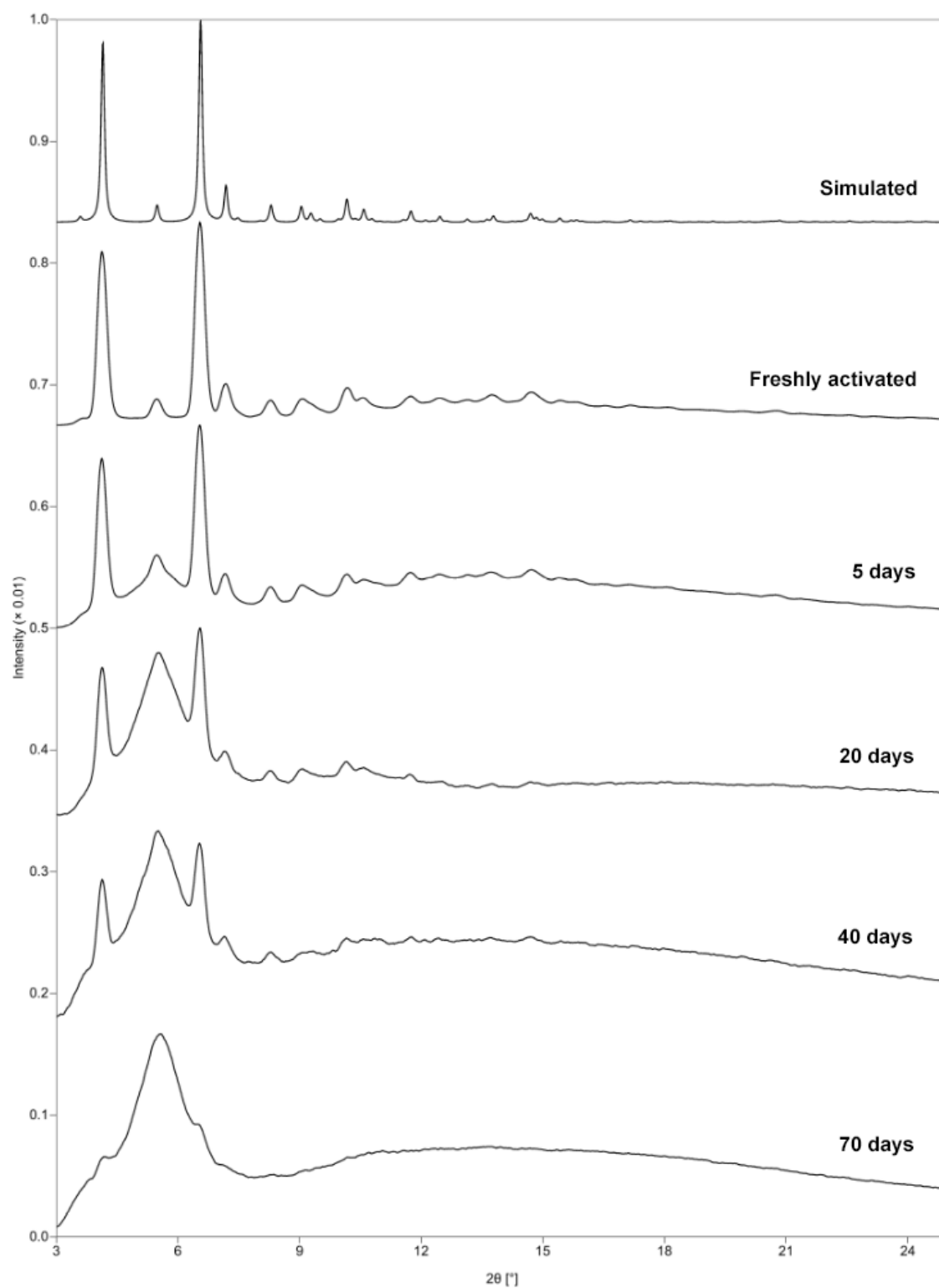


**Figure B.12** Gravimetric  $\text{CH}_4$  adsorption (filled circles) and desorption (open circles) isotherms measured at 298 K for MUF-7a and MUF-77s.



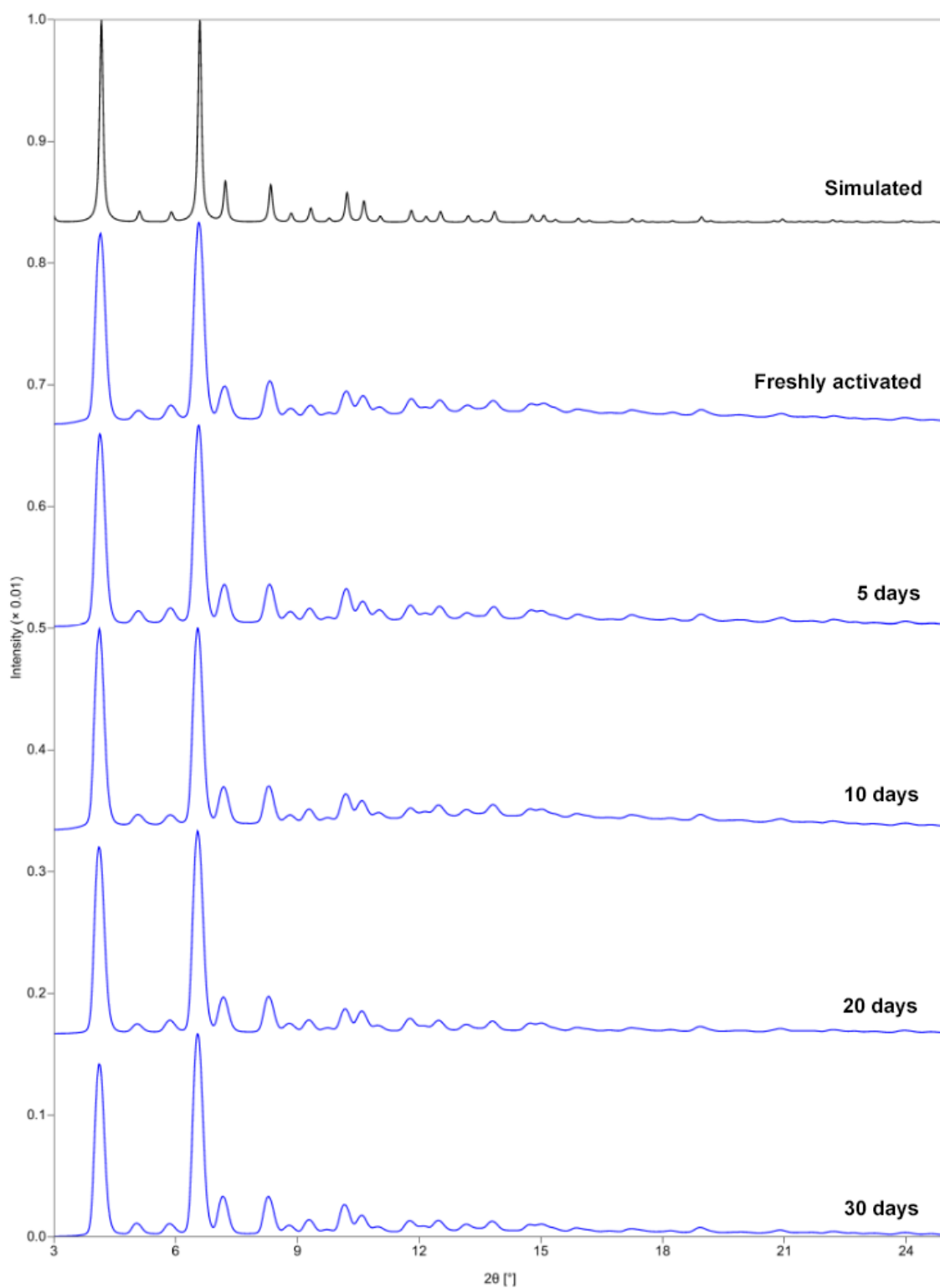
**Figure B.13** Volumetric  $\text{CH}_4$  adsorption (filled circles) and desorption (open circles) isotherms measured at 298 K for MUF-7a and MUF-77s.

## 5. Aging experiments data

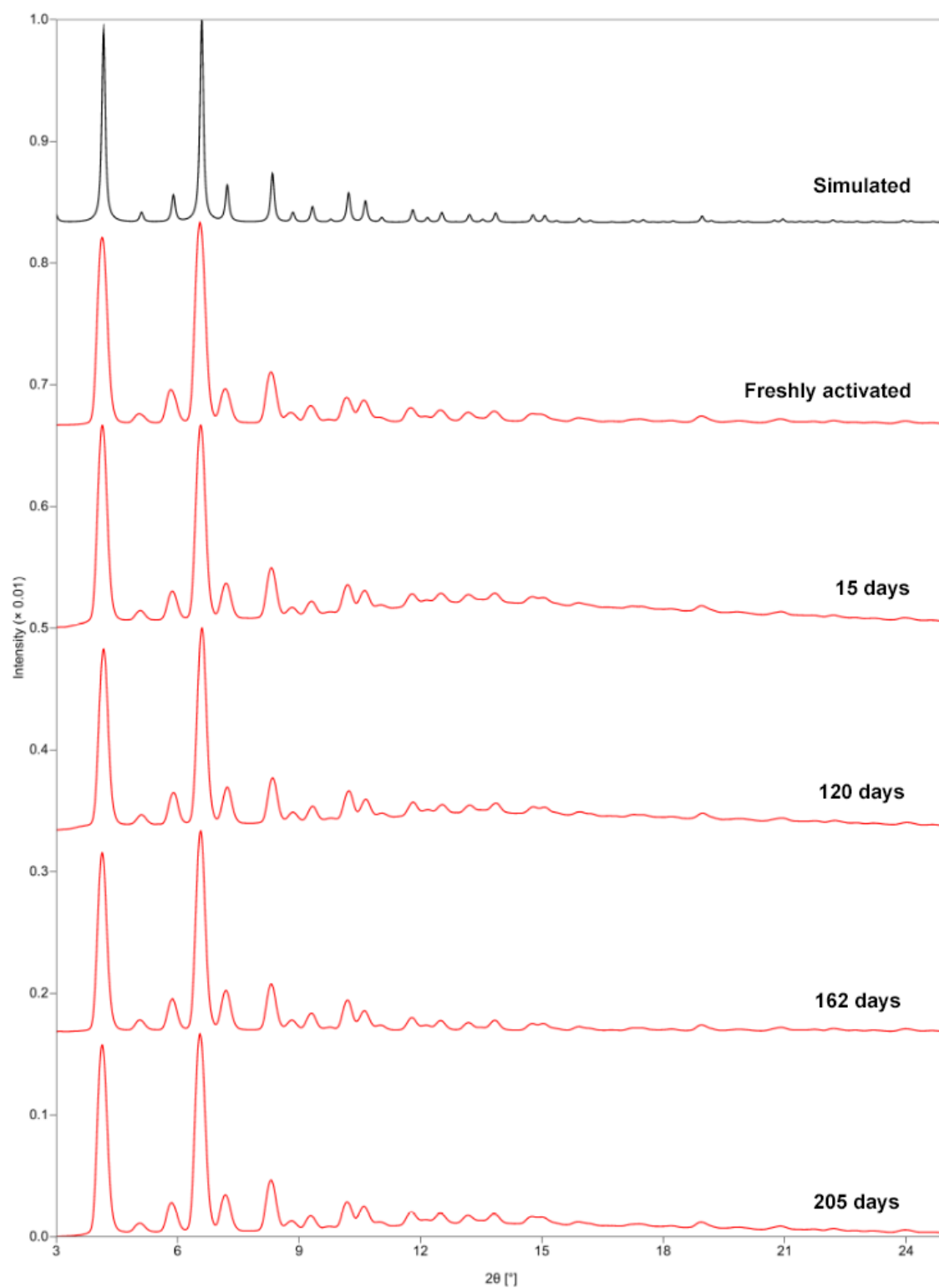


**Figure B.14** PXRD patterns of simulated, pristine and aged MUF-7a under 40-50 % RH.

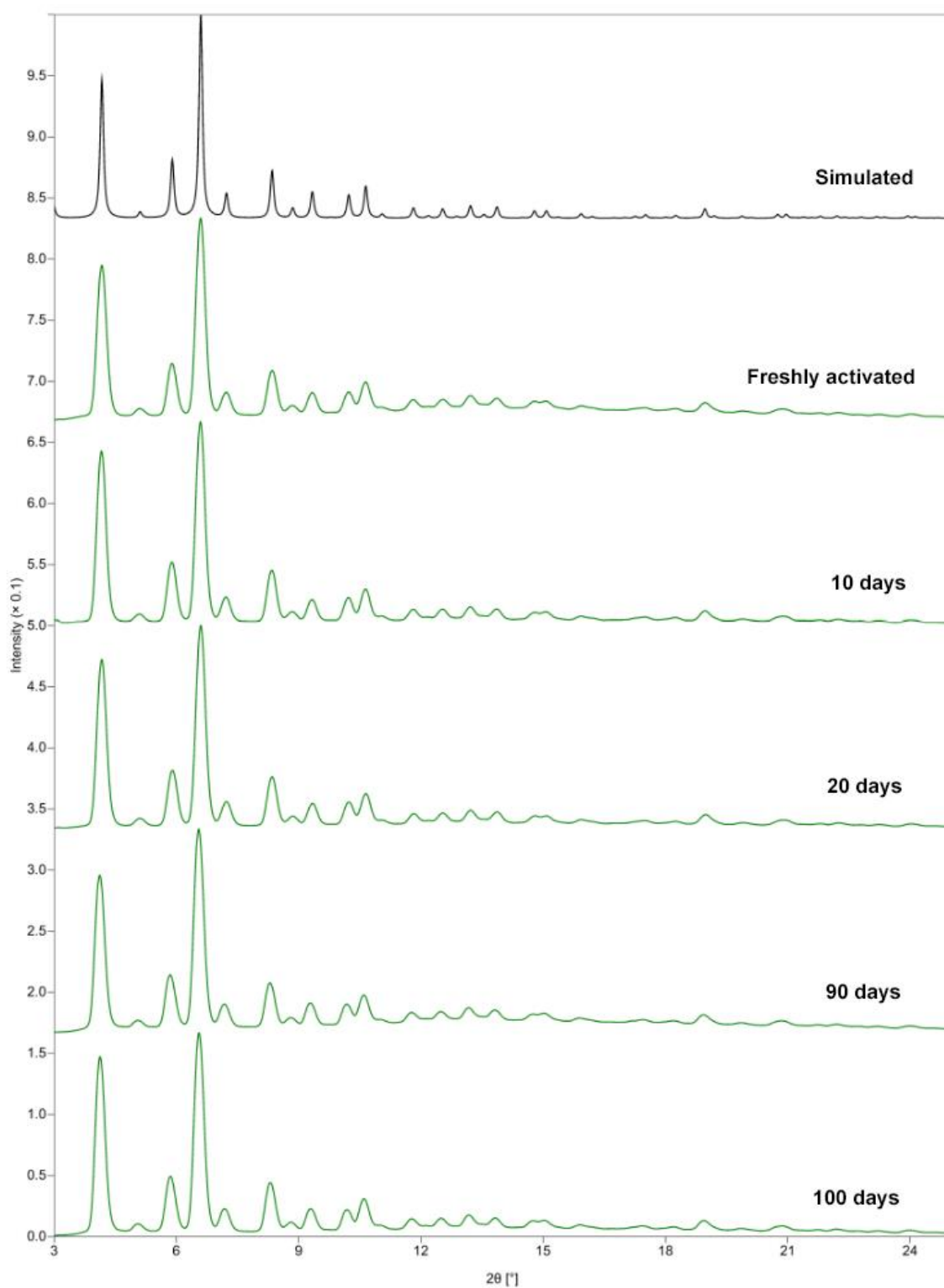




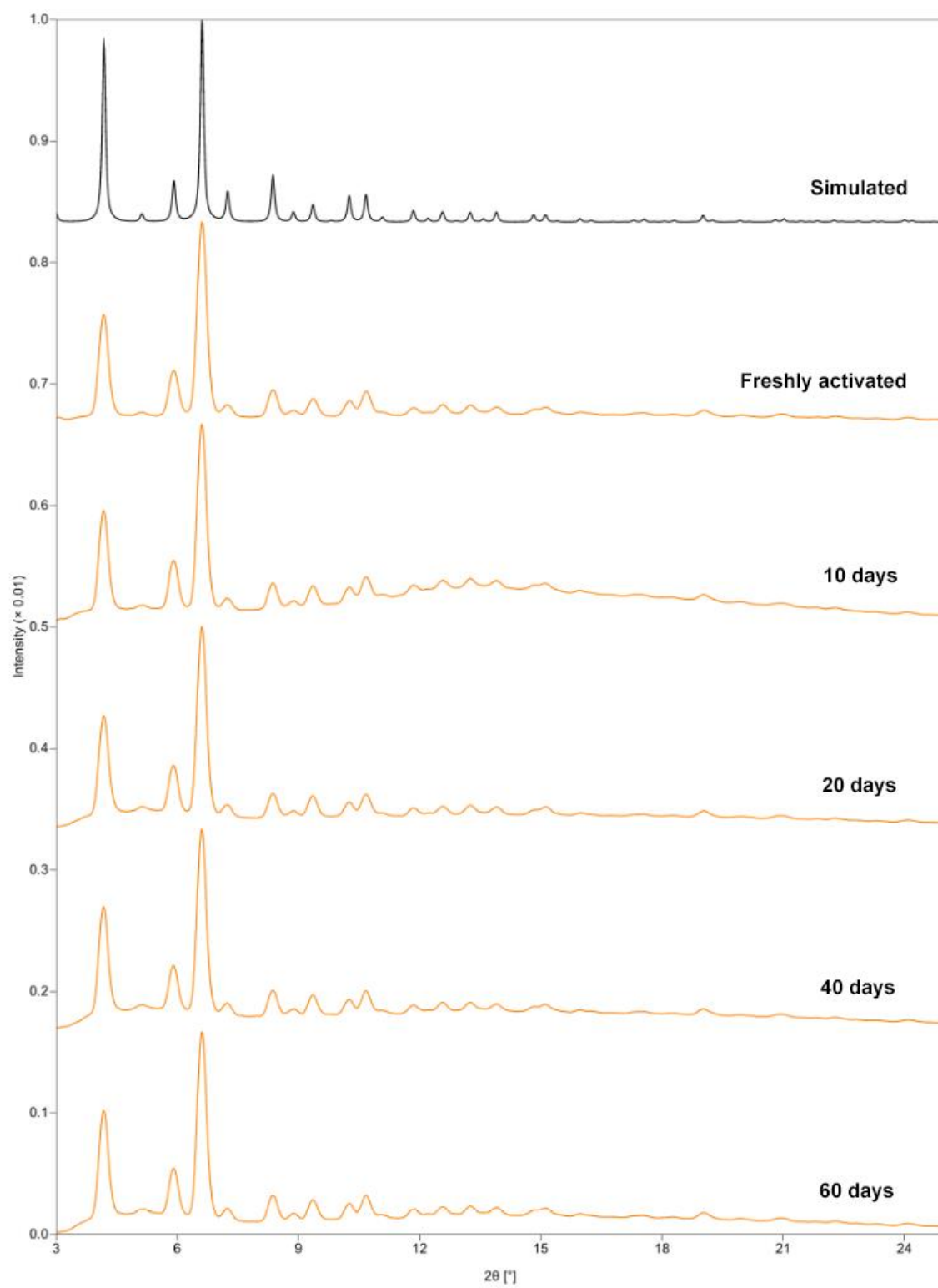
**Figure B.15** PXRD patterns of simulated, pristine and aged MUF-77-methyl under 40-50 % RH.



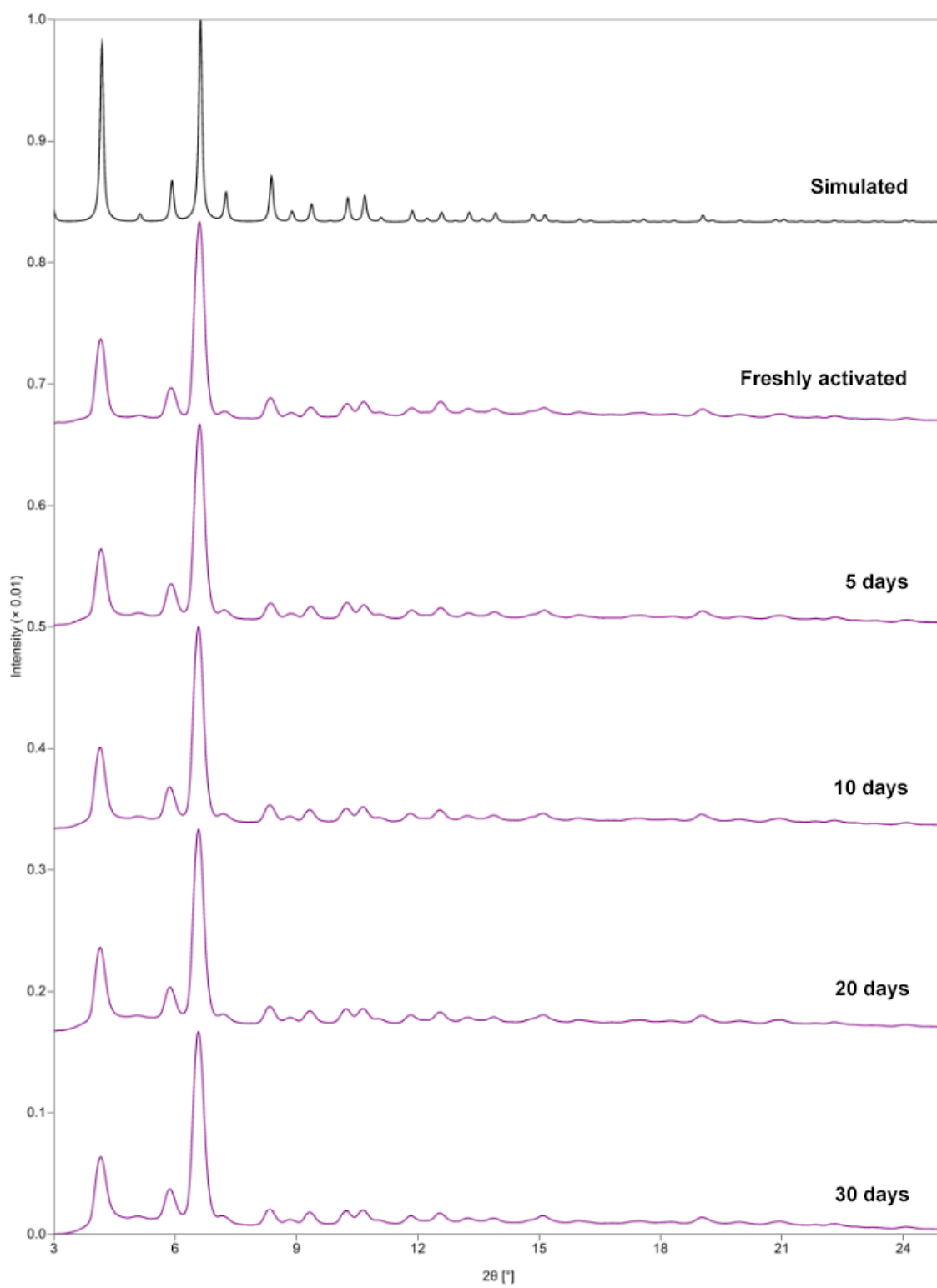
**Figure B.16** Additional PXRD patterns of simulated, pristine and aged MUF-77-ethyl under 40-50 % RH.



