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Supporting Information

Synthesis of Chiral MOF-74 Frameworks by Post-Synthetic Modification by Using an Amino Acid

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Supplementary information

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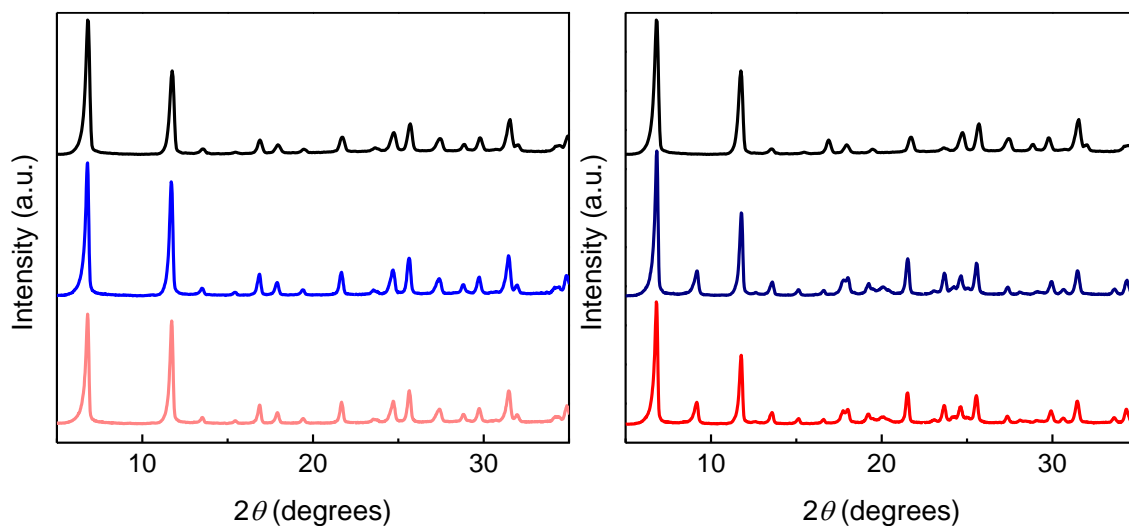


Figure S1. PXRD patterns of Zn-MOF-74 (black), MOFs synthesised in MeOH with *L*-Pro (blue) and with *D*-Pro (red) (left) and MOFs synthesised in DMF with *L*-Pro (red) and with *D*-Pro (blue) (right).

