SUPPORTING INFORMATION

# Solvent free base Catalysis and Transesterification over basic functionalised Metal-Organic Frameworks

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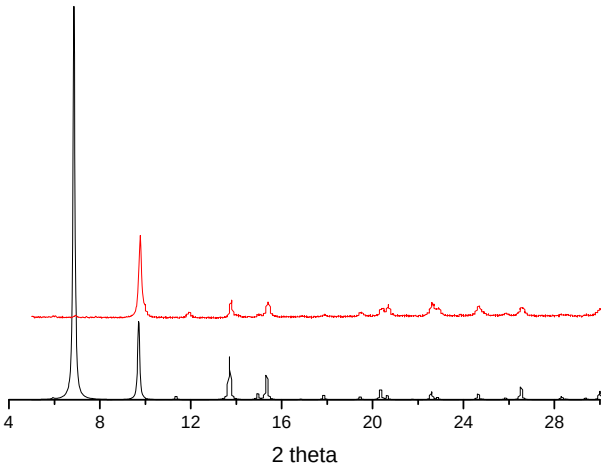



Figure 1. Powder X-Ray diffraction patterns of IRMOF-3 **1a**. Experimental result (top), simulated pattern from IRMOF-3.cif file (bottom).

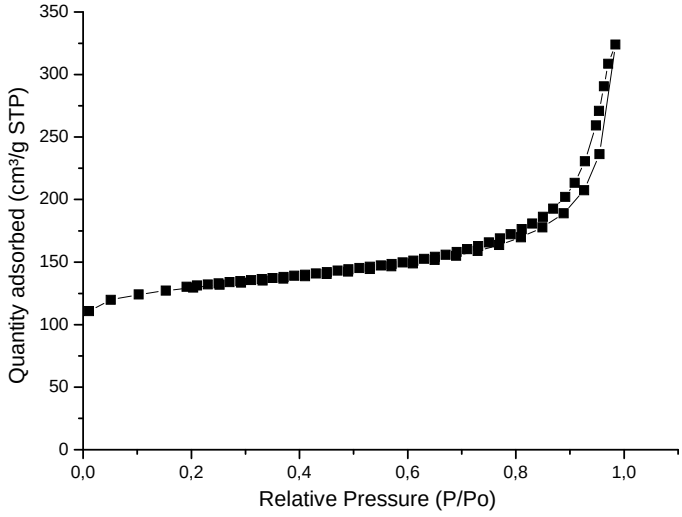



Figure 2. $N_2$ isotherm at 77K of IRMOF-3 **1a**

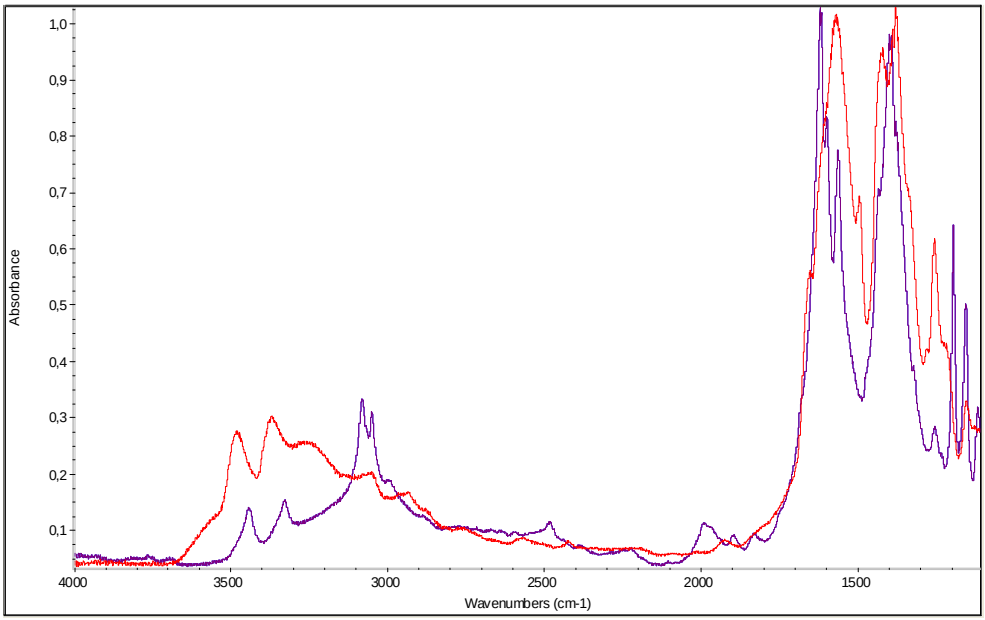
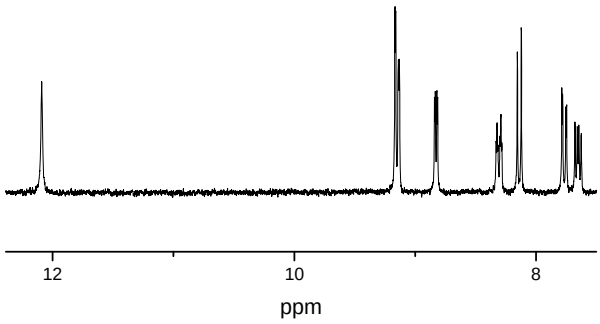
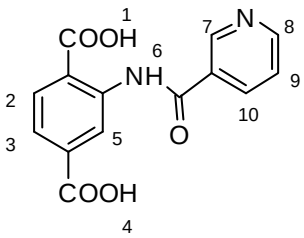



Figure 3. FT-IR spectrum of as-synthesized (red) **1a** and modified IRMOF-3 **1b** (blue).