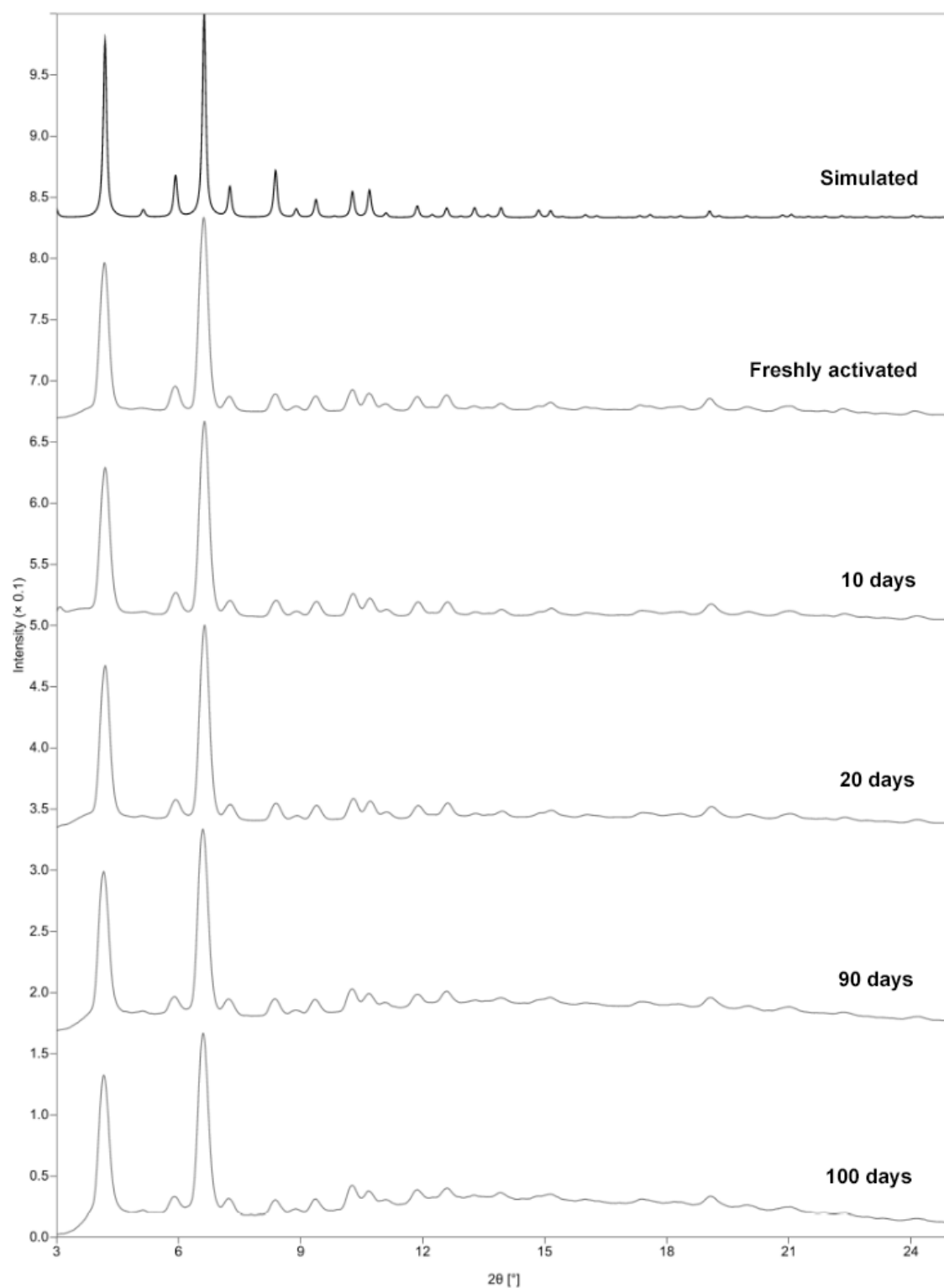
**Figure B.17** PXRd patterns of simulated, pristine and aged MUF-77-butyl under 40-50 % RH.



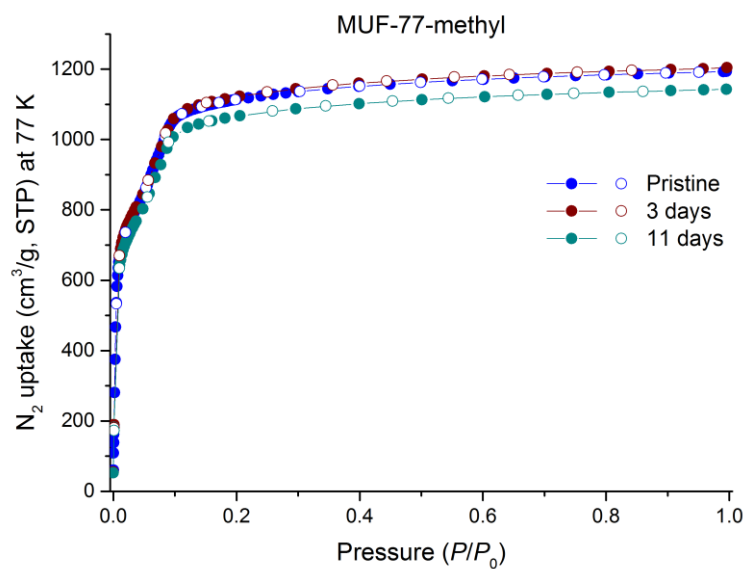
**Figure B.18** PXRD patterns of simulated, pristine and aged MUF-77-hexyl under 40-50 % RH.



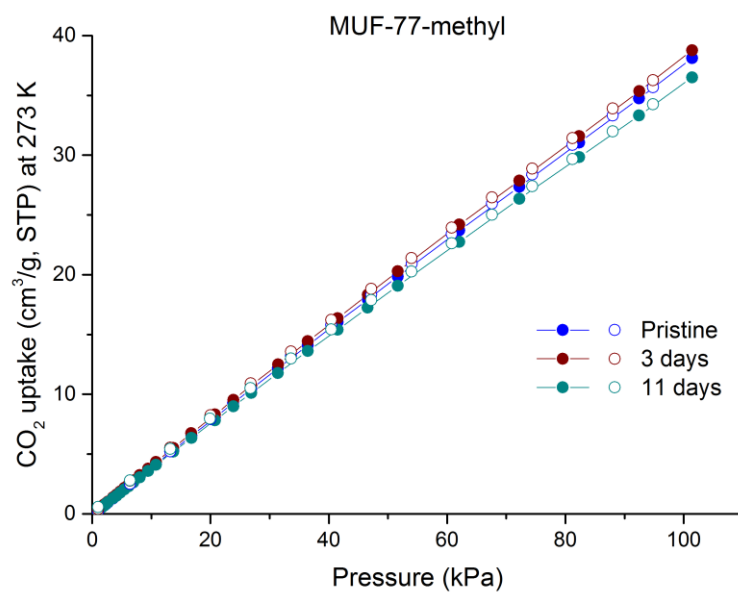
**Figure B.19** PXRD patterns of simulated, pristine and aged MUF-77-octyl under 40-50 % RH.



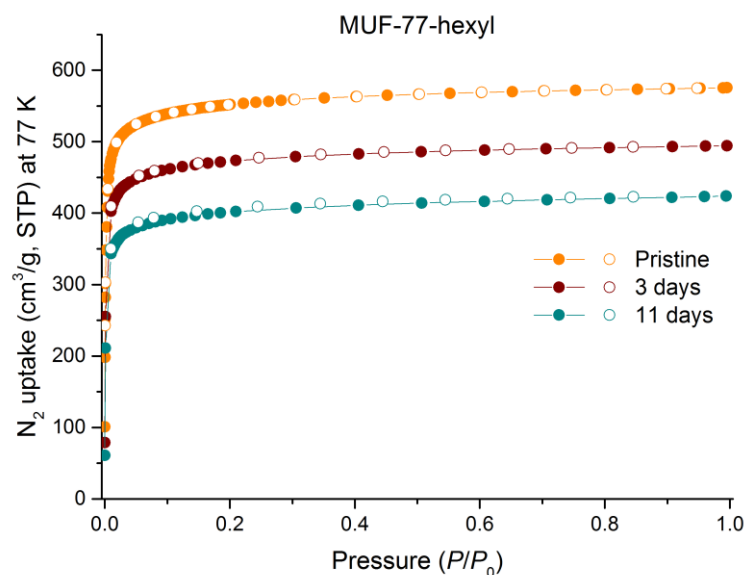
**Figure B.20** PXRD patterns of simulated, pristine and aged MUF-77-decyl under 40-50 % RH.



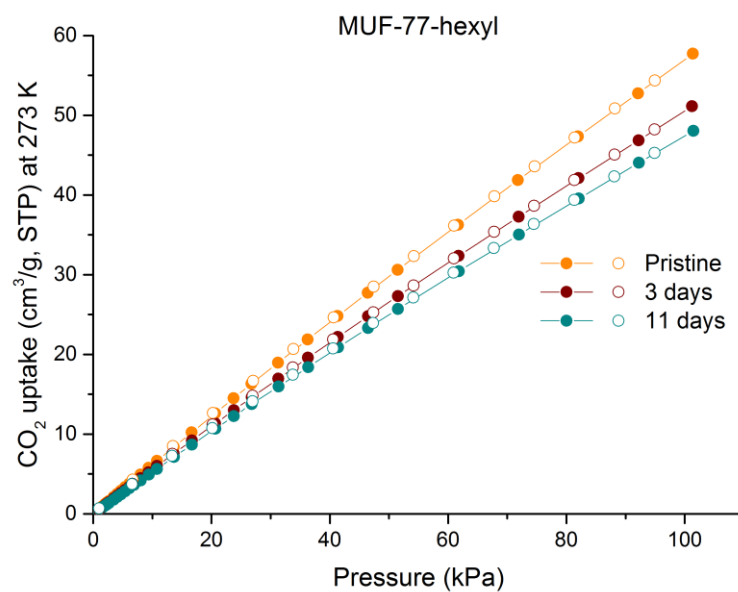
**Figure B.21** Nitrogen adsorption (filled circles) and desorption (open circles) isotherms measured at 77 K for pristine and aged MUF-77-methyl under 40-50 % RH.



**Figure B.22** CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for pristine and aged MUF-77-methyl under 40-50 % RH.

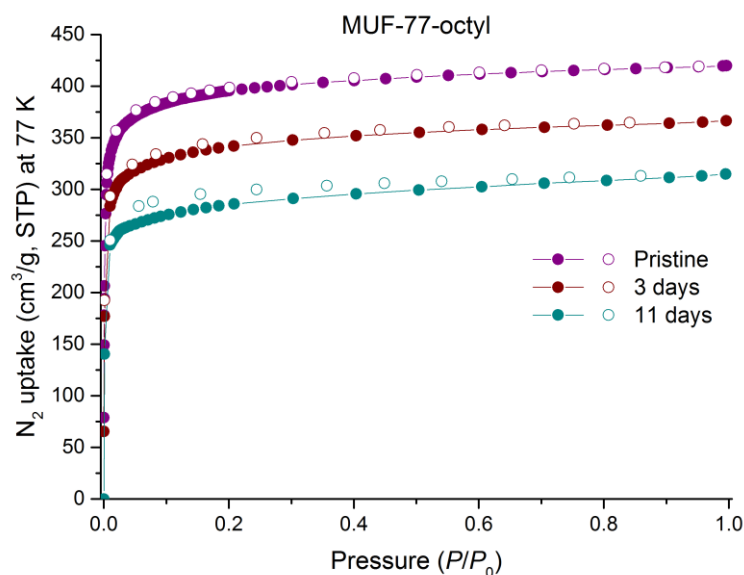


**Figure B.23** Nitrogen adsorption (filled circles) and desorption (open circles) isotherms measured at 77 K for pristine and aged MUF-77-hexyl under 40-50 % RH.

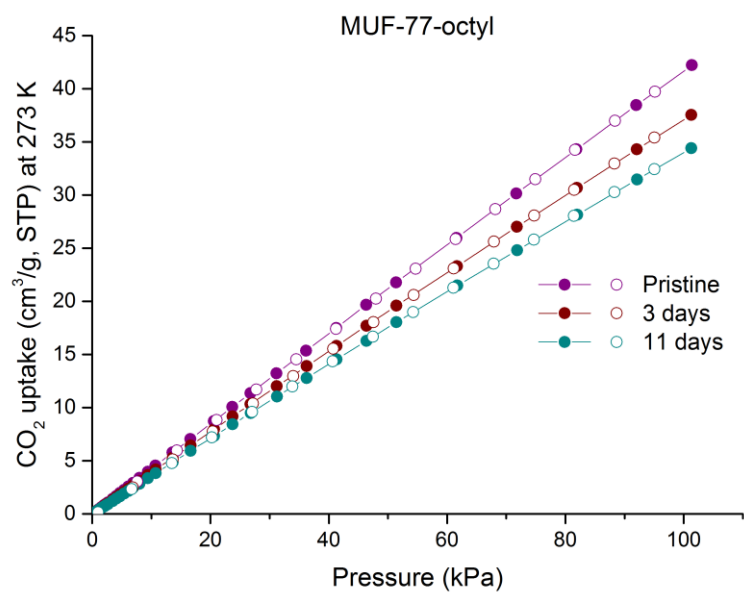


**Figure B.24** CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for pristine and aged MUF-77-hexyl under 40-50 % RH.

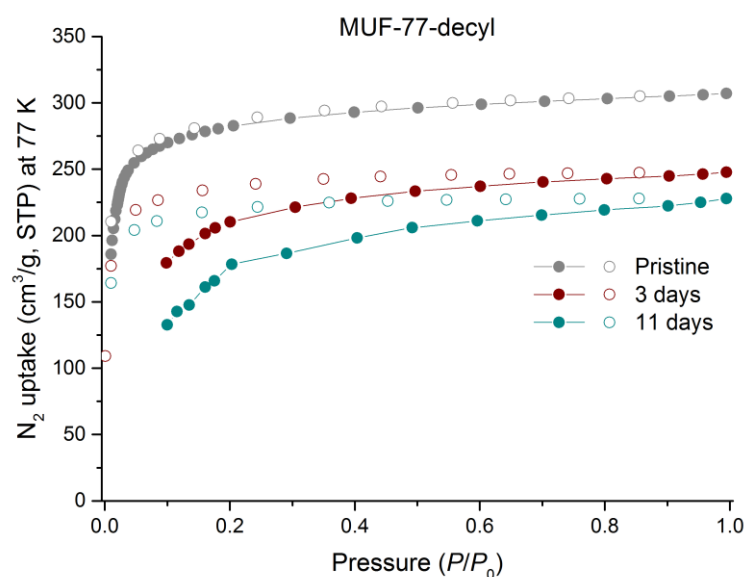




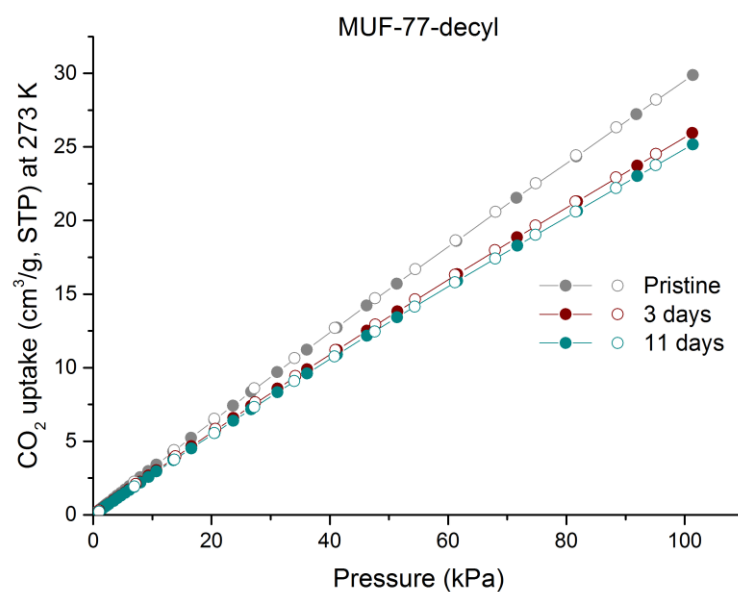
**Figure B.25** Nitrogen adsorption (filled circles) and desorption (open circles) isotherms measured at 77 K for pristine and aged MUF-77-octyl under 40-50 % RH.



**Figure B.26**  $\text{CO}_2$  adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for pristine and aged MUF-77-octyl under 40-50 % RH.

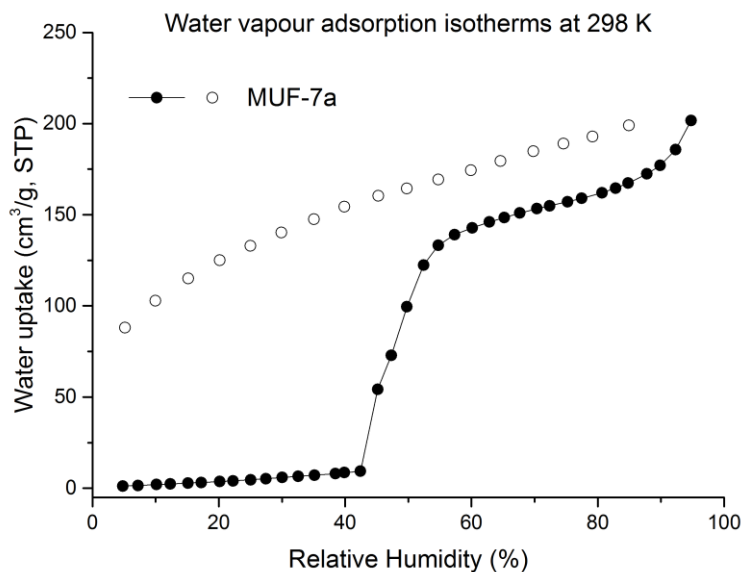


**Figure B.27** Nitrogen adsorption (filled circles) and desorption (open circles) isotherms measured at 77 K for pristine and aged MUF-77-decyl under 40-50 % RH. Due to extremely slow adsorption kinetics, data points below  $P/P_0 = 0.1$  for aged samples were not collected. Increased hysteresis for aged sample also indicates pore collapse.

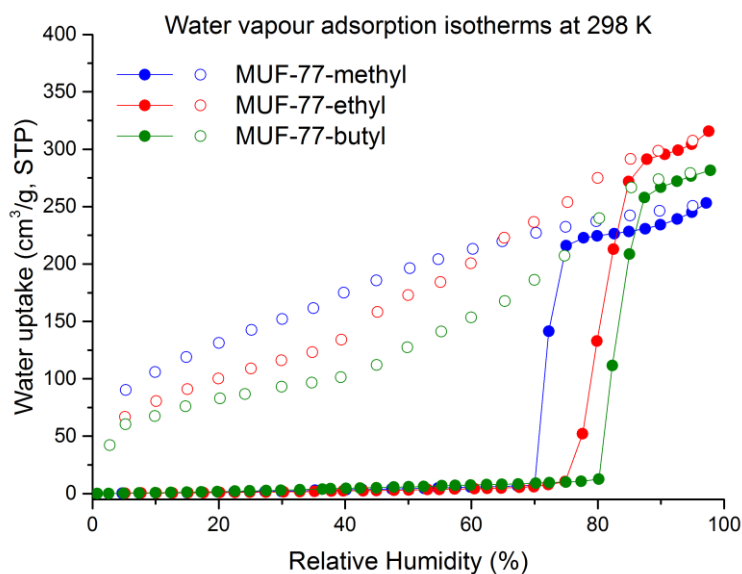


**Figure B.28** CO<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms measured at 273 K for pristine and aged MUF-77-decyl under 40-50 % RH.