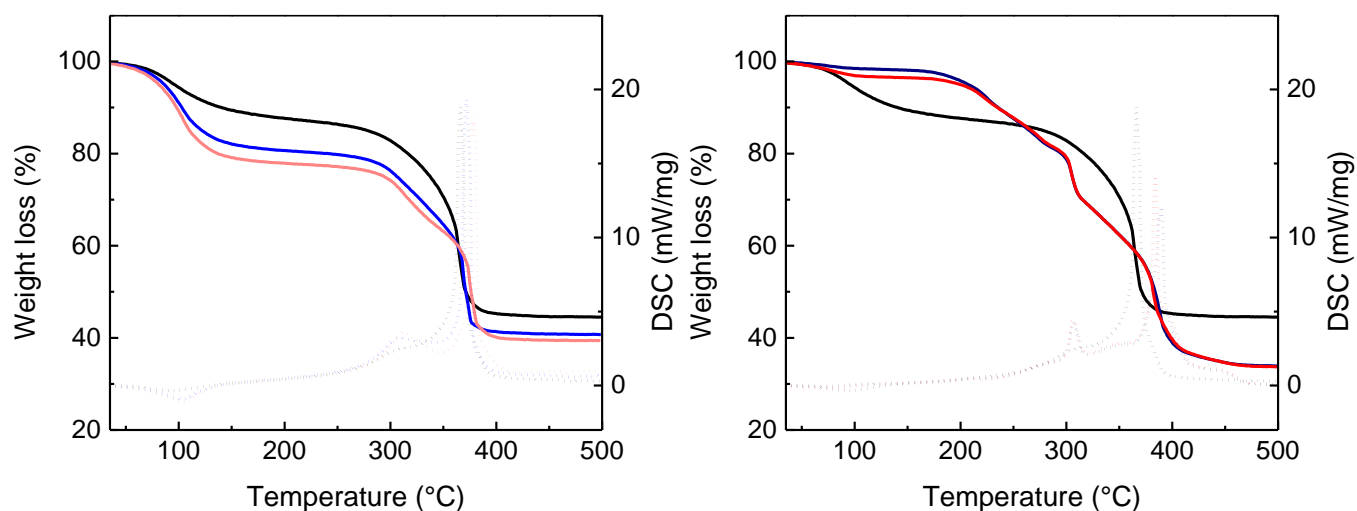


Figure S2. TGA/DSC curves of Zn-MOF-74 (black), MOFs synthesised in MeOH with *L*-Pro (blue) and with *D*-Pro (red) (left) and MOFs synthesised in DMF with *L*-Pro (red) and with *D*-Pro (blue) (right).

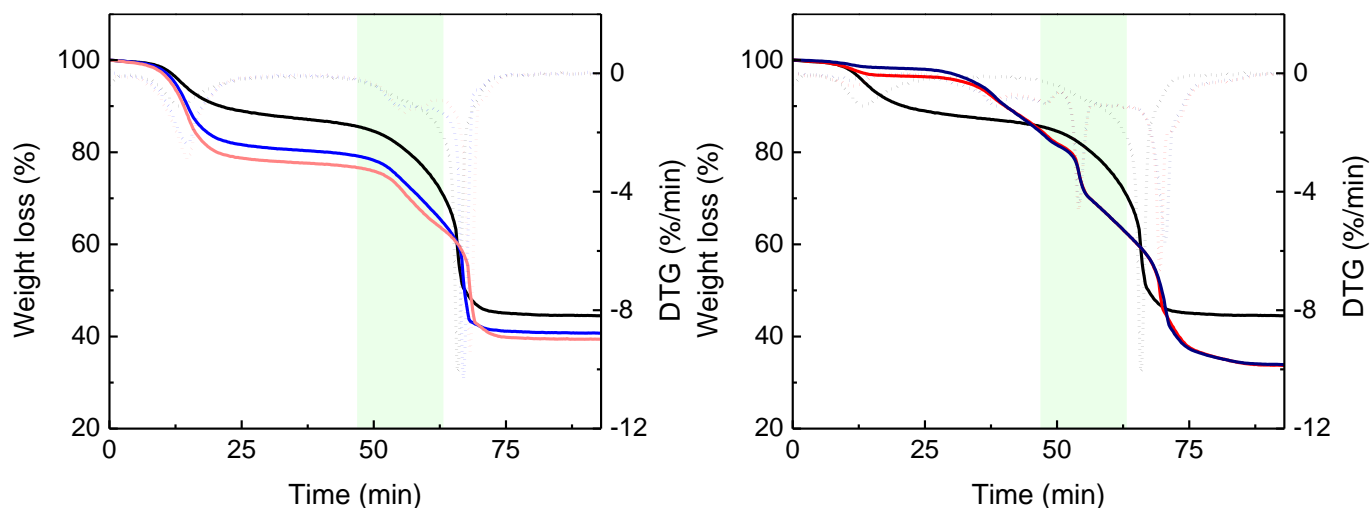


Figure S3. TGA/DTG curves of Zn-MOF-74 (black), MOFs synthesised in MeOH with *L*-Pro (blue) and with *D*-Pro (red) (left) and MOFs synthesised in DMF with *L*-Pro (red) and with *D*-Pro (blue) (right).