The functionalised ligand was obtained by acylation of dimethylaminoterephthalate (1.5 g) with nicotinoyl chloride (3 g) in a dichloromethane solution containing triethylamine (9 mL) and DMAP (0.7 g) at room temperature for 5 h. The ligand is obtained after saponification, followed by acidification on Amberlite IR-120 resin.




**$^{1}$H RMN:** (DMSO, $D_2O$/DCl, 250 MHz): δ (ppm) 13.44 (s, 2H, $H_1$, $H_4$), 12.09 (s, 1H, $H_6$), 9.16 (d, 1H, $^{4}J_{HH}$ = 1.58 Hz, $H_5$), 9.13 (d, 1H, $^{4}J_{HH}$ = 1.9 Hz, $H_7$), 8.82 (dd, $^{4}J_{HH}$ = 1.58 Hz, $^{3}J_{HH}$ = 4.9 Hz, $H_8$), 8.30 (ddd, $^{4}J_{HH}$ = 1.9 Hz, $^{4}J_{HH}$ = 1.58 Hz $^{3}J_{HH}$ = 8 Hz, $H_{10}$), 8.14 (d, 1H, $^{1}J_{HH}$ = 8 Hz, $H_2$), 7.76 (dd, 1H, $^{3}J_{CH}$ = 1.58 Hz, $^{3}J_{CH}$ = 8 Hz, $H_3$), 7.64 (dd, 1H, $^{3}J_{CH}$ = 4.9 Hz, $^{3}J_{CH}$ = 8 Hz, $H_9$

Figure 4. $^{1}$H-NMR results of the functionalised ligand.

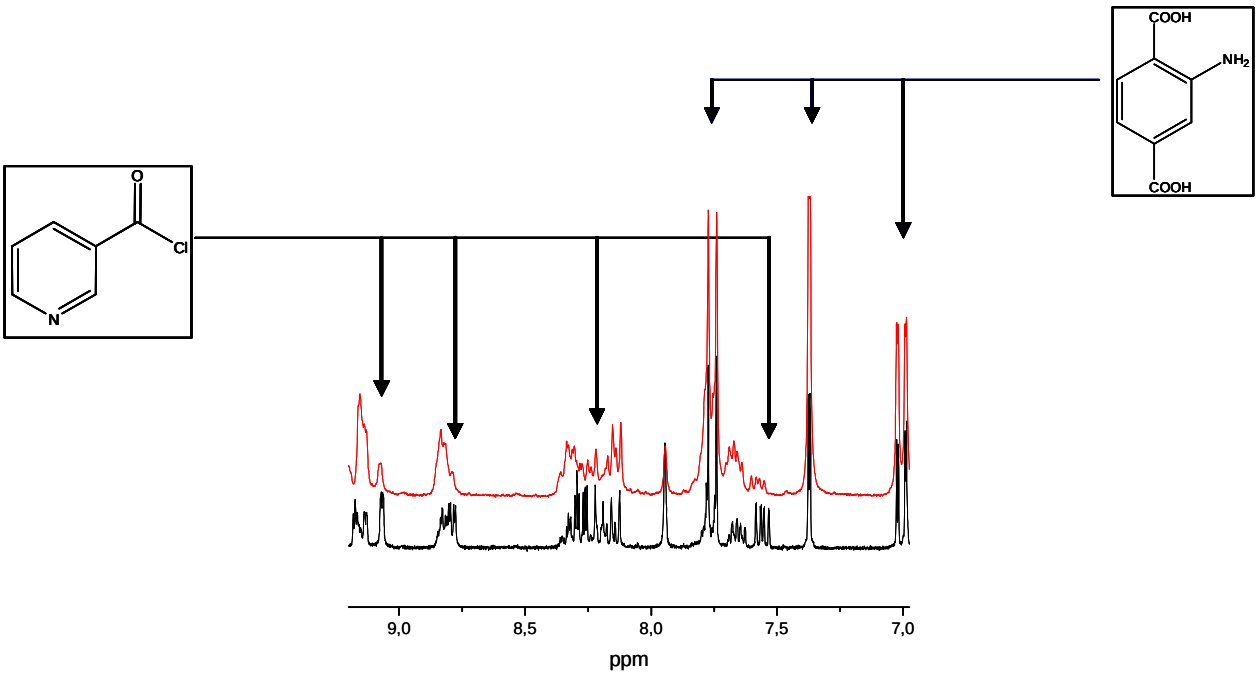



Figure 5. $^{1}$H-NMR results of digested modified IRMOF-3 **1b** without washing (black) and digested modified IRMOF-3 **1b** with repeated washings (red).