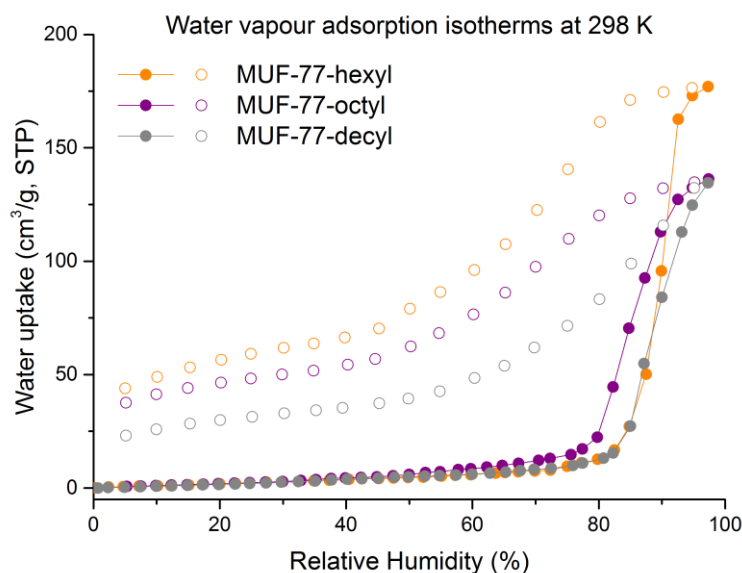
## Water vapor adsorption and desorption isotherms



**Figure B.29** Water vapour adsorption and desorption isotherms of MUF-7a.



**Figure B.30** Water vapour adsorption and desorption isotherms of MUF-77-methyl, -ethyl and -butyl.



**Figure B.31** Water vapour adsorption and desorption isotherms of MUF-77-hexyl, -octyl and -decyl.

## 7. The number of theoretical competing phases in multicomponent MOFs

To calculate theoretical number of competing phases during the synthesis of multicomponent MOFs where all ligands are topologically distinct, i.e., all ligands are different in their shapes and / or lengths, the following two assumptions are given to simplify the calculations. First, each ligand will form and only forms one phase (or one MOF) with metal or metal cluster. Second, any given combinations of different ligands will form and only form one phase (or one MOF) with metal or metal cluster. Thus, total number of possible phases ( $N_{\text{total}}$ ) during a synthesis with  $n$  distinct ligands can be described with the following equation:

$$N_{\text{total}} = \binom{n}{1} + \binom{n}{2} + \binom{n}{3} + \cdots \binom{n}{n} = \sum_{i=1}^n \binom{n}{i},$$

where  $\binom{n}{i}$  denotes the number of possible different phases generated by a number of  $i$  distinct ligands out of a total number of  $n$  distinct ligands, and the formula is known as:

$$\binom{n}{i} = \frac{n!}{i!(n-i)!}, \text{ for } 0 \leq i \leq n,$$

where  $n!$  denotes the fraction of  $n$ :

$$n! = n \times (n-1) \times (n-2) \times \cdots 2 \times 1.$$

Thus  $N_{\text{total}}$  can be deduced as:

$$N_{\text{total}} = \sum_{i=1}^n \frac{n!}{i!(n-i)!}.$$

Because there is only one possible phase comprising all  $n$  distinct ligands out of a total number of  $n$  distinct ligands,

$$\binom{n}{n} = \frac{n!}{n! (n - n)!} = 1.$$

The number of possible competing phases  $N$  is:

$$N = N_{total} - 1 = \sum_{i=1}^n \frac{n!}{i! (n - i)!} - 1.$$

As an example, the number of possible competing phases involving 5 distinct ligands is

$$\sum_{i=1}^5 \frac{5!}{i! (5 - i)!} - 1 = \frac{5!}{1! \times 4!} + \frac{5!}{2! \times 3!} + \frac{5!}{3! \times 2!} + \frac{5!}{4! \times 1!} + \frac{5!}{5! \times 0!} - 1 = 30.$$

Some numbers of possible competing phases in respect to the total number of topologically distinct ligands are listed in table B.5.

**Table B.5** Number of possible competing phases in multicomponent MOFs.

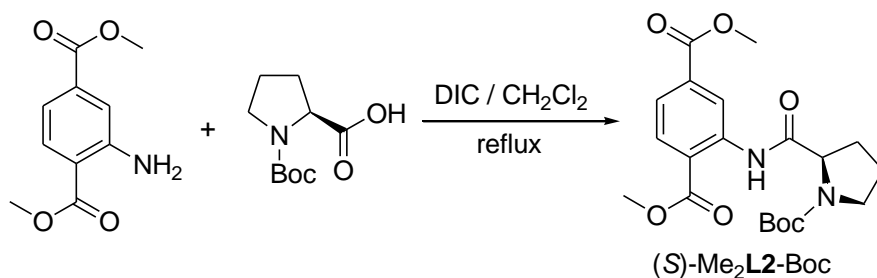
| Number of distinct ligands $n$ | Number of possible competing phases $N$ |
|--------------------------------|---|
| 1                              | 0                                       |
| 2                              | 2                                       |
| 3                              | 6                                       |
| 4                              | 14                                      |
| 5                              | 30                                      |
| 6                              | 62                                      |
| 7                              | 126                                     |
| 8                              | 254                                     |
| 9                              | 510                                     |
| 10                             | 1022                                    |

## Appendix C for Chapter 5

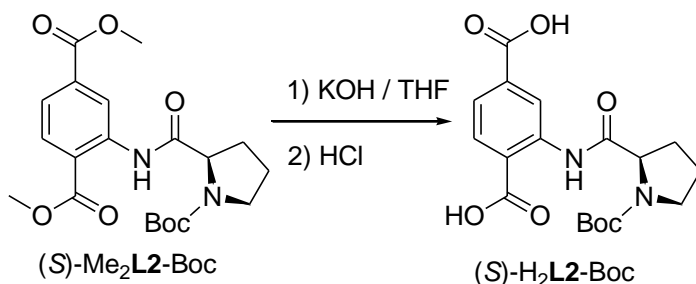
### Experimental Details and Supporting Information for Chapter 5

#### 1. Ligand synthesis

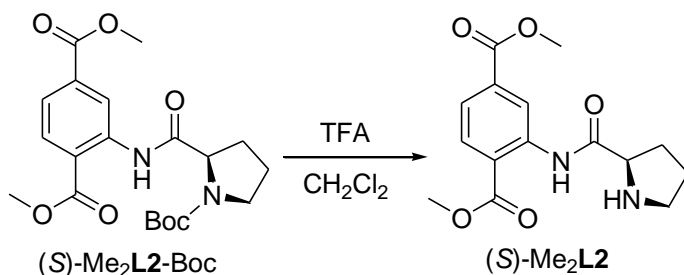
##### (*S*)-Me<sub>2</sub>L2-Boc and (*R*)-Me<sub>2</sub>L2-Boc



(*S*)-Me<sub>2</sub>L2-Boc: To a solution of *N*-Boc-L-Proline (4.74 g, 22.0 mmol) and DMAP (69 mg, 0.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), *N,N'*-diisopropylcarbodiimide (1.72 mL, 11.0 mmol) was added dropwise at 0 °C over an hour. The resulting suspension was gradually added to a solution of dimethyl aminoterephthalate (2.09g, 10.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at 0 °C. The resulting mixture was then refluxed for 3 days. The reaction mixture was concentrated to ~25 mL by evaporating CH<sub>2</sub>Cl<sub>2</sub> *in vacuo* and the insoluble material was removed by filtration. The remaining CH<sub>2</sub>Cl<sub>2</sub> was removed under reduced pressure from the filtrate to afford a pink oil. To this oil, small amount of 96 % ethanol was added and the product was crystallized as large block colorless crystals. Yield: 3.36g (57 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, complicated by two conformers): δ 1.35-1.50 (s, s, 9H), 1.92-1.96 (m, 2H), 2.19-2.32 (m, 2H), 3.49-3.75 (m, 2H), 3.94 (s, 6H), 4.32-4.47 (s, s, 1 H), 7.75 (s, s, 1H), 8.09 (s, s, 1H), 9.39 (s, 1H), 11.45-11.52 (s, s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, complicated by two conformers): δ 23.97, 24.52, 28.38, 28.58, 30.55, 31.69, 46.99, 47.32, 52.66, 52.96, 62.22, 62.82, 80.54, 118.71, 121.16, 121.44, 123.59, 130.92, 131.18, 135.52, 141.04, 141.27, 154.39, 155.26, 166.29, 167.77, 172.19, 172.69 ppm. ES-MS (positive mode, CH<sub>3</sub>OH): *m/z* = 430.11 ([C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>7</sub>Na]<sup>+</sup>, calcd. 429.16). HPLC: Daicel Chiralpak AS. Hexane / *i*-PrOH, 95 : 5, 1 mL min<sup>-1</sup>, 254 nm: *t*R = 15.2 min. *e.e.* = 100 %. (*R*)-Me<sub>2</sub>L2-Boc was prepared with the same procedure with its <sup>1</sup>H NMR data identical to the *S* enantiomer. *t*R = 11.3 min. *e.e.* = 100 %. Alternative HPLC condition: Daicel Chiralpack AS. Hexane / *i*-PrOH, 90 : 10, 1 mL min<sup>-1</sup>, 254 nm: *t*R (*S* enantiomer) = 10.1 min, *t*R (*R* enantiomer) = 7.7 min.

**(S)-H<sub>2</sub>L2-Boc**

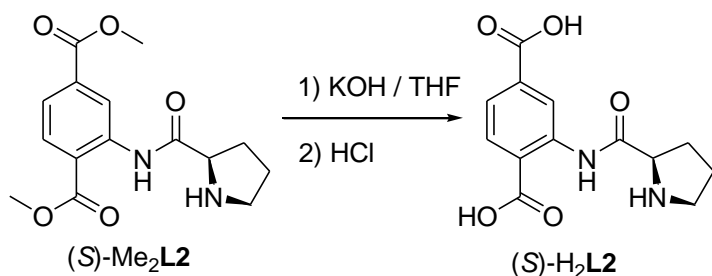
(S)-Me<sub>2</sub>L<sub>2</sub>-Boc (1.076 g, 2.647 mmol) was suspended in a 1 : 1 (v/v) mixture of THF and 1 M aq. KOH (50 mL). The suspension was heated to 50 °C and the reaction was monitored by TLC. Reaction was completed in 3 hours and THF was removed *in vacuo*. The remaining solution was acidified with 1 M aq. HCl to pH = 2. The white precipitate was isolated by filtration and washed with H<sub>2</sub>O then dried under dynamic vacuum. Yield: 0.923 g (92%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, complicated by two conformers): δ 1.24-1.41 (s, s, 9H), 1.83-1.87 (m, 2H), 1.95-1.99 (m, 1H), 2.20-2.32 (m, 1H) 3.39-3.44 (m, 1H), 3.49-3.55 (m, 1H), 4.16-4.20 (m, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 9.16-9.20 (s, s, 1H), 11.7 (s, 1H), 11.3-14.1 (s, s, br, 2H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 23.28, 23.94, 27.83, 28.02, 30.05, 30.95, 46.50, 46.77, 61.81, 62.07, 79.03, 79.31, 120.08, 123.13, 131.42, 135.47, 140.52, 153.06, 154.02, 166.48, 168.96, 169.08, 171.77, 172.00 ppm. <sup>13</sup>C NMR (100 MHz, KOH / D<sub>2</sub>O / dioxane): δ 24.23, 24.61, 28.17, 28.33, 30.94, 31.55, 47.39, 47.91, 63.38, 82.59, 121.09, 121.14, 124.69, 127.62, 131.31, 137.86, 140.08, 156.41, 157.11, 174.39, 174.66, 175.13 ppm. ES-MS (negative mode, CH<sub>3</sub>OH): *m/z* = 378.04 ([C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>7</sub>]<sup>−</sup>, calcd. 377.13).

**(S)-Me<sub>2</sub>L<sub>2</sub> and (R)-Me<sub>2</sub>L<sub>2</sub>**

(S)-Me<sub>2</sub>L<sub>2</sub>: To a solution of (S)-Me<sub>2</sub>L<sub>2</sub>-Boc (1.204 g, 2.962 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL), trifluoroacetic acid (25 mL) was added dropwise at 0 °C. After 10 minutes, the reaction mixture was allowed to warm to room temperature and reacted for a further 30 minutes. Solvents were removed under reduced pressure and the remaining material was partitioned

between  $\text{CH}_2\text{Cl}_2$  and saturated aq.  $\text{NaHCO}_3$ . The organic layer was dried over  $\text{Na}_2\text{SO}_4$  to afford the product as a white solid after evaporating the solvent from the filtrate. Yield: 0.857 g (95 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.71-1.84 (m, 2H), 2.03-2.10 (m, 1H), 2.19-2.27 (m, 1H), 3.05-3.10 (m, 1H), 3.13-3.18 (m, 1H), 3.92-3.96 (m, 7H), 7.55 (dd,  $J = 8.2$  Hz, 1.5 Hz, 1H), 8.08 (d,  $J = 8.3$  Hz, 1H), 9.39 (d,  $J = 1.4$  Hz, 1H), 12.2 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.33, 31.28, 47.55, 52.61, 52.72, 61.95, 119.52, 121.61, 123.43, 131.16, 135.18, 140.81, 166.38, 167.38, 175.18 ppm. ES-MS (positive mode,  $\text{CH}_3\text{OH}/\text{TFA}$ ):  $m/z = 307.67$  ( $[\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_5]^+$ , calcd. 307.13). HPLC: Daicel Chiralpak AD. Hexane / *i*-PrOH, 45 : 55 to 20 : 80 gradient,  $0.75 \text{ mL min}^{-1}$ , 254 nm:  $t_R = 13.3$  min. *e.e.* = 100 %. (*R*)- $\text{Me}_2\text{L2}$  was prepared with the same procedure with its  $^1\text{H}$  NMR data identical to *S* enantiomer.  $t_R = 7.8$  min. *e.e.* = 100 %.

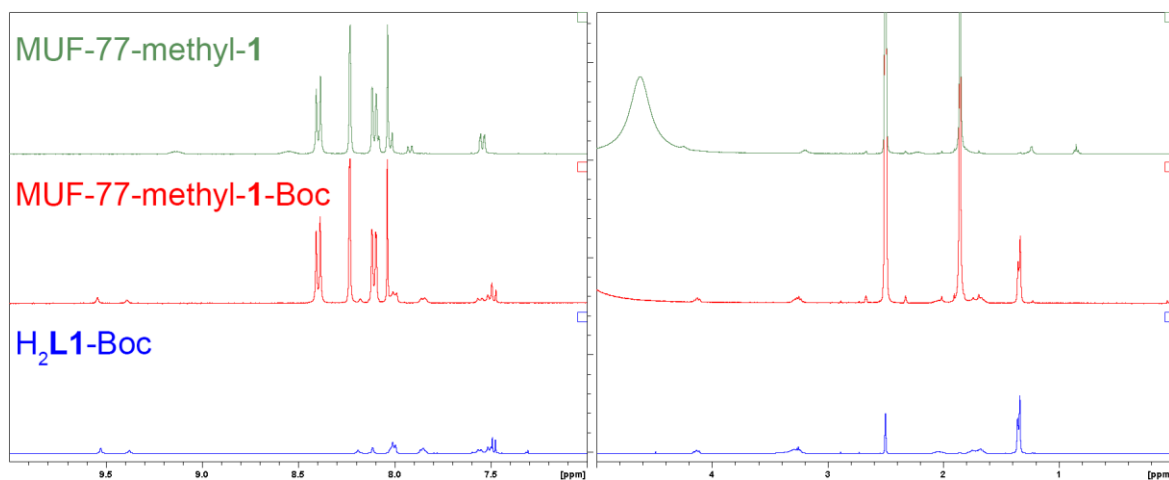
### (*S*)- $\text{H}_2\text{L2}$



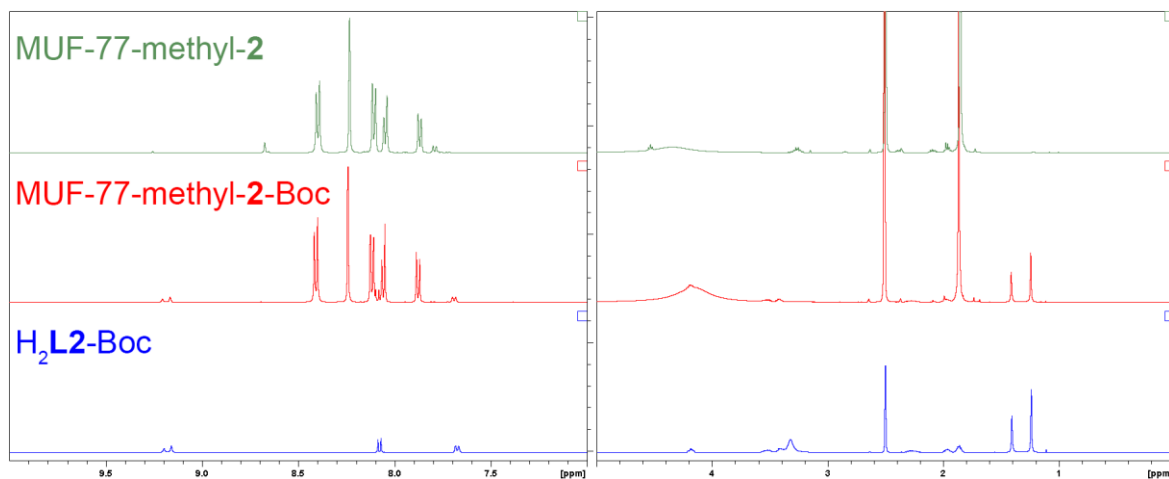
(*S*)- $\text{Me}_2\text{L2}$  (225 mg, 0.735 mmol) was suspended in a 1 : 1 (v/v) mixture of THF and 1 M aq. KOH (10 mL). The suspension was refluxed for 14 hours. After the reaction, THF was removed *in vacuo*. The remaining solution was acidified with 3 M then 0.2 M aq. HCl to pH = 2. The yellow precipitate was isolated by filtration and washed with  $\text{H}_2\text{O}$  and dried under dynamic vacuum to afford the product as its hydrochloric salt. Yield: 134.3 mg (58%).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  1.94-2.00 (m, 2H), 2.03-2.10 (m, 1H), 2.34-2.41 (m, 1H), 3.21-3.31 (m, 2H) 4.53 (t,  $J = 7.6$  Hz, 1H), 7.64 (dd,  $J = 8.2$  Hz, 1.3 Hz, 1H), 8.06 (d,  $J = 7.9$  Hz, 1H), 8.9 (s, 1H).  $^{13}\text{C}$  NMR (175 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  23.84, 29.02, 45.46, 60.90, 119.68, 123.04, 131.13, 132.30, 139.81, 167.11, 168.37 ppm. ES-MS (negative mode,  $\text{CH}_3\text{OH}$ ):  $m/z = 277.86$  ( $[\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_5]^-$ , calcd. 277.08). ES-MS (positive mode,  $\text{CH}_3\text{OH}$ ):  $m/z = 279.38$  ( $[\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_5]^+$ , calcd. 279.10).



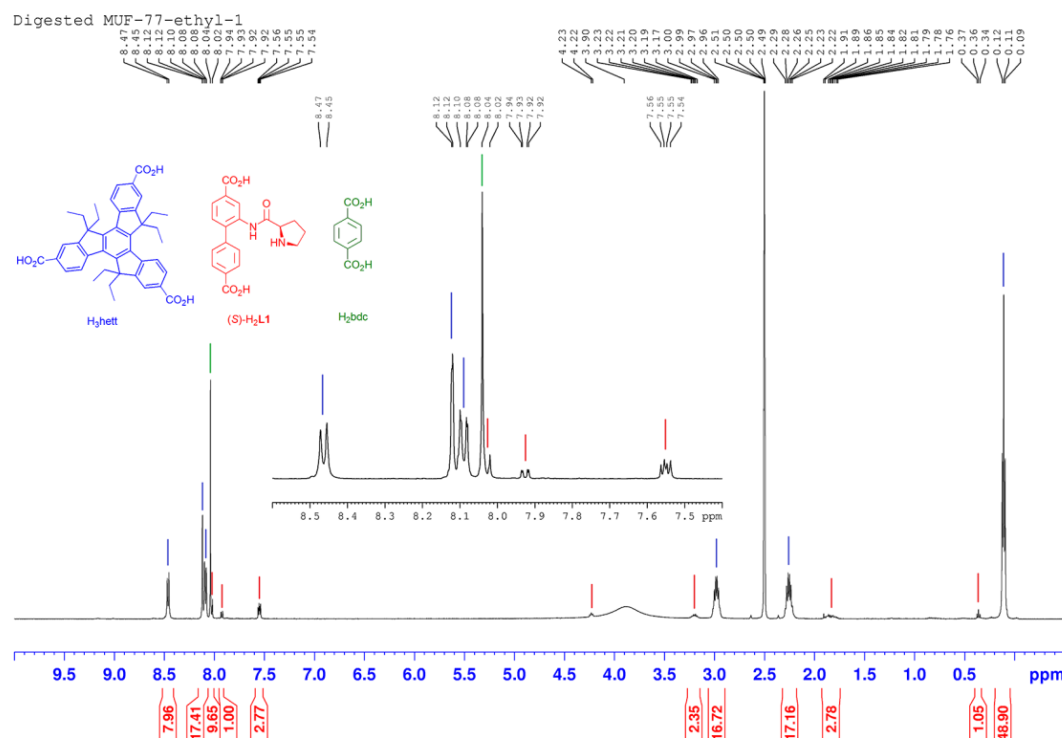
## 2. $^1\text{H}$ NMR of digested MOFs



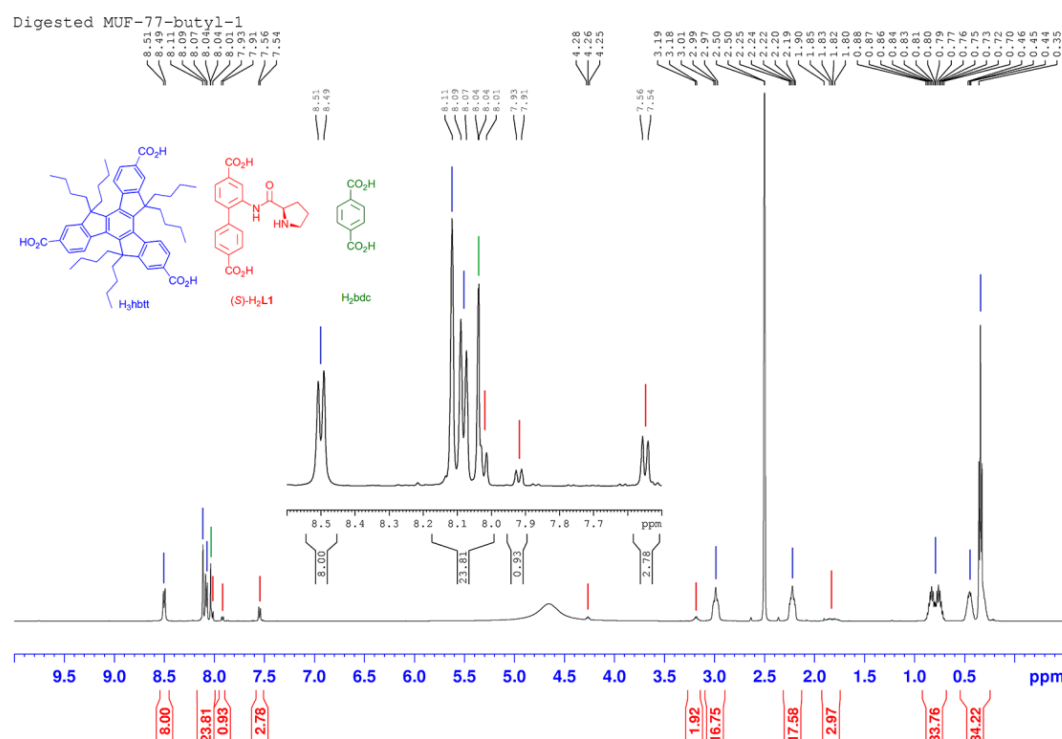
**Figure C.1** Overlay of  $^1\text{H}$  NMR spectra of  $\text{H}_2\text{L1-Boc}$ , MUF-77-methyl-1-Boc and MUF-77-methyl-1 showing the Boc protecting group was completely removed after heating MUF-77-methyl-1-Boc at 200  $^\circ\text{C}$  for 10 hours under dynamic vacuum.