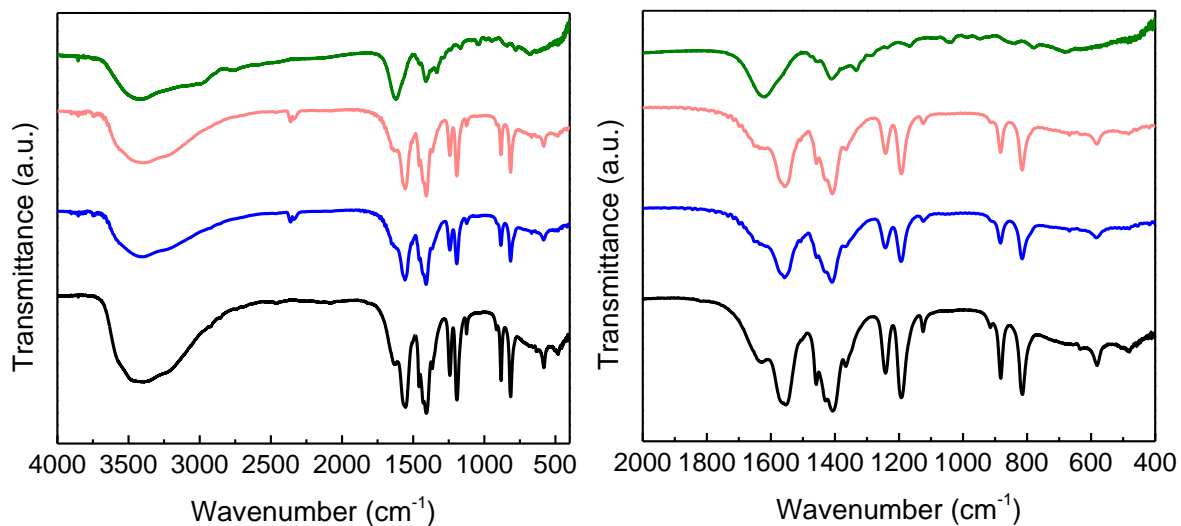


Figure S4. FTIR spectra of *L*-Pro (green), Zn-MOF-74 (black), MOFs synthesised in MeOH with *L*-Pro (blue) and with *D*-Pro (red) (left) and FTIR with zoom in on the fingerprint region (right).

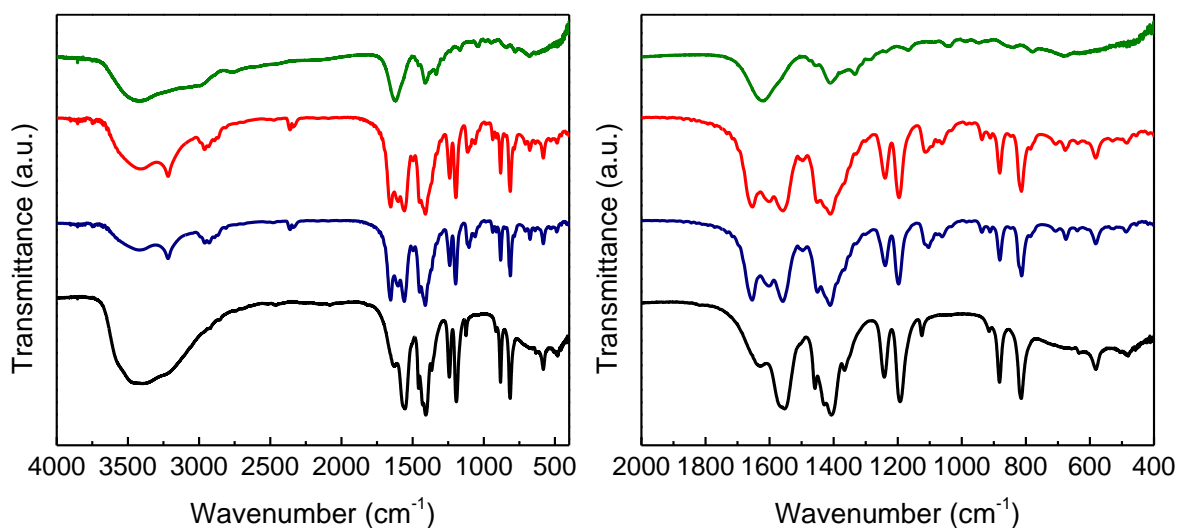


Figure S5. FTIR spectra of *L*-Pro (purple), Zn-MOF-74 (black), MOFs synthesised in DMF with *L*-Pro (red) and with *D*-Pro (blue) (left) and FTIR with zoom in on the fingerprint region (right).