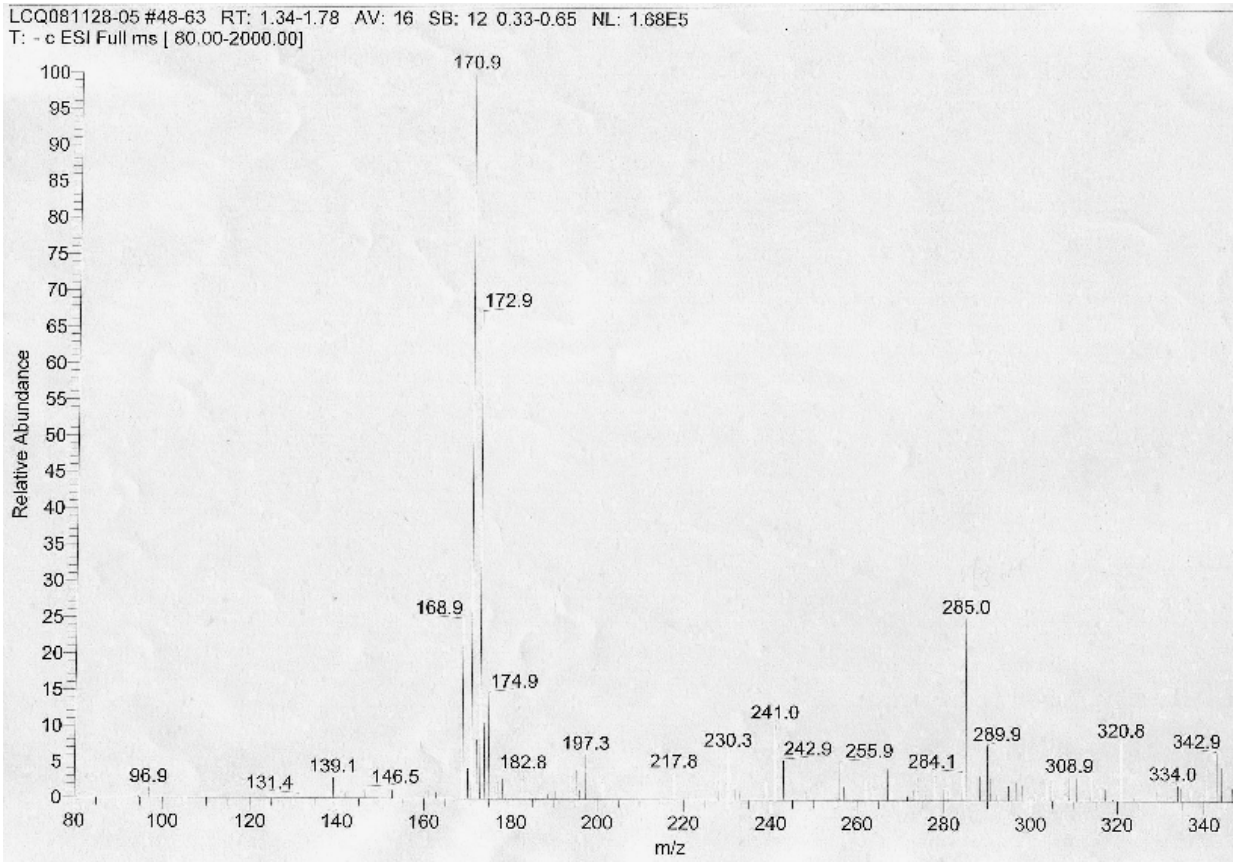



Figure 6. Negative ion mode ESI-MS of digested modified IRMOF-3 **1b**

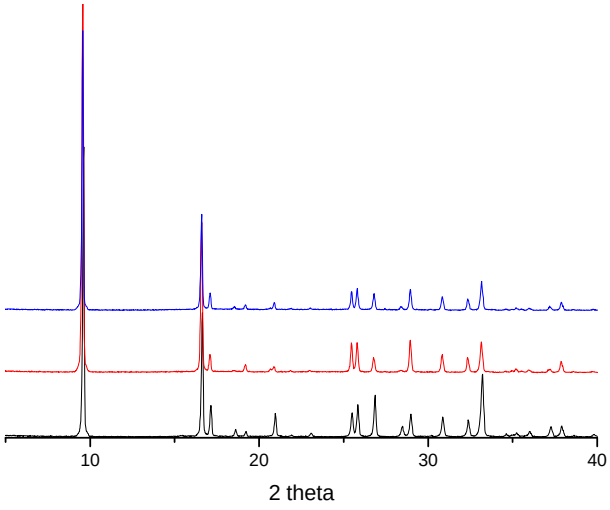



Figure 7. Powder X-Ray diffraction patterns of ZnF($Am_2$TAZ) 2a (black), post-functionalized ZnF($Am_2$TAZ) 2b (red) and post-functionalised ZnF($Am_2$TAZ) 2b after reaction.