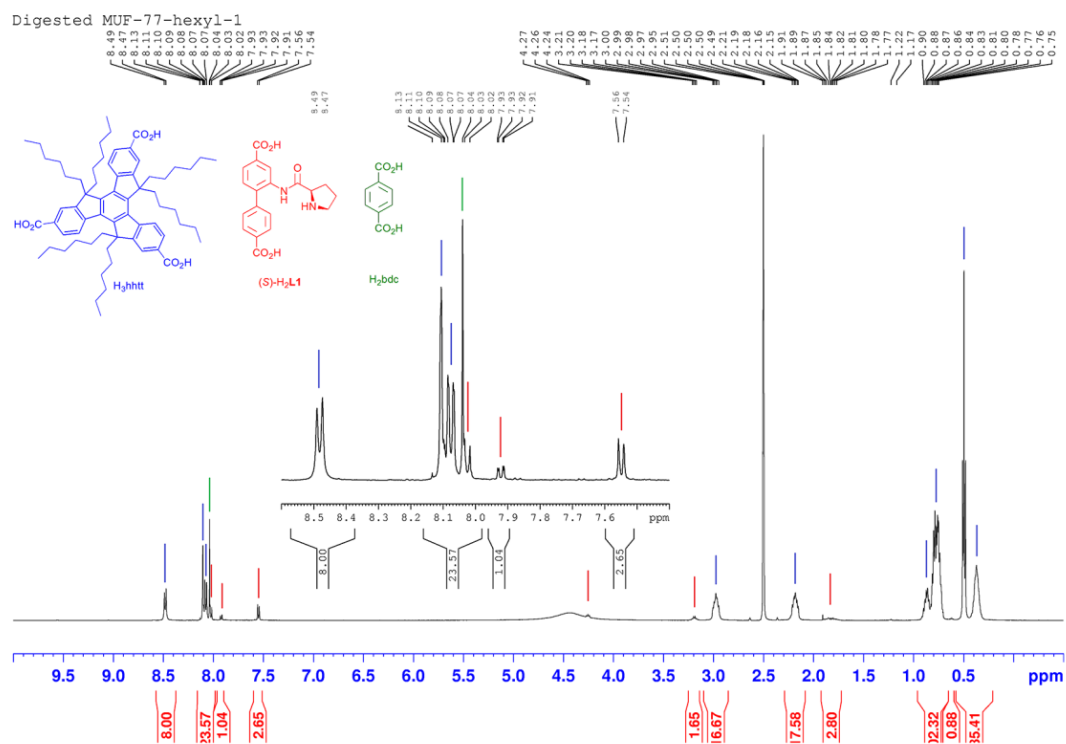
**Figure C.2** Overlay of  $^1\text{H}$  NMR spectra of  $\text{H}_2\text{L2-Boc}$ , MUF-77-methyl-2-Boc and MUF-77-methyl-2 showing the Boc protecting group was completely removed after heating MUF-77-methyl-2-Boc at 200  $^\circ\text{C}$  for 10 hours under dynamic vacuum.



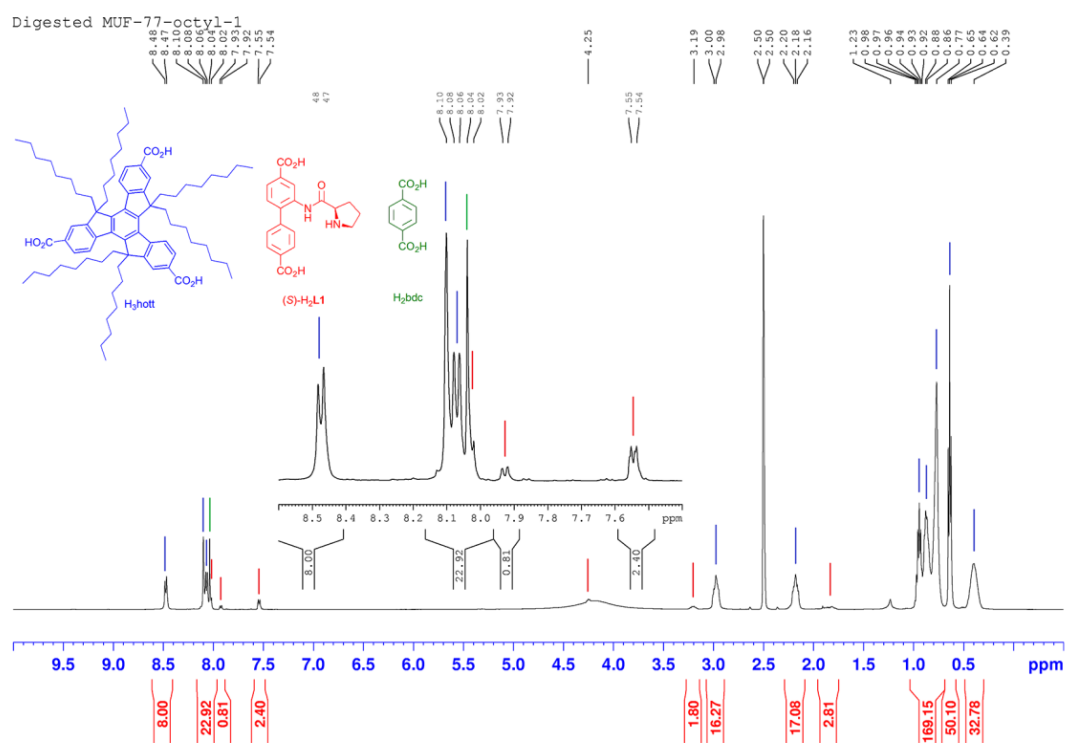
**Figure C.3**  $^1H$  NMR spectrum of digested MUF-77-ethyl-1 showing the Boc group was completely removed after being heated to 200 °C for 10 hours under dynamic vacuum.



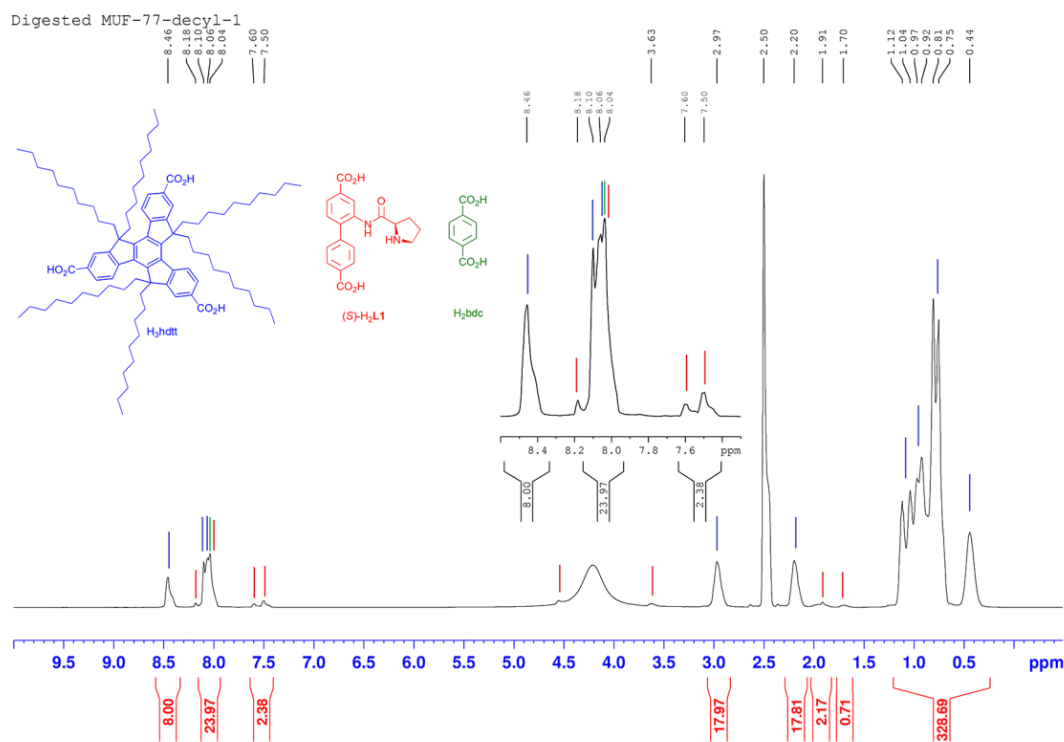
**Figure C.4**  $^1H$  NMR spectrum of digested MUF-77-butyl-1 showing the Boc group was completely removed after being heated to 200 °C for 10 hours under dynamic vacuum.



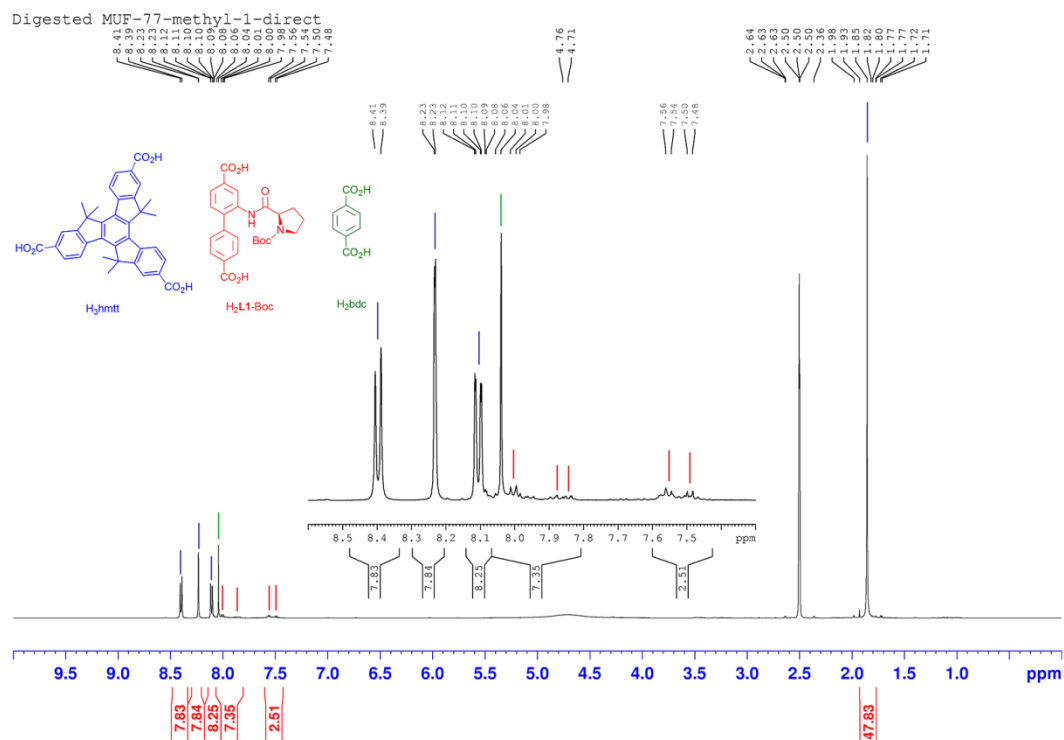
**Figure C.5**  $^1H$  NMR spectrum of digested MUF-77-hexyl-1 showing the Boc group was completely removed after being heated to 200 °C for 20 hours under dynamic vacuum.



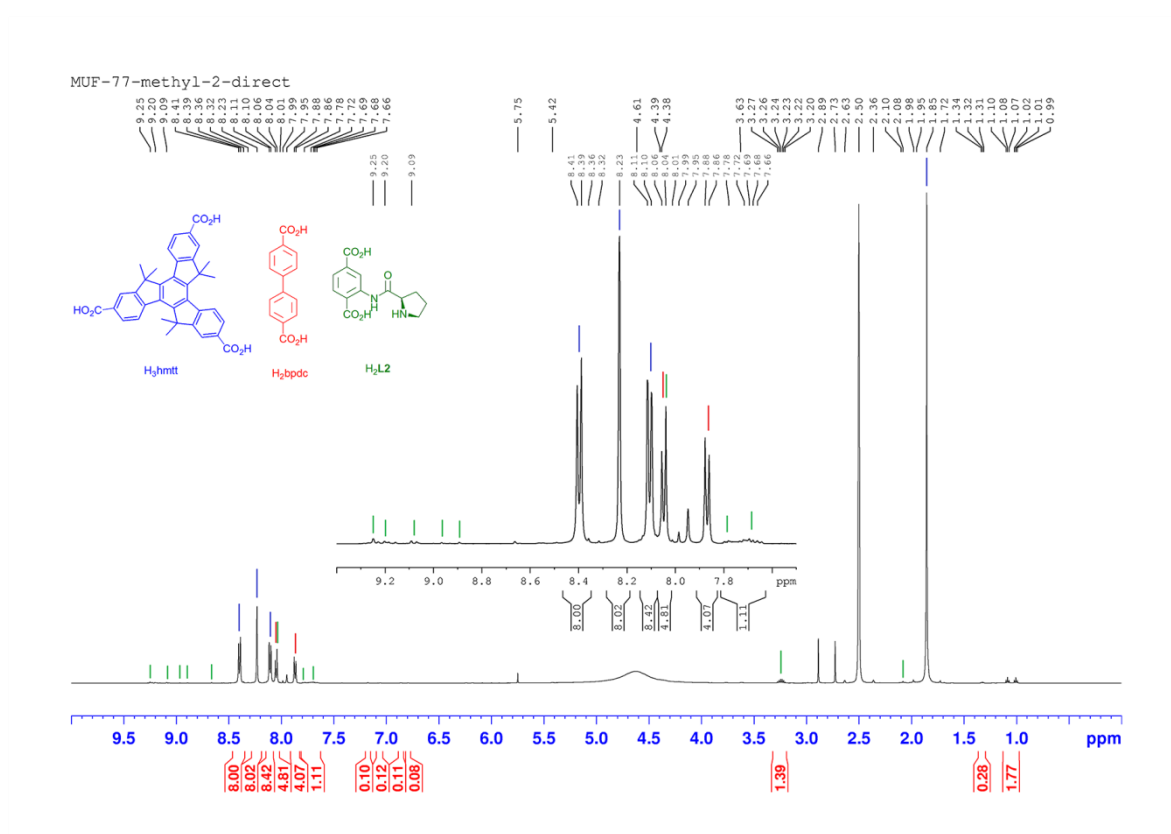
**Figure C.6**  $^1H$  NMR spectrum of digested MUF-77-octyl-1 showing the Boc group was completely removed after being heated to 200 °C for 20 hours under dynamic vacuum.



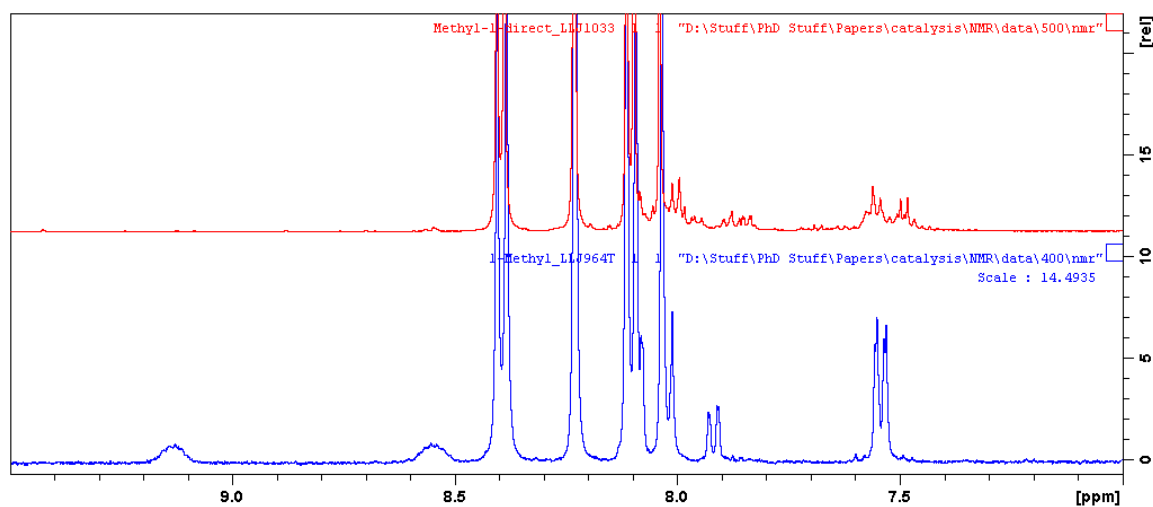
**Figure C.7**  $^1H$  NMR spectrum of digested MUF-77-decyl-1 showing the Boc group was completely removed after being heated to 200 °C for 20 hours under dynamic vacuum.



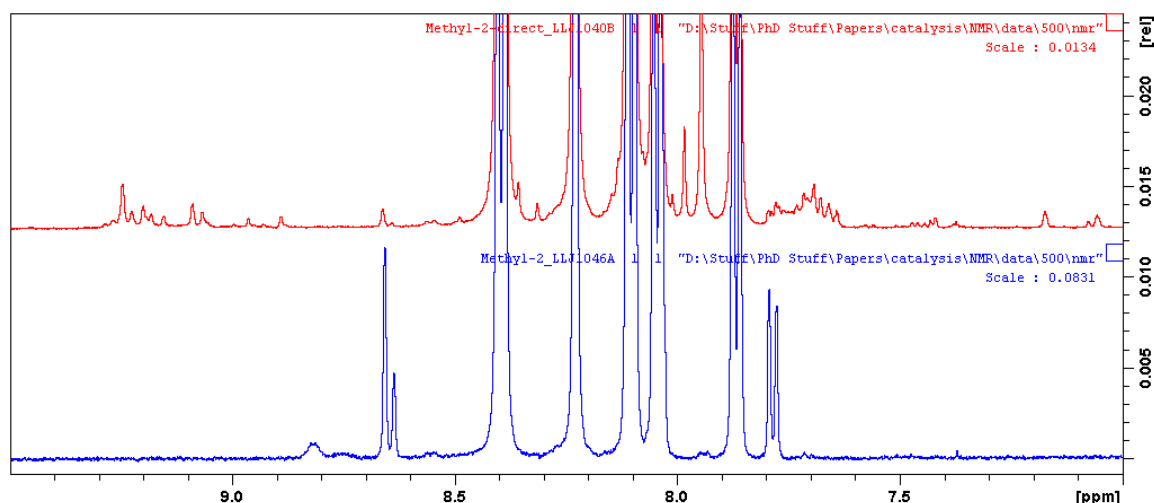
**Figure C.8**  $^1H$  NMR spectrum of digested MUF-77-methyl-1-direct.



**Figure C.9**  $^1\text{H}$  NMR spectrum of digested MUF-77-methyl-2-direct.



**Figure C.10** Overlaid  $^1\text{H}$  NMR spectra of digested MUF-77-methyl-1 (blue) and MUF-77-methyl-1-direct (red) showing their aromatic regions. The aromatic proton peaks of **L1** in MUF-77-methyl-1-direct are complicated, indicating **L1** could undergo side reactions during the MOF synthesis without BOC protecting group.



**Figure C.11** Overlaid  $^1\text{H}$  NMR spectra of digested MUF-77-methyl-2 (blue) and MUF-77-methyl-2-direct (red) showing their aromatic regions. The aromatic proton peaks of **L2** in MUF-77-methyl-2-direct are complicated, indicating **L2** could undergo side reactions during the MOF synthesis without BOC protecting group.

### 3. Crystallography of (*S*)-Me<sub>2</sub>L2-Boc and (*R*)-Me<sub>2</sub>L2-Boc

Data collections were carried out at  $-120\text{ }^\circ\text{C}$ . All carbon, oxygen and nitrogen atoms were found in the electron density difference maps and refined anisotropically. Due to the excellent data quality, all hydrogen atoms were found in the electron density difference maps and refined isotropically. Totally refined hydrogen atoms aroused some alerts from the checkcif reports. To eliminate these alerts, only six hydrogen atoms on the two *tert*-butyl groups of (*R*)-Me<sub>2</sub>L2-Boc were placed on their calculated positions. Extinction corrections were used for both structures.