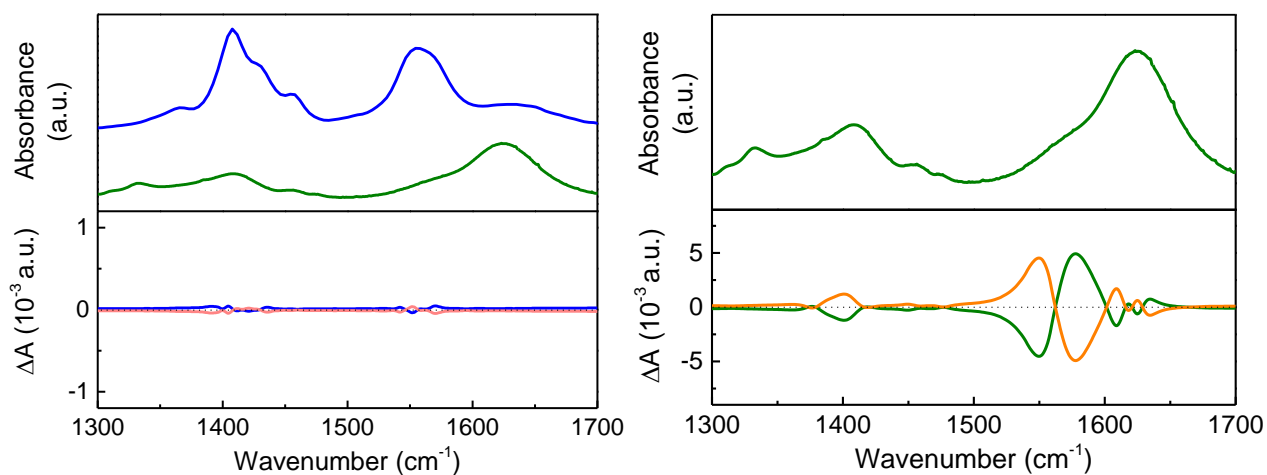


Figure S6. Left: FTIR spectra of *L*-Pro (green), MOFs synthesised with *L*-Pro in MeOH (blue) (top) and refined VCD spectra of MOFs synthesised in MeOH with *L*-Pro (blue) and with *D*-Pro (red) (bottom). Right: FTIR spectra of *L*-Pro (green) (top) and refined VCD spectra of *L*-Pro (green) and *D*-Pro (orange) (bottom) (right).

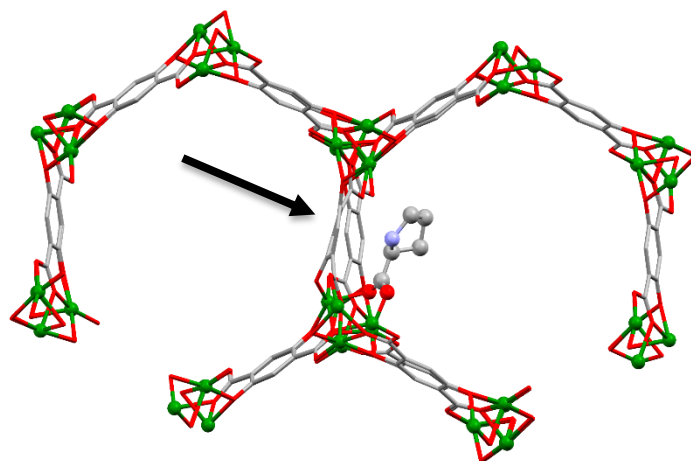


Figure S7. View along the c axis of the MOF-74 framework with induced strain by coordination of one proline molecule to two consecutive Zn²⁺ ions in a bidentate fashion.