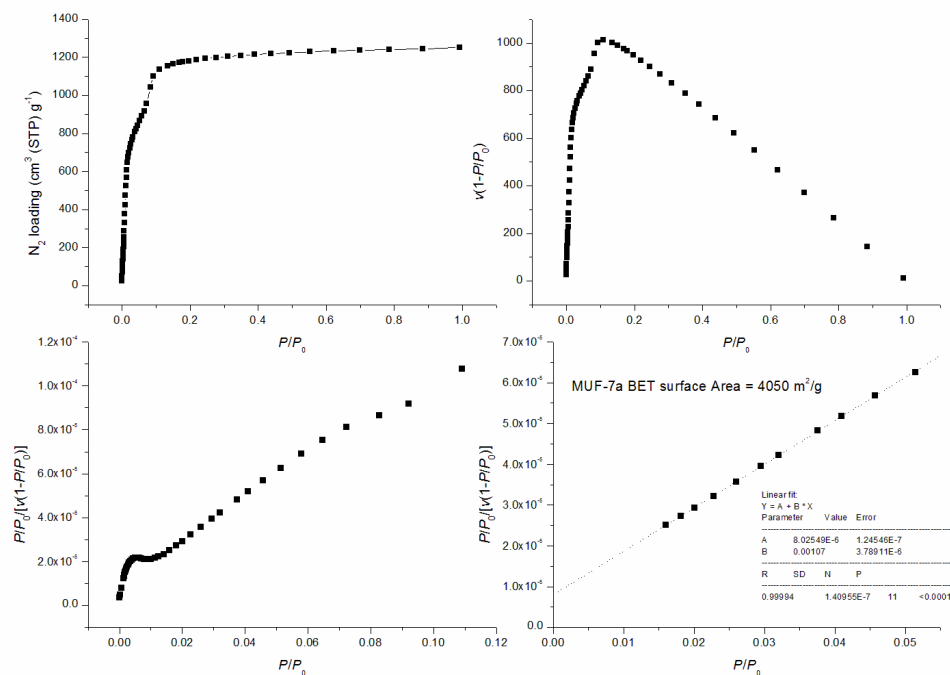
**Table C.1** Crystallography data summary for (*R*)-Me<sub>2</sub>L2-Boc and (*S*)-Me<sub>2</sub>L2-Boc

| Compound  | ( <i>R</i> )-Me <sub>2</sub> L2-Boc                             | ( <i>S</i> )-Me <sub>2</sub> L2-Boc                             |
|---|---|---|
| Formula   | C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O <sub>7</sub>   | C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O <sub>7</sub>   |
| Formula weight  | 406.43  | 406.43  |
| Crystal size (mm)                                     | 0.587 × 0.432 × 0.355   | 1.312 × 1.163 × 0.433   |
| Temperature (K)                                       | 153(2)  | 153(2)  |
| Wavelength (Å)  | 1.54178   | 1.54178   |
| Crystal system  | orthorhombic  | orthorhombic  |
| Space group   | <i>C</i> 222 <sub>1</sub>                                       | <i>C</i> 222 <sub>1</sub>                                       |
| Unit cell lengths (Å)                                 | <i>a</i> = 12.0860(2)   | <i>a</i> = 12.1049(3)   |
|   | <i>b</i> = 15.1870(3)   | <i>b</i> = 15.1987(3)   |
|   | <i>c</i> = 22.6210(16)  | <i>c</i> = 22.6397(16)  |
| Unit cell volume (Å <sup>3</sup> )                    | 4152.1(3)   | 4165.2(3)   |
| <i>Z</i>  | 8   | 8   |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )        | 1.300   | 1.296   |
| $\mu$ (mm <sup>-1</sup> )                             | 0.826   | 0.824   |
| <i>F</i> (000)  | 1728  | 1728  |
| Reflns coll./unique, <i>R</i> <sub>int</sub>          | 20026 / 4011, 0.0347  | 16530 / 3980, 0.0428  |
| Theta range for data                                  | 7.0° < $\theta$ < 72° or $6.3\text{Å} > d > 0.81\text{Å}$       | 7.0° < $\theta$ < 72° or $6.3\text{Å} > d > 0.81\text{Å}$       |
| Index ranges  | -14 ≤ <i>h</i> ≤ 10, -18 ≤ <i>k</i> ≤ 18, -27 ≤ <i>l</i> ≤ 24   | -15 ≤ <i>h</i> ≤ 36, -36 ≤ <i>k</i> ≤ 33, -36 ≤ <i>l</i> ≤ 21   |
| Completeness  | 99.7%   | 99.6%   |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>     | 0.81, 1.00  | 0.75, 1.00  |
| R indices for data with <i>I</i> > 2σ( <i>I</i> )     | <i>R</i> <sub>1</sub> = 0.0296; <i>wR</i> <sub>2</sub> = 0.0699 | <i>R</i> <sub>1</sub> = 0.0307; <i>wR</i> <sub>2</sub> = 0.0714 |
| R indices for all data                                | <i>R</i> <sub>1</sub> = 0.0342; <i>wR</i> <sub>2</sub> = 0.0741 | <i>R</i> <sub>1</sub> = 0.0360; <i>wR</i> <sub>2</sub> = 0.0849 |
| Absolute structure parameter                          | 0.02(5)   | 0.01(7)   |
| Extinction coefficient                                | 0.00054(7)  | 0.00111(9)  |
| Largest difference peak and hole (e Å <sup>-3</sup> ) | 0.18 / -0.14  | 0.17 / -0.19  |

## Appendix D Additional Isotherm Plots

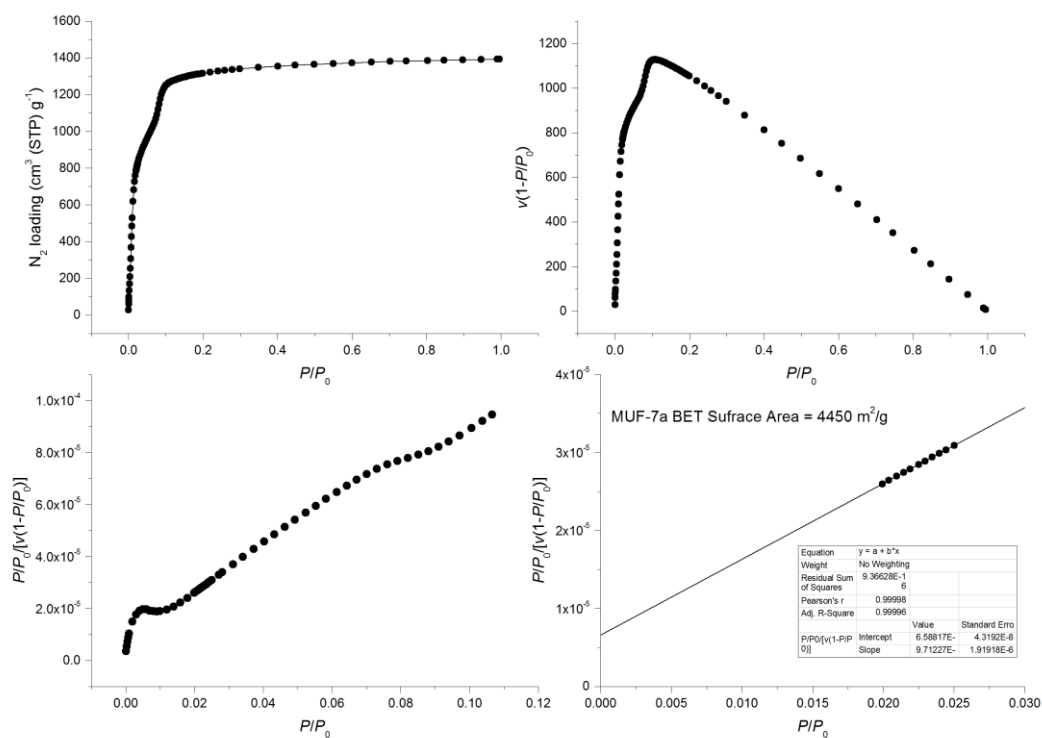
### Isotherm Fitting Figures and Parameters for Chapter 2-4

#### 1. BET surface area plots

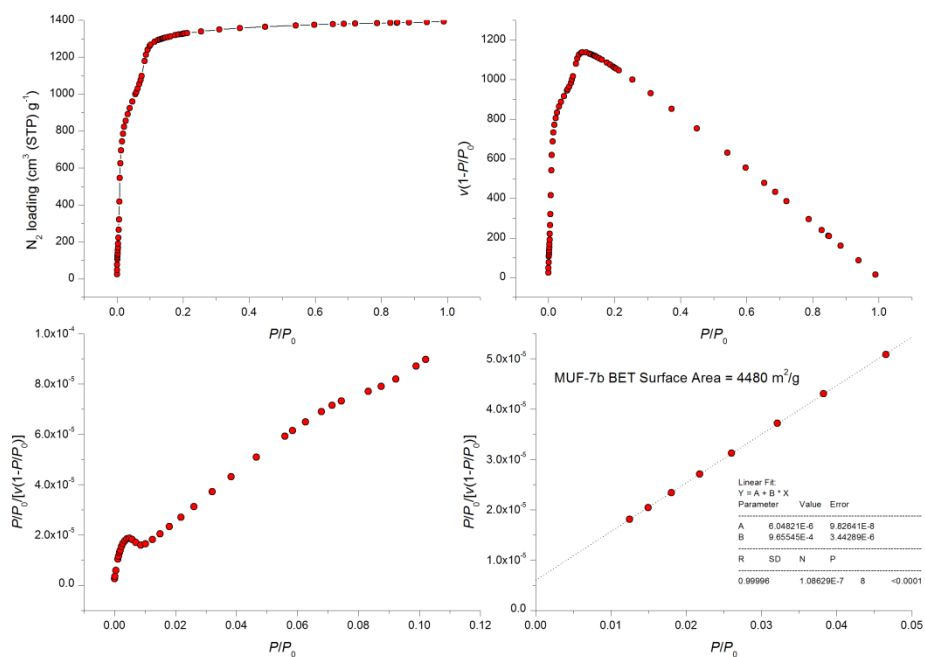


**Figure D.1**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-7a synthesized in DEF.

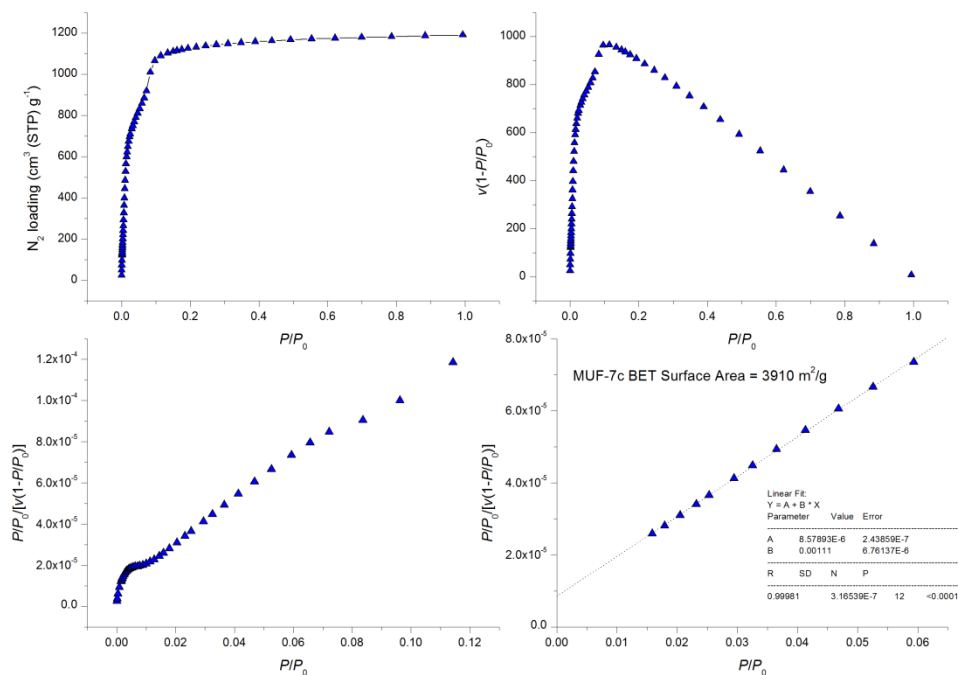




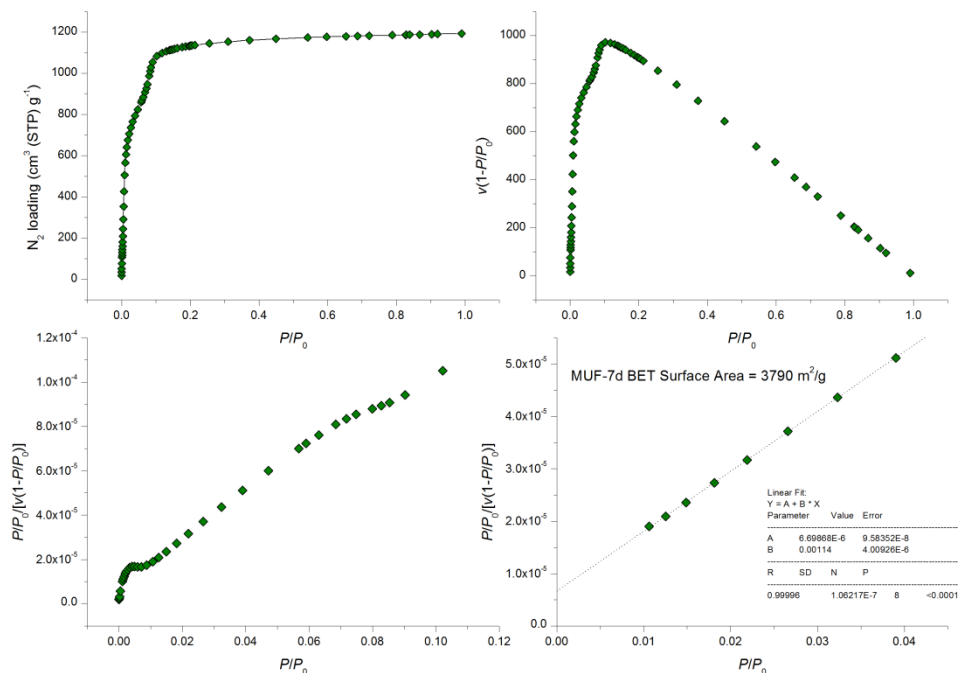
**Figure D.2** N<sub>2</sub> adsorption isotherm at 77 K and BET surface area plots for MUF-7a synthesized in DMF.



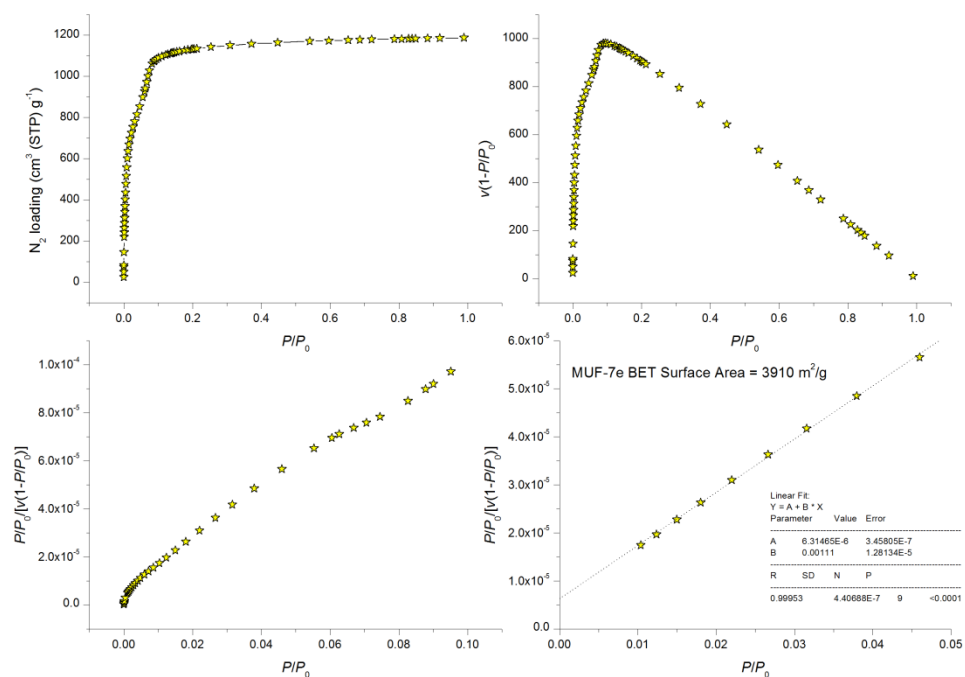
**Figure D.3** N<sub>2</sub> adsorption isotherm at 77 K and BET surface area plots for MUF-7b.



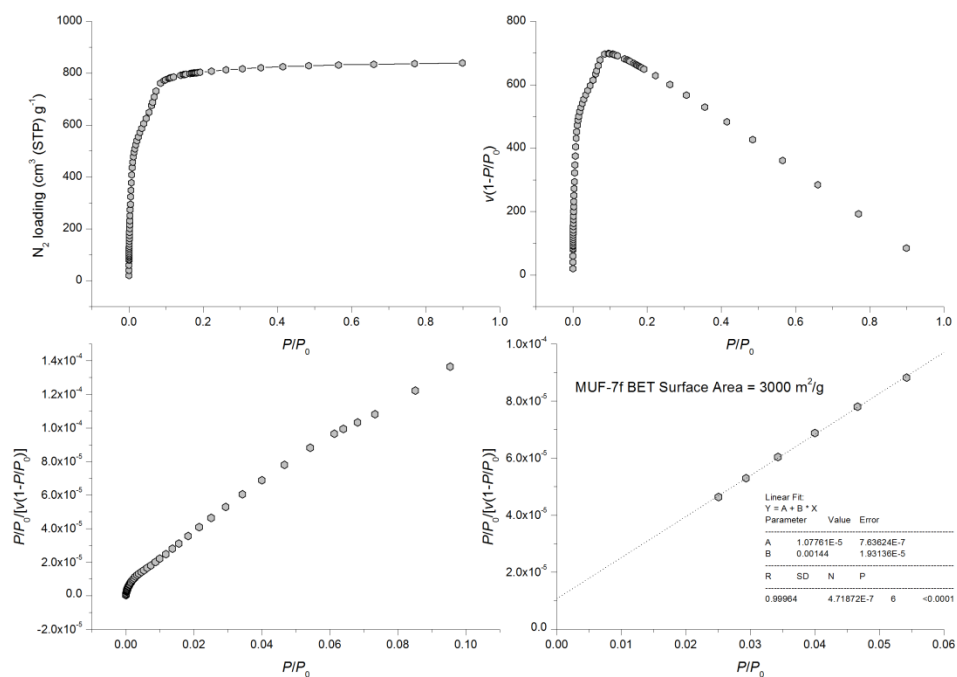
**Figure D.4**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-7c.



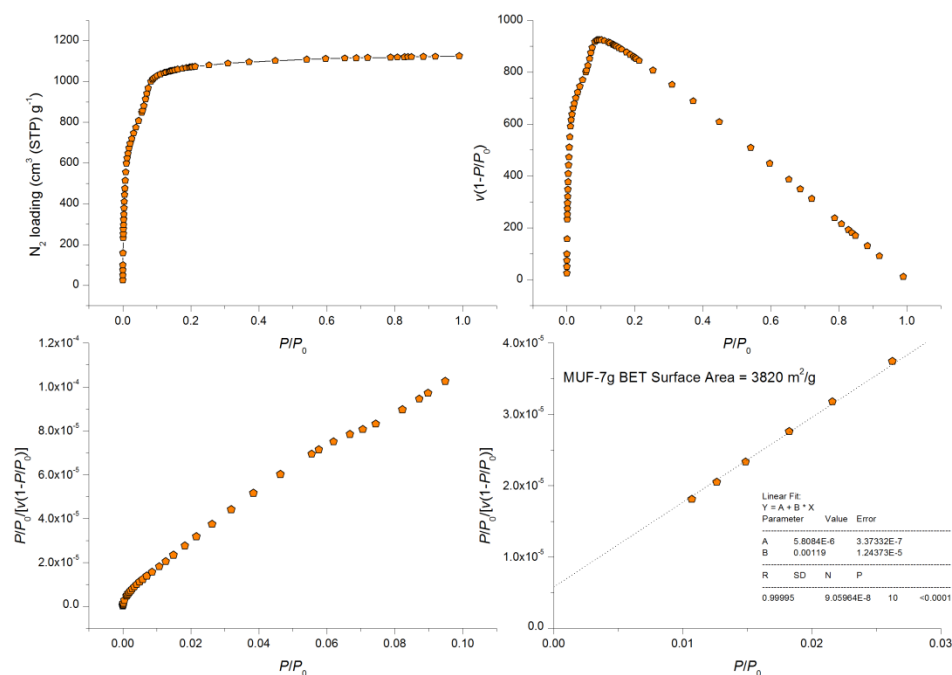
**Figure D.5**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-7d.



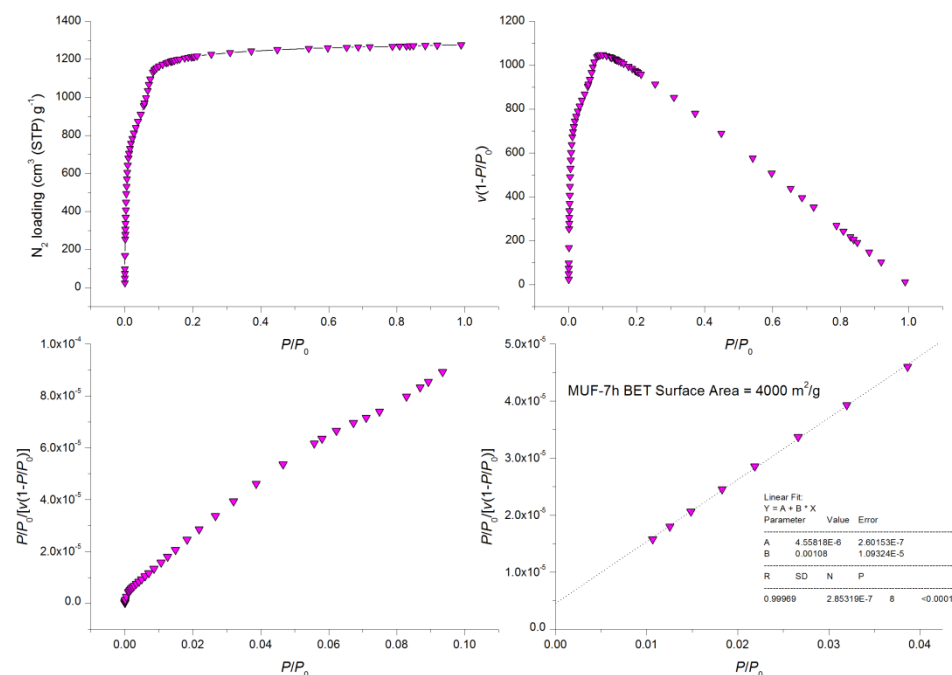
**Figure D.6** N<sub>2</sub> adsorption isotherm at 77 K and BET surface area plots for MUF-7e.



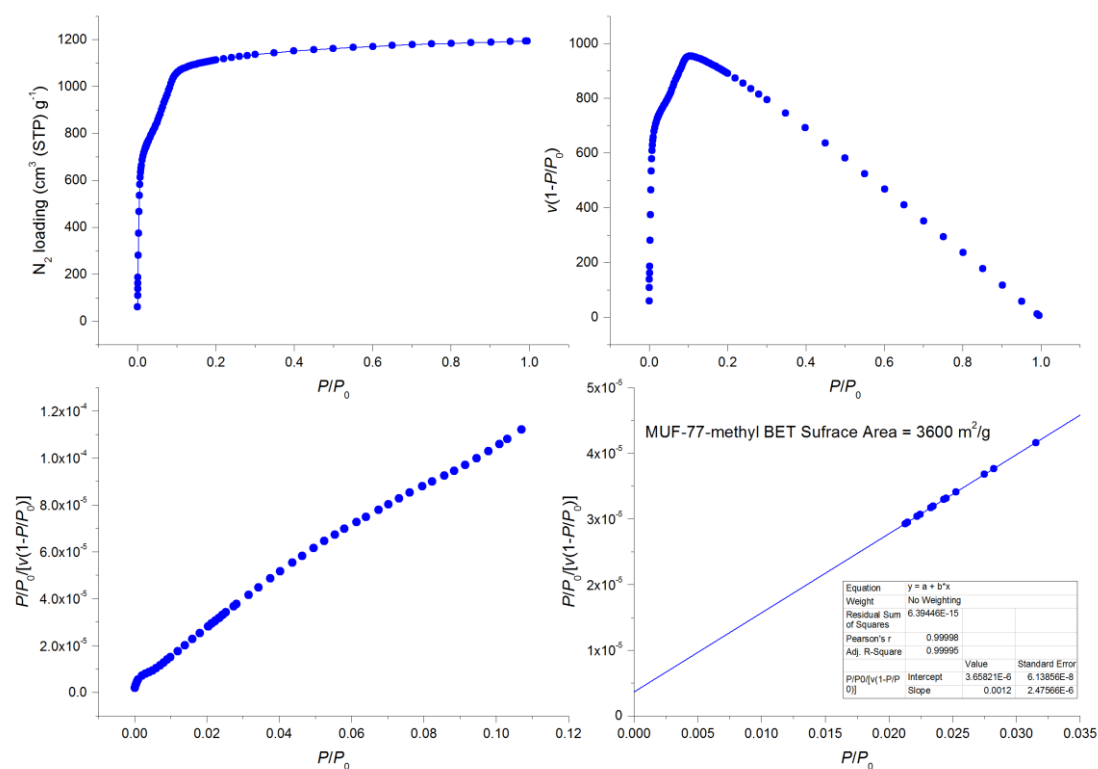
**Figure D.7** N<sub>2</sub> adsorption isotherm at 77 K and BET surface area plots for MUF-7f.



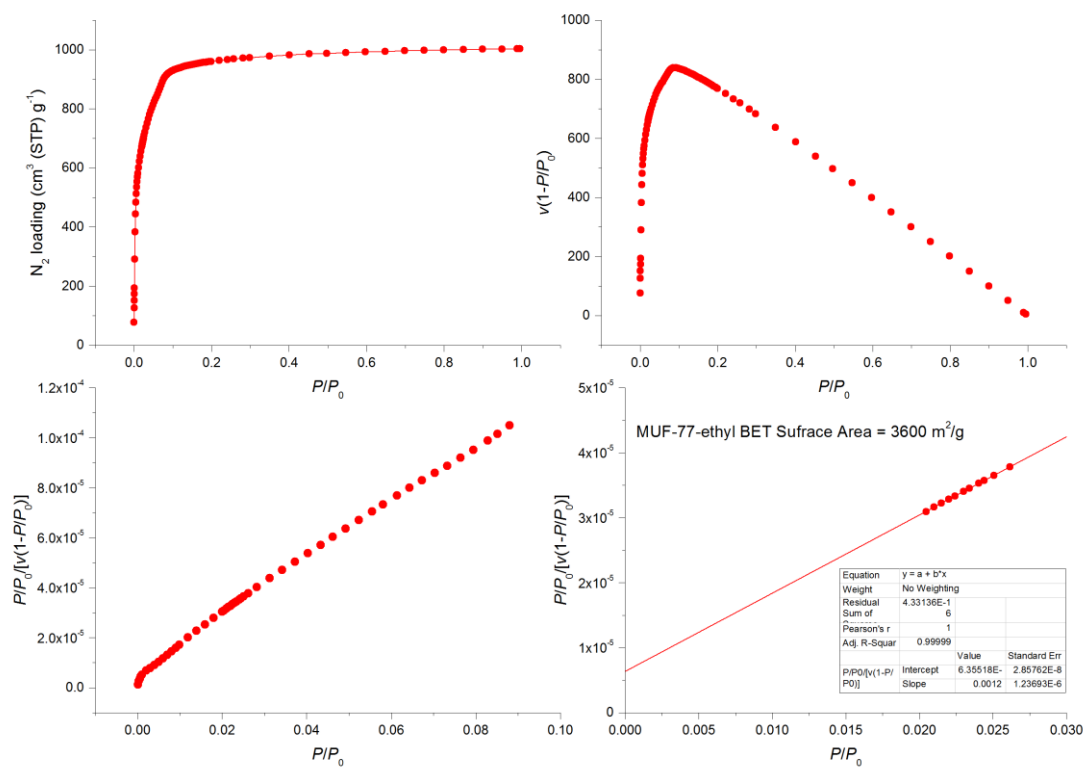
**Figure D.8** N<sub>2</sub> adsorption isotherm at 77 K and BET surface area plots for MUF-7g.



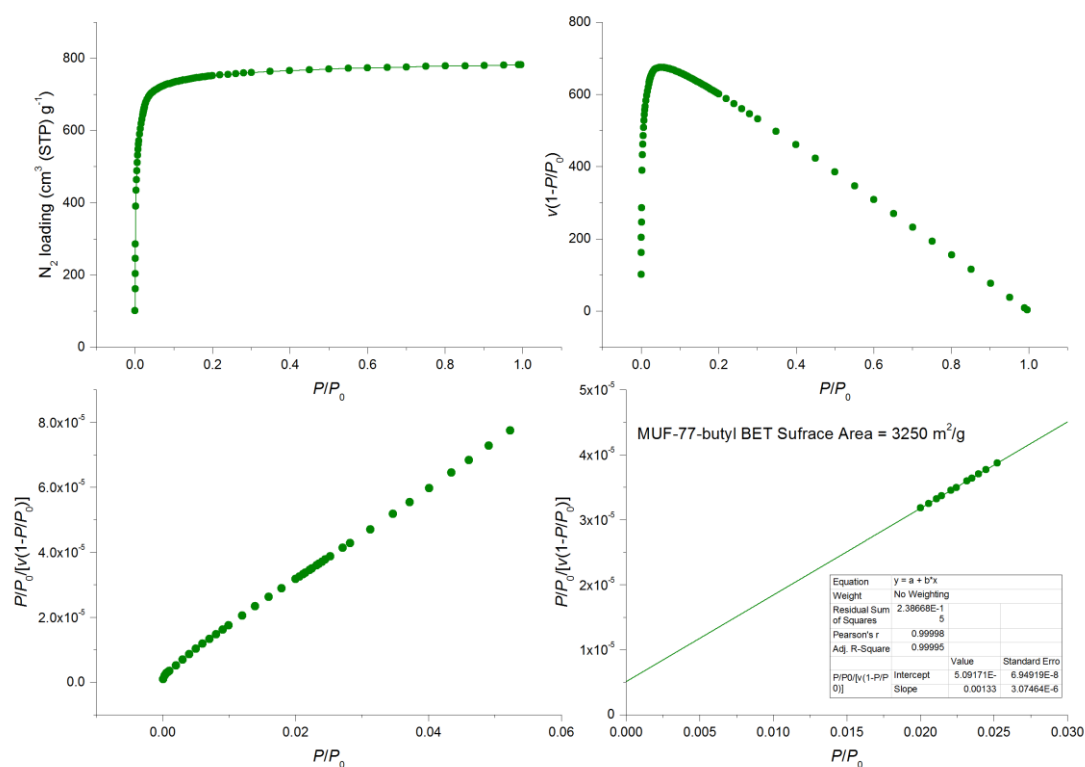
**Figure D.9** N<sub>2</sub> adsorption isotherm at 77 K and BET surface area plots for MUF-7h.



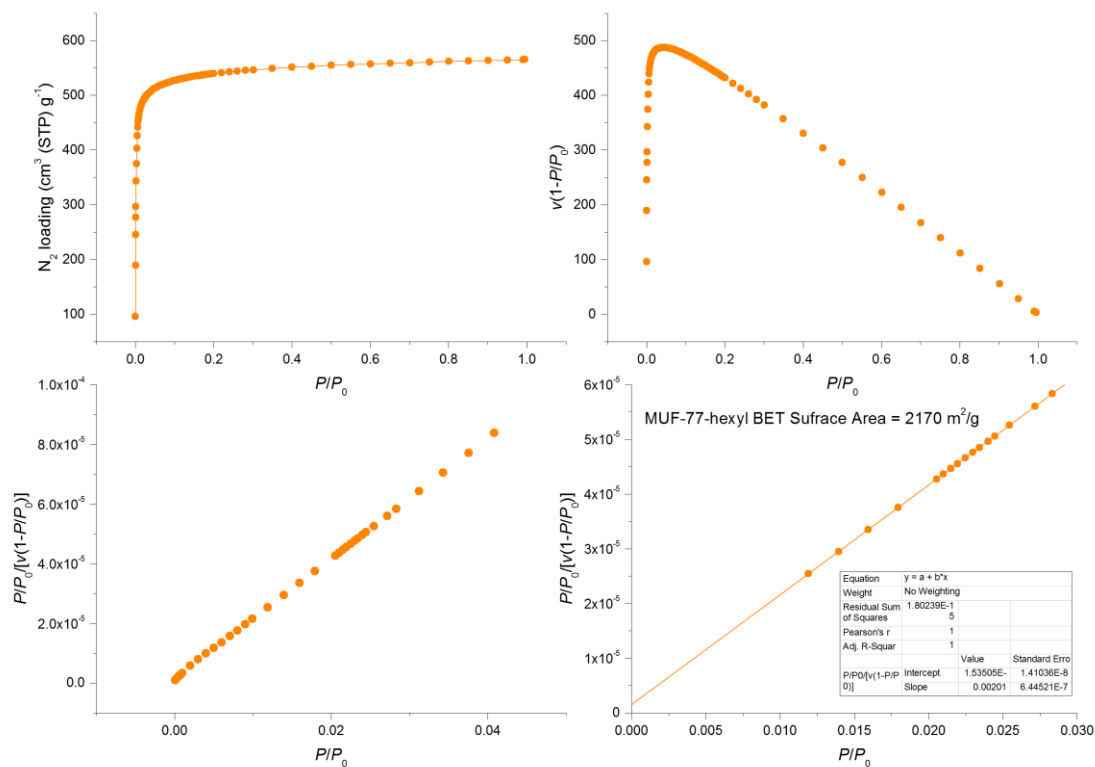
**Figure D.10**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-77-methyl.



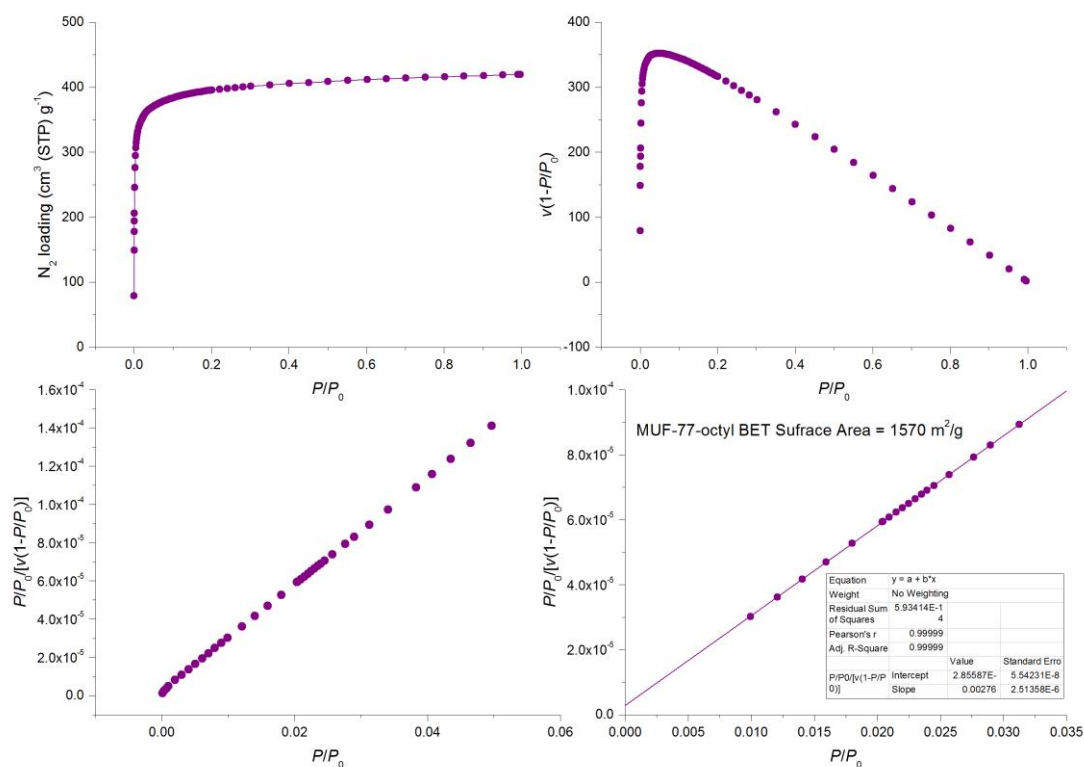
**Figure D.11**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-77-ethyl.



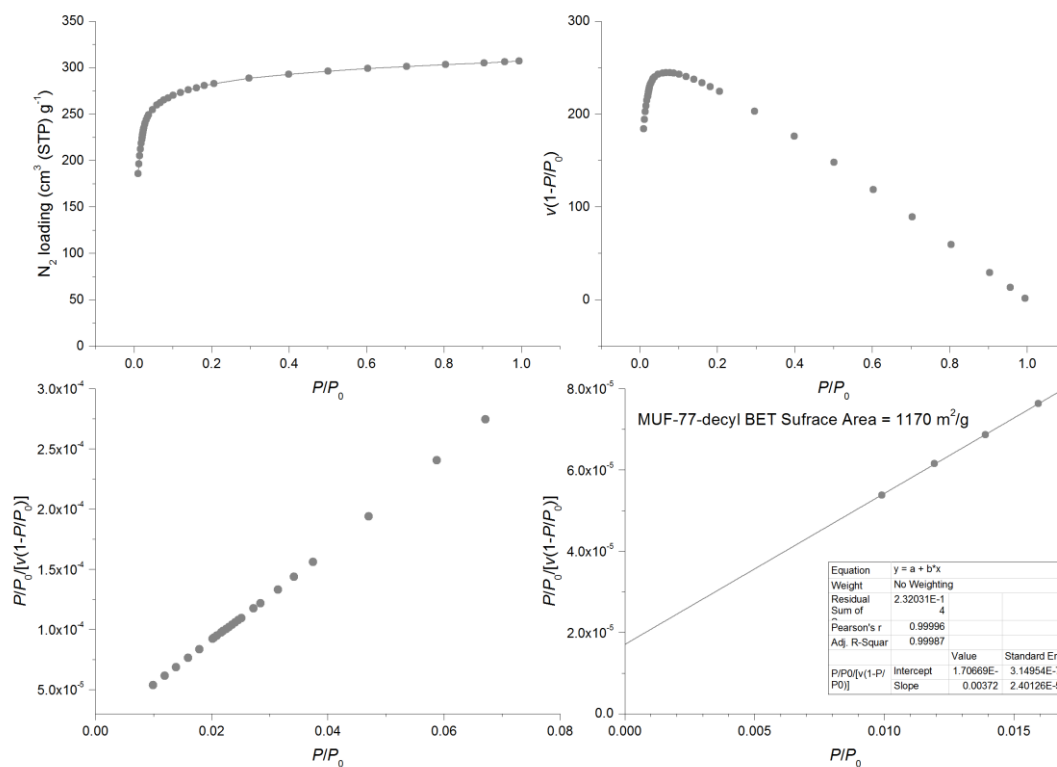
**Figure D.12**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-77-butyl.



**Figure D.13**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-77-hexyl.

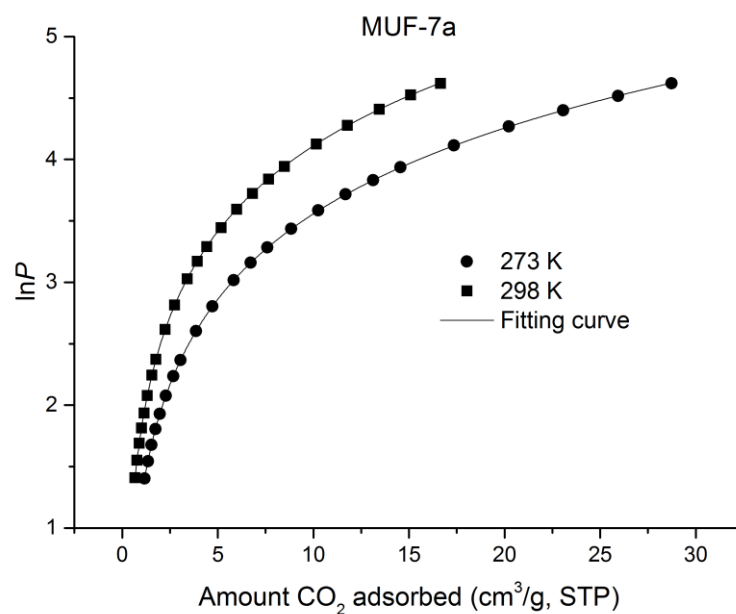


**Figure D.14**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-77-octyl.



**Figure D.15**  $N_2$  adsorption isotherm at 77 K and BET surface area plots for MUF-77-decyl.

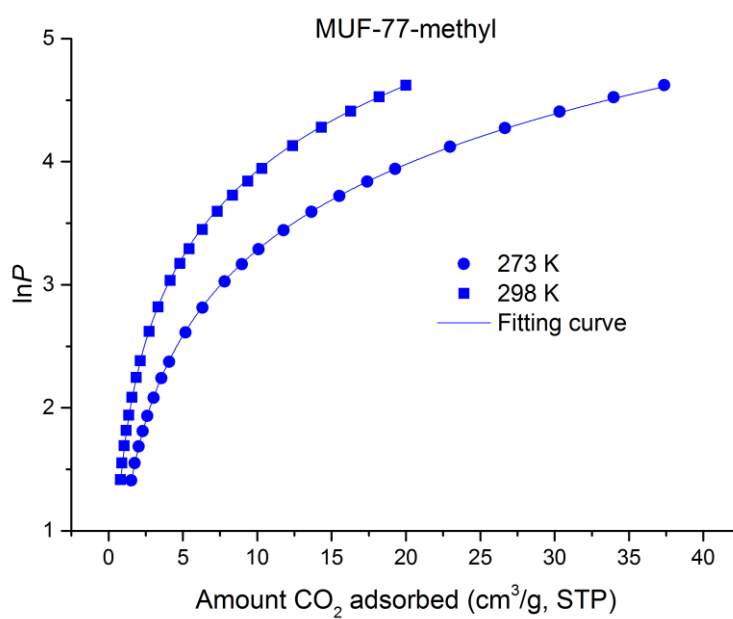
## 2. Isostatic heat of adsorption: plots and fitting parameters



**Figure D.16** Virial equation fit for CO<sub>2</sub> adsorption isotherms of MUF-7a.

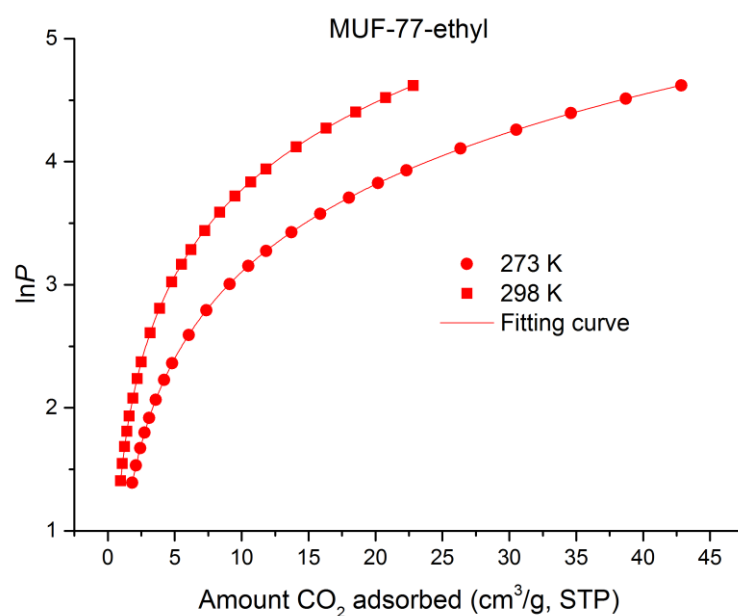
|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99999     |                |
|               | Value       | Standard Error |
| a0            | -1799.22245 | 3.34766        |
| a1            | 0.13877     | 0.02005        |
| b0            | 7.83958     | 0.0116         |
| T1            | 273         | 0              |
| T2            | 298         | 0              |





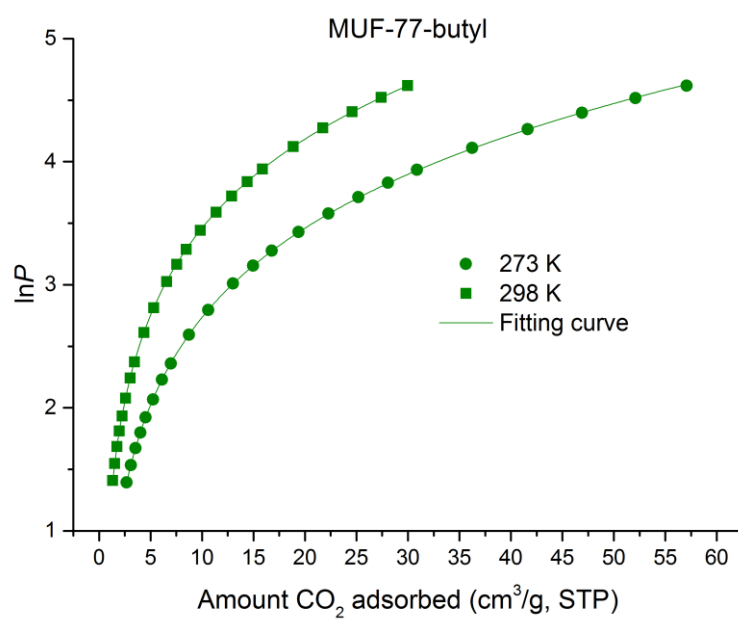
**Figure D.17** Virial equation fit for CO<sub>2</sub> adsorption isotherms of MUF-77-methyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99983     |                |
|               | Value       | Standard Error |
| a0            | -2092.38795 | 13.43359       |
| a1            | 0.09314     | 0.0617         |
| b0            | 8.64007     | 0.04649        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



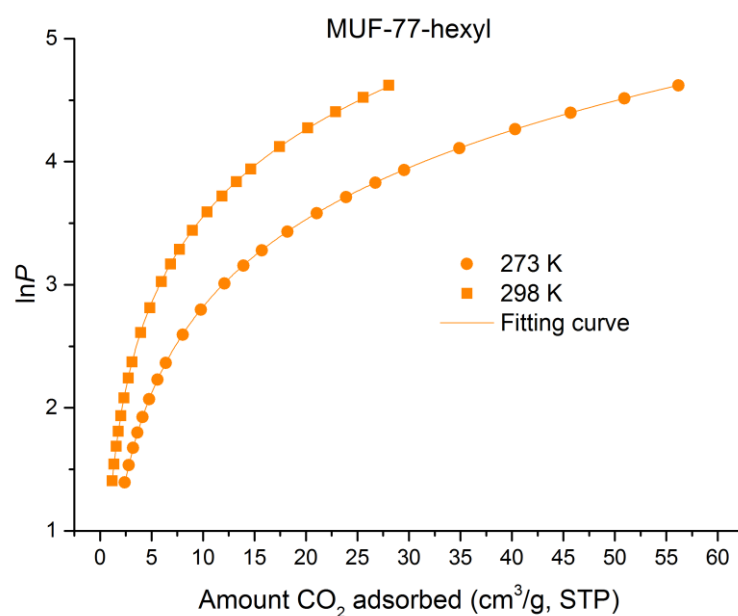
**Figure D.18** Virial equation fit for  $\text{CO}_2$  adsorption isotherms of MUF-77-ethyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99999     |                |
|               | Value       | Standard Error |
| a0            | -2177.74754 | 2.48365        |
| a1            | 0.51957     | 0.00999        |
| b0            | 8.75879     | 0.00859        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



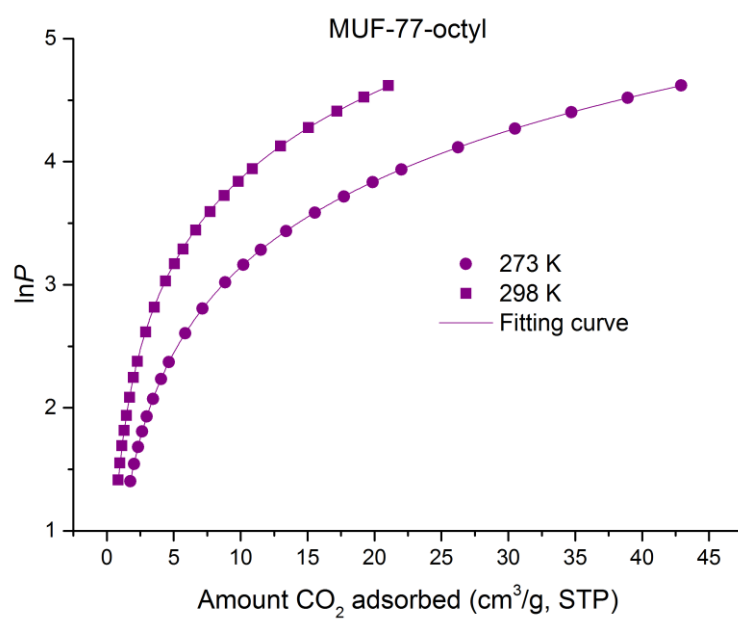
**Figure D.19** Virial equation fit for CO<sub>2</sub> adsorption isotherms of MUF-77-butyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99999     |                |
|               | Value       | Standard Error |
| a0            | -2371.24937 | 3.93032        |
| b1            | 0.87906     | 0.01174        |
| b0            | 9.08537     | 0.01358        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



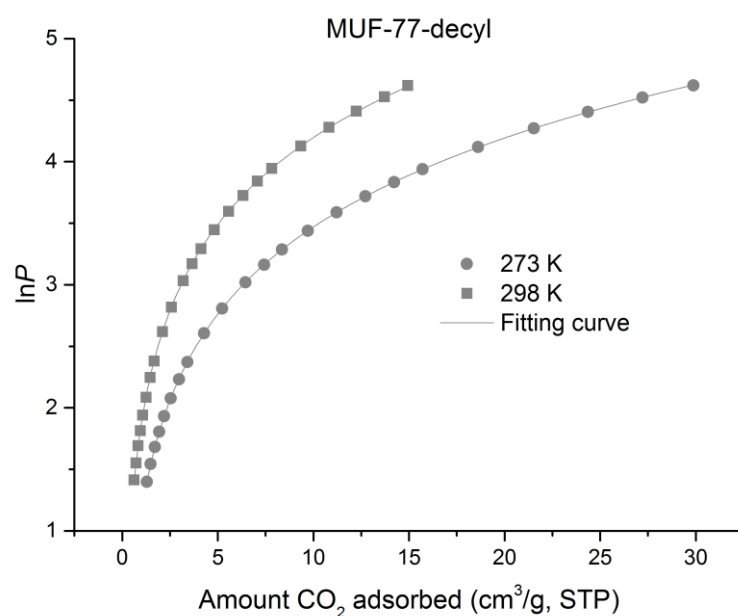
**Figure D.20** Virial equation fit for  $\text{CO}_2$  adsorption isotherms of MUF-77-hexyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99998     |                |
|               | Value       | Standard Error |
| a0            | -2387.80176 | 5.13824        |
| a1            | 0.43749     | 0.01573        |
| b0            | 9.24845     | 0.01776        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



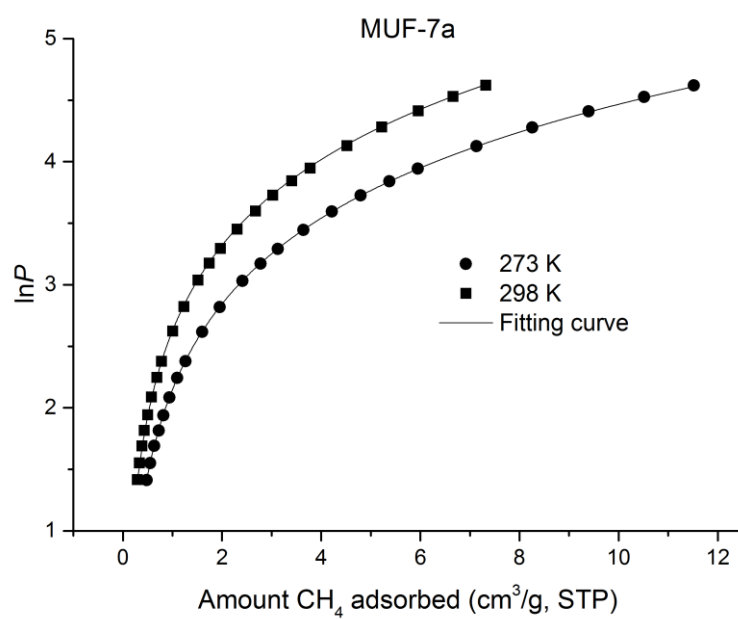
**Figure D.21** Virial equation fit for  $\text{CO}_2$  adsorption isotherms of MUF-77-octyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99997     |                |
|               | Value       | Standard Error |
| a0            | -2345.81371 | 5.62184        |
| a1            | 0.16015     | 0.02263        |
| b0            | 9.42616     | 0.01944        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



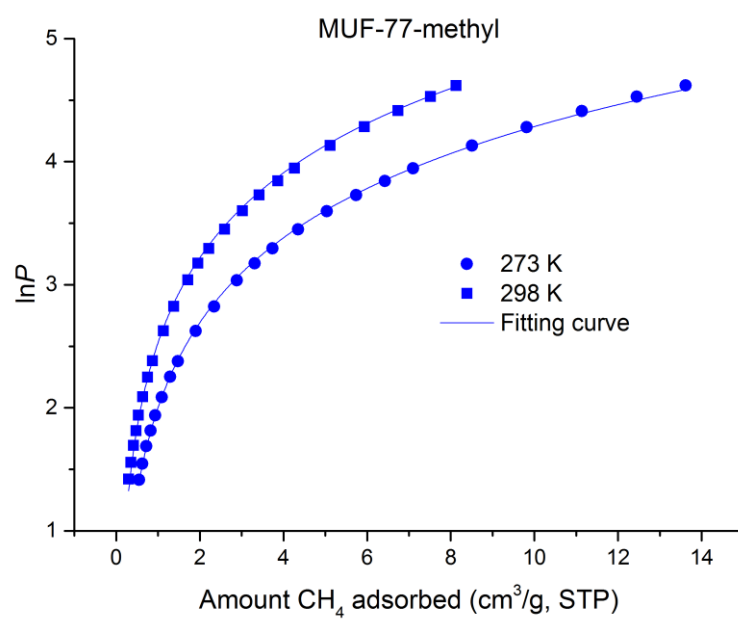
**Figure D.22** Virial equation fit for  $\text{CO}_2$  adsorption isotherms of MUF-77-decyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99998     |                |
|               | Value       | Standard Error |
| a0            | -2371.83705 | 4.16584        |
| a1            | 0.81979     | 0.02393        |
| b0            | 9.82433     | 0.0144         |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



**Figure D.23** Virial equation fit for  $\text{CH}_4$  adsorption isotherms of MUF-7a.

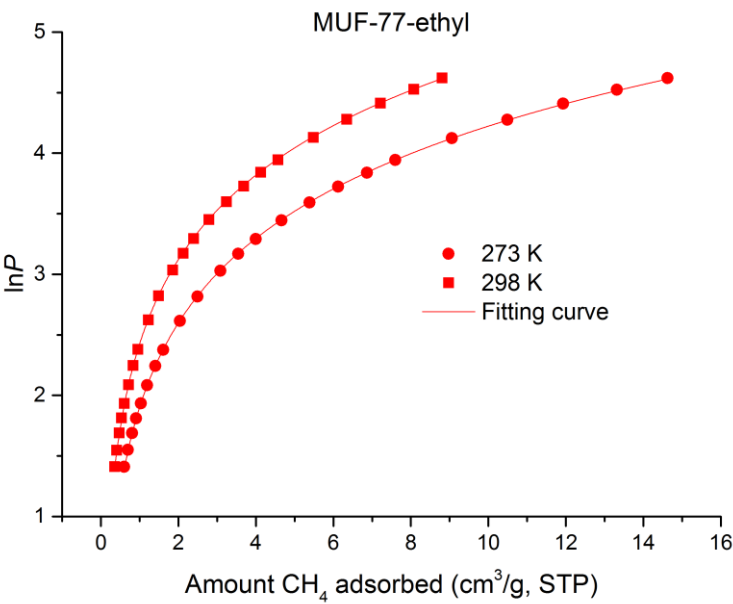
|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99988     |                |
|               | Value       | Standard Error |
| a0            | -1550.33029 | 11.36895       |
| a1            | 0.41996     | 0.16653        |
| b0            | 7.82715     | 0.03944        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



**Figure D.24** Virial equation fit for CH<sub>4</sub> adsorption isotherms of MUF-77-methyl.

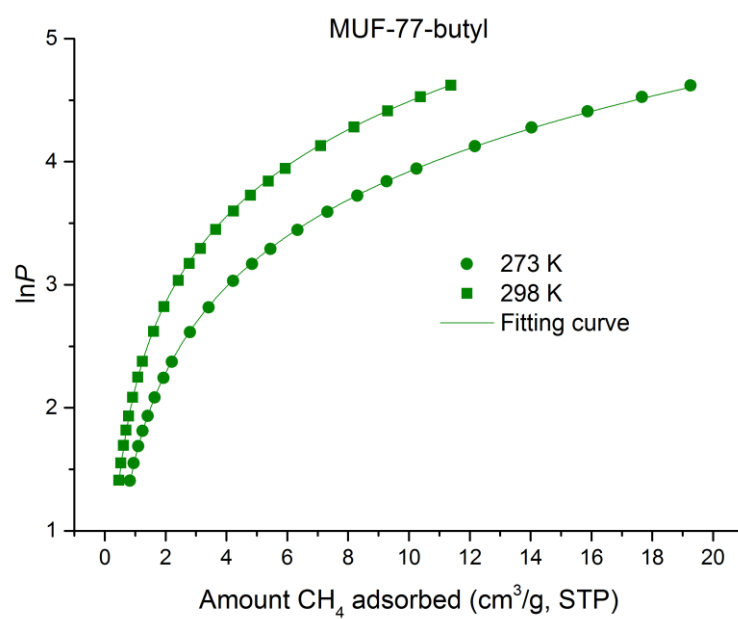
|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99927     |                |
|               | Value       | Standard Error |
| a0            | -1715.48478 | 27.85012       |
| a1            | -0.55596    | 0.34531        |
| b1            | 8.28673     | 0.09653        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |





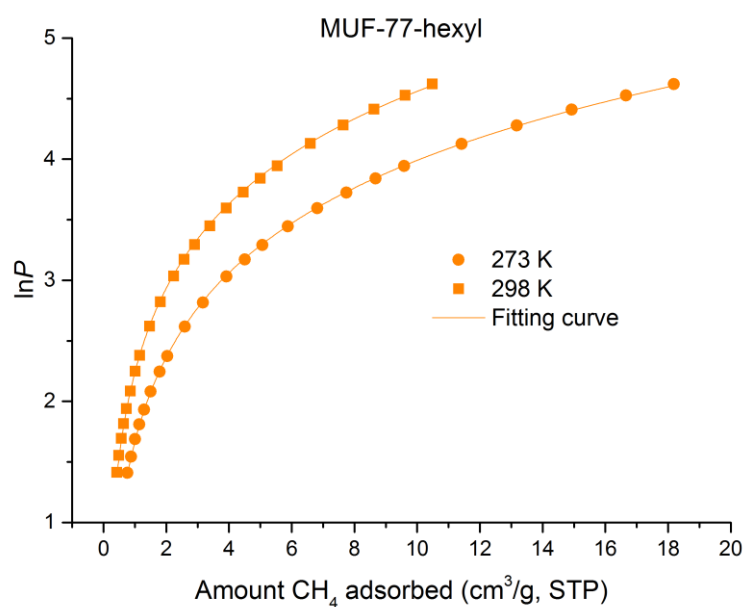
**Figure D.25** Virial equation fit for CH<sub>4</sub> adsorption isotherms of MUF-77-ethyl.

|               |            |                |
|---------------|------------|----------------|
| Adj. R-Square | 0.99994    |                |
|               | Value      | Standard Error |
| a0            | -1702.9994 | 8.04157        |
| a1            | 0.51714    | 0.0933         |
| b0            | 8.13952    | 0.02787        |
| T1            | 273        | 0              |
| T2            | 298        | 0              |



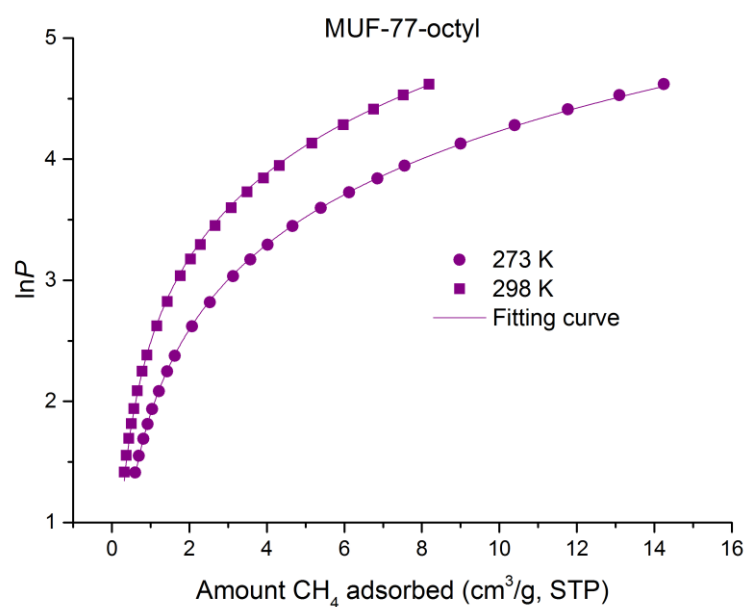
**Figure D.26** Virial equation fit for  $\text{CH}_4$  adsorption isotherms of MUF-77-butyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99985     |                |
|               | Value       | Standard Error |
| a0            | -1862.72476 | 12.21191       |
| a1            | 0.90107     | 0.10703        |
| b0            | 8.40673     | 0.04229        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



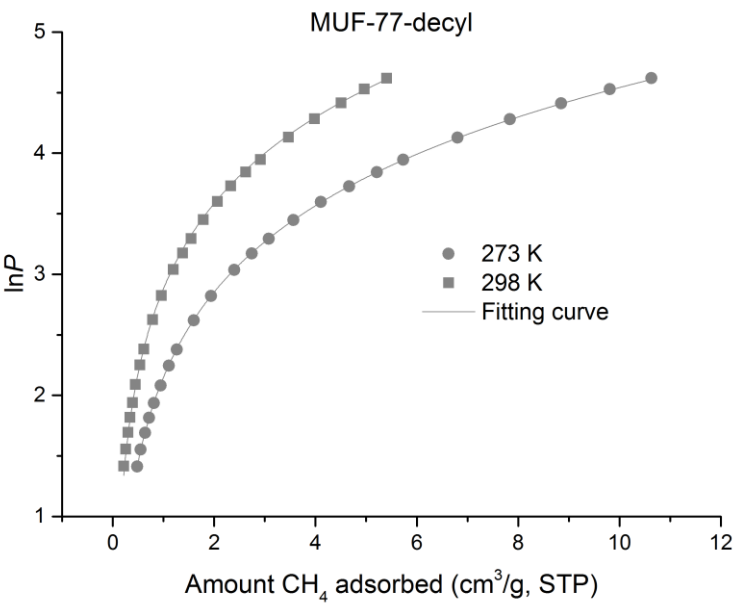
**Figure D.27** Virial equation fit for  $\text{CH}_4$  adsorption isotherms of MUF-77-hexyl.

| Adj. R-Square | 0.99985     |                |
|---------------|-------------|----------------|
|               | Value       | Standard Error |
| a0            | -1858.39728 | 12.75972       |
| a1            | 0.60658     | 0.11889        |
| b0            | 8.4729      | 0.04419        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



**Figure D.28** Virial equation fit for CH<sub>4</sub> adsorption isotherms of MUF-77-octyl.

|               |             |                |
|---------------|-------------|----------------|
| Adj. R-Square | 0.99958     |                |
|               | Value       | Standard Error |
| a0            | -1921.33228 | 21.17864       |
| a1            | 0.9525      | 0.25117        |
| b0            | 8.93251     | 0.07332        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |



**Figure D.29** Virial equation fit for CH<sub>4</sub> adsorption isotherms of MUF-77-decyl.

| Adj. R-Square | 0.99965     |                |
|---------------|-------------|----------------|
|               | Value       | Standard Error |
| a0            | -2384.34249 | 19.81814       |
| a1            | 2.69393     | 0.31559        |
| b0            | 10.87385    | 0.06847        |
| T1            | 273         | 0              |
| T2            | 298         | 0              |

## 3. Isotherm fitting plots

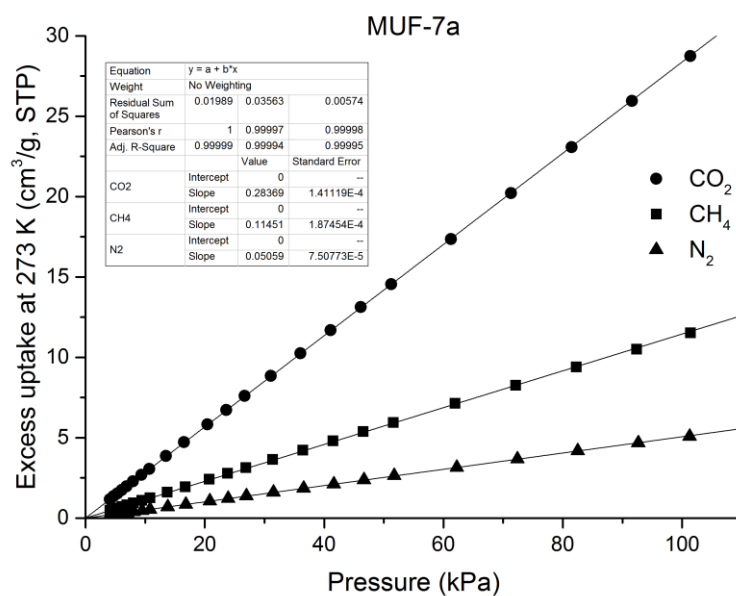


Figure D.30 Isotherm fitting parameters for MUF-7a at 273 K.

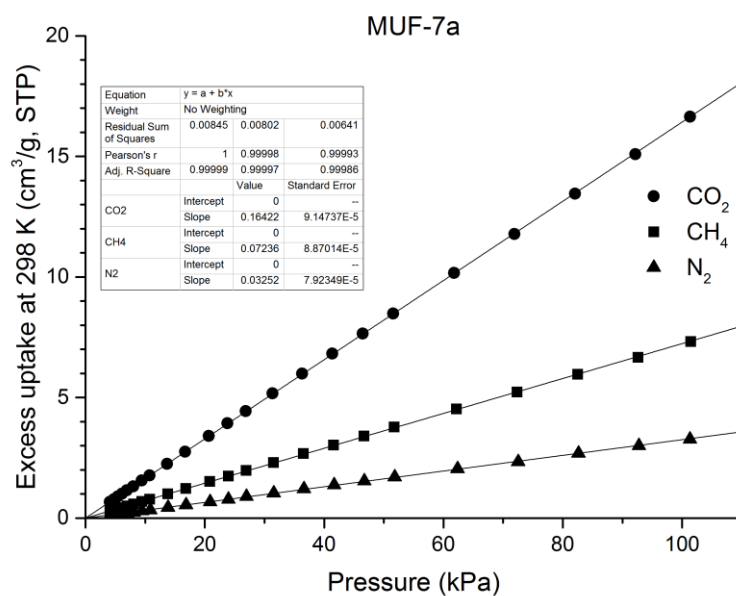
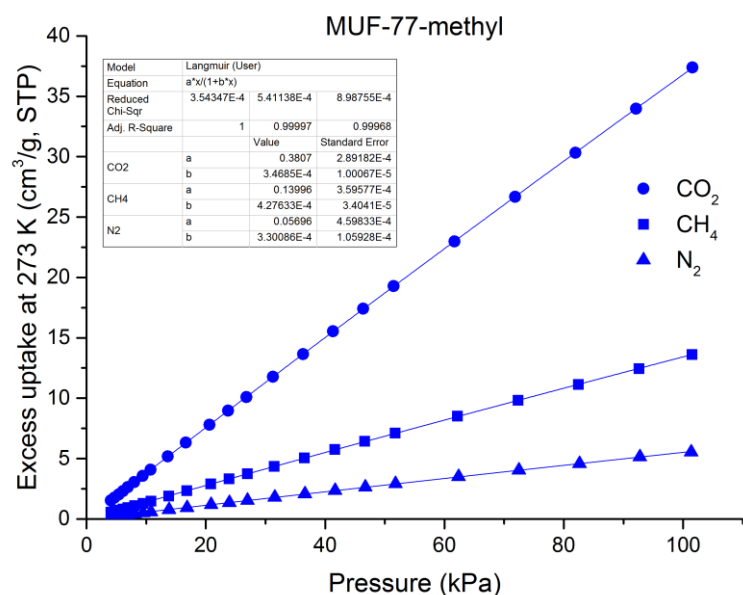
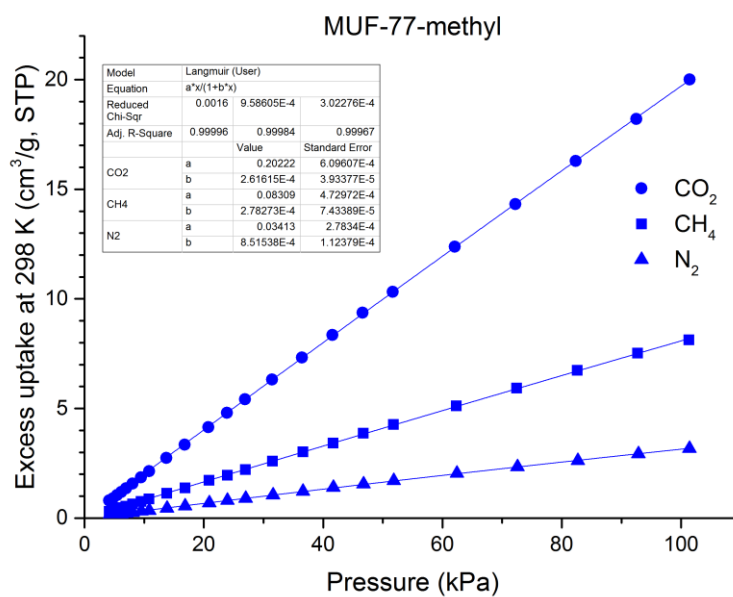


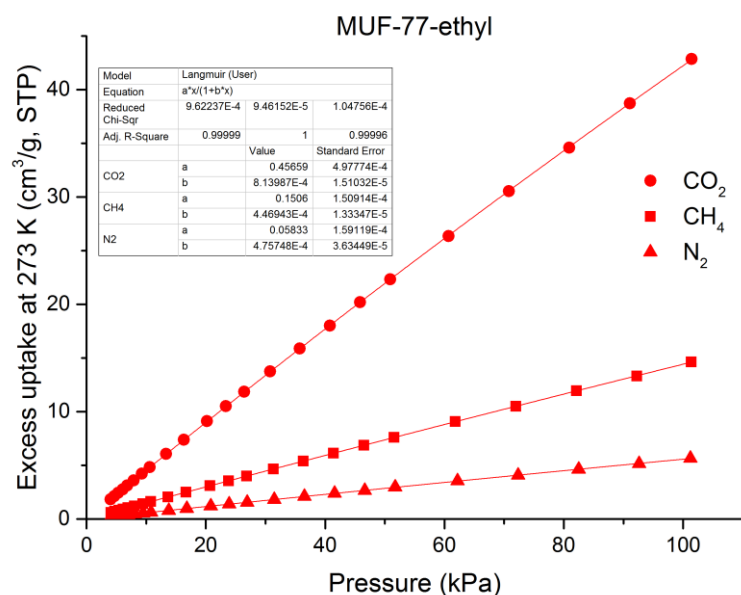
Figure D.31 Isotherm fitting parameters for MUF-7a at 298 K.



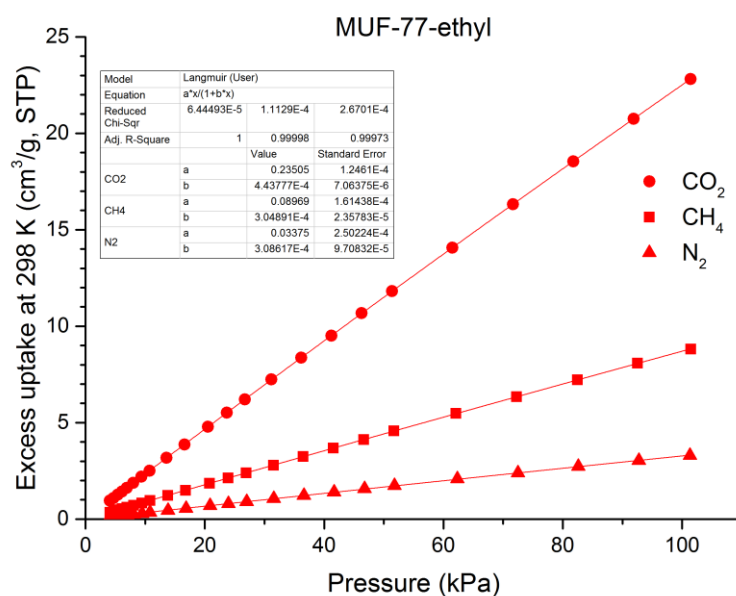
**Figure D.32** Isotherm fitting parameters for MUF-77-methyl at 273 K.



**Figure D.33** Isotherm fitting parameters for MUF-77-methyl at 298 K.

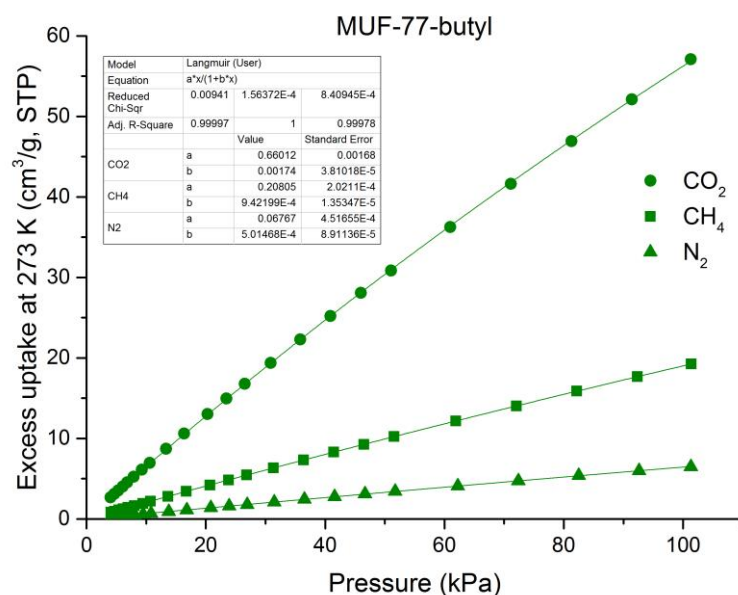


**Figure D.34** Isotherm fitting parameters for MUF-77-ethyl at 273 K.

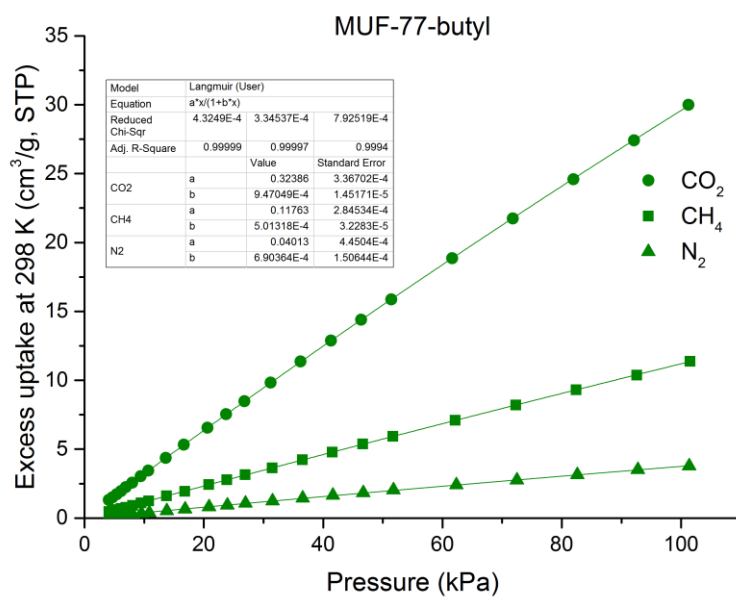


**Figure D.35** Isotherm fitting parameters for MUF-77-ethyl at 298 K.

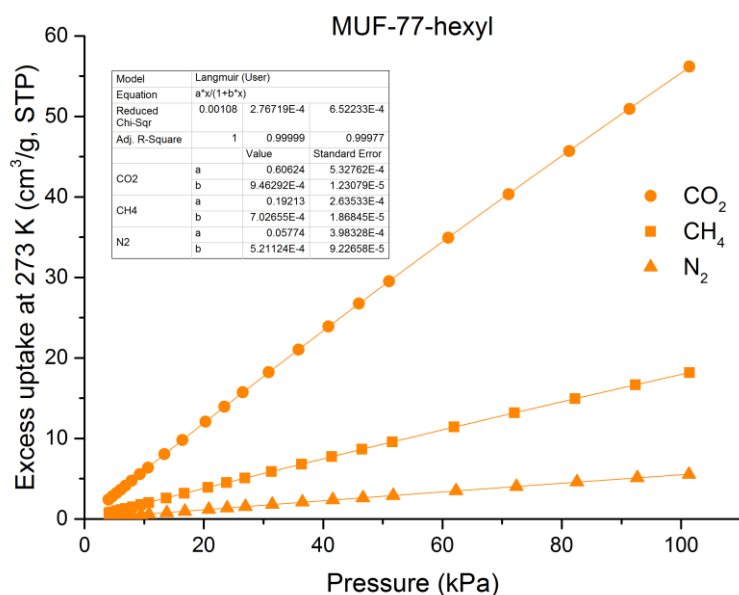




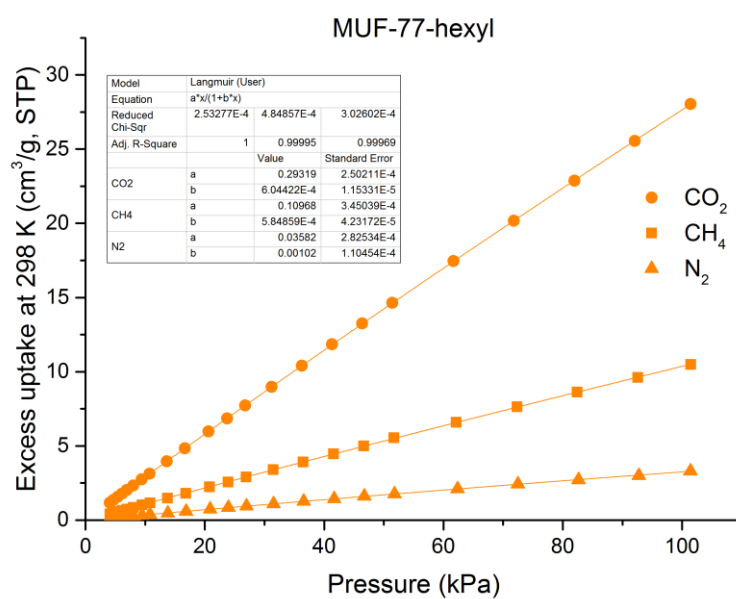
**Figure D.36** Isotherm fitting parameters for MUF-77-butyl at 273 K.



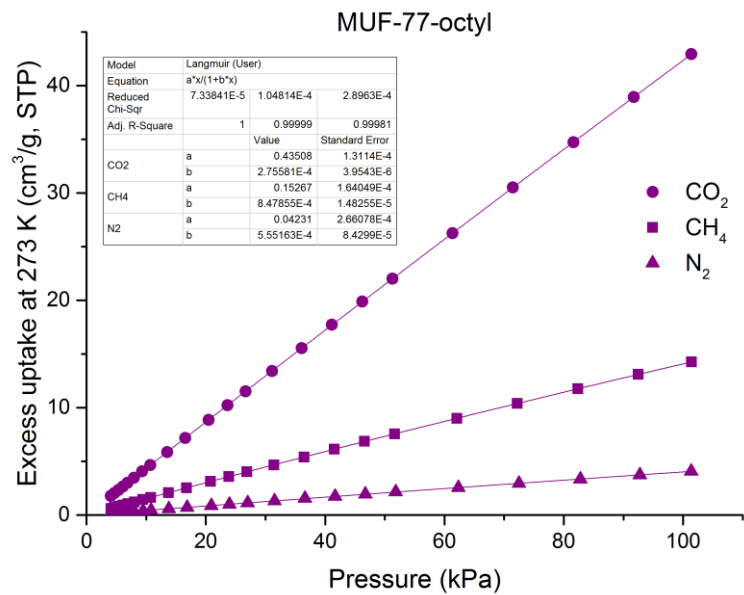
**Figure D.37** Isotherm fitting parameters for MUF-77-butyl at 298 K.



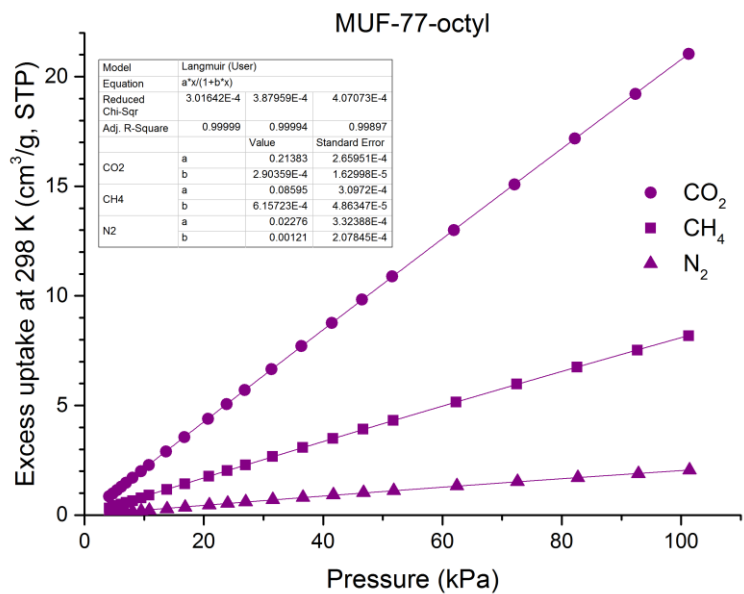
**Figure D.38** Isotherm fitting parameters for MUF-77-hexyl at 273 K.



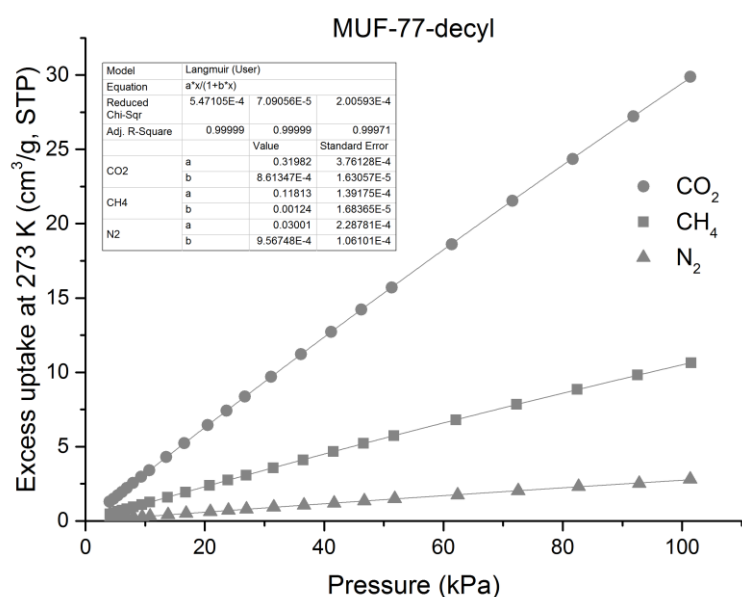
**Figure D.39** Isotherm fitting parameters for MUF-77-hexyl at 298 K.



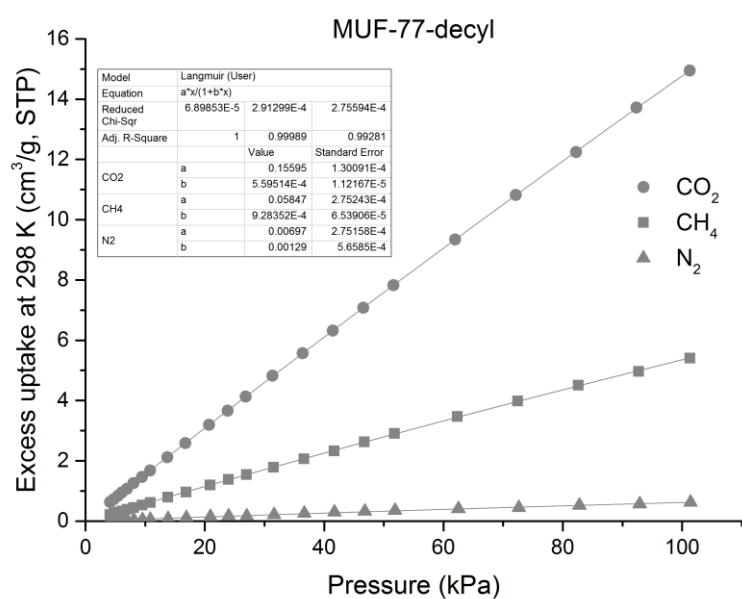
**Figure D.40** Isotherm fitting parameters for MUF-77-octyl at 273 K.



**Figure D.41** Isotherm fitting parameters for MUF-77-octyl at 298 K.



**Figure D.42** Isotherm fitting parameters for MUF-77-decyl at 273 K.



**Figure D.43** Isotherm fitting parameters for MUF-77-decyl at 298 K.

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