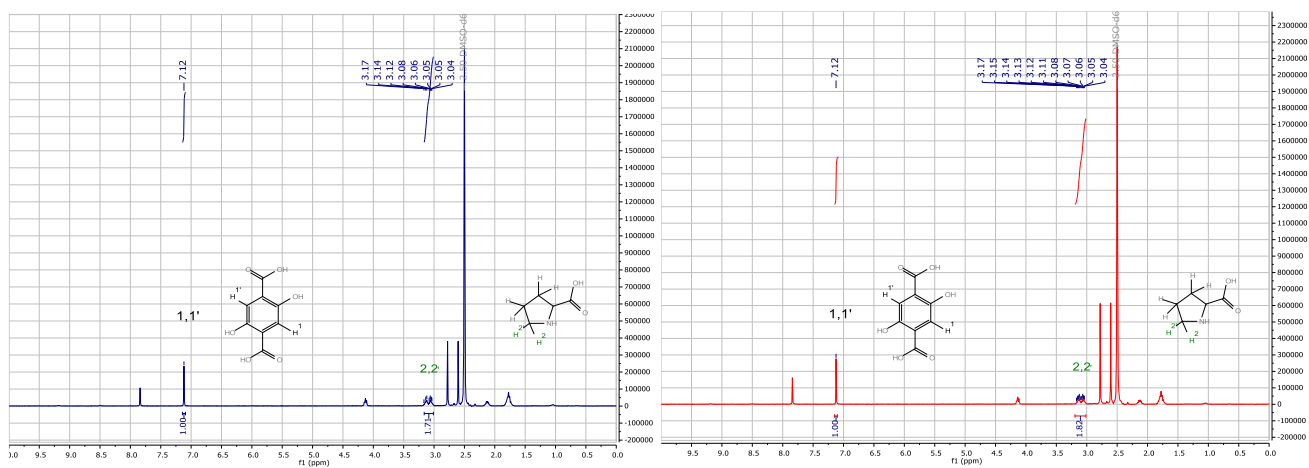
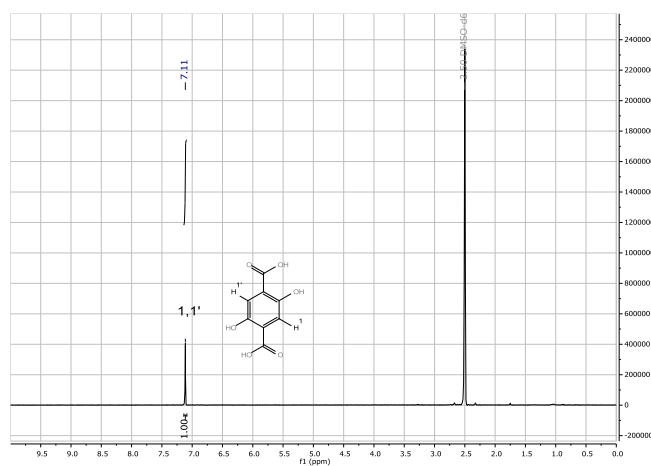


Figure S8. ¹H NMR analysis of the digested Zn-MOF-74 (black) and of the MOFs synthesised in DMF with D-Pro (blue) (left) and with L-Pro (red) (right).

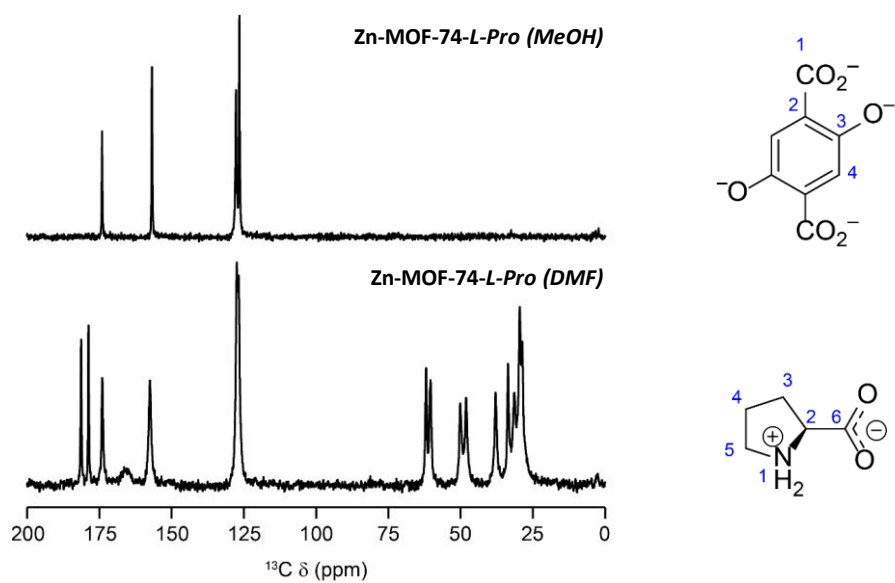


Figure S9. ^{13}C CP MAS NMR spectra of Zn-MOF-74-L-Pro synthesised in MeOH and DMF and the numbering used for dobdc^{4-} and L-Pro.

Table S1. Textural values of Zn-MOF-74 and Zn-MOF-74-L-Pro synthesised in MeOH and DMF.

Sample	S_{Langmuir} ($\text{m}^2 \text{g}^{-1}$)	$D_{\text{micropore}}$ (nm)	$V_{\text{micropore}}^{\text{a}}$ ($\text{cm}^3 \text{g}^{-1}$)
Zn-MOF-74	1168	1.6	0.4
Zn-MOF-74-L-Pro (MeOH)	264	1.5	0.09
Zn-MOF-74-L-Pro (DMF)	37	2.0	0.02

a. The Saito-Foley volume is calculated using the range p/p^0 0.001-0.4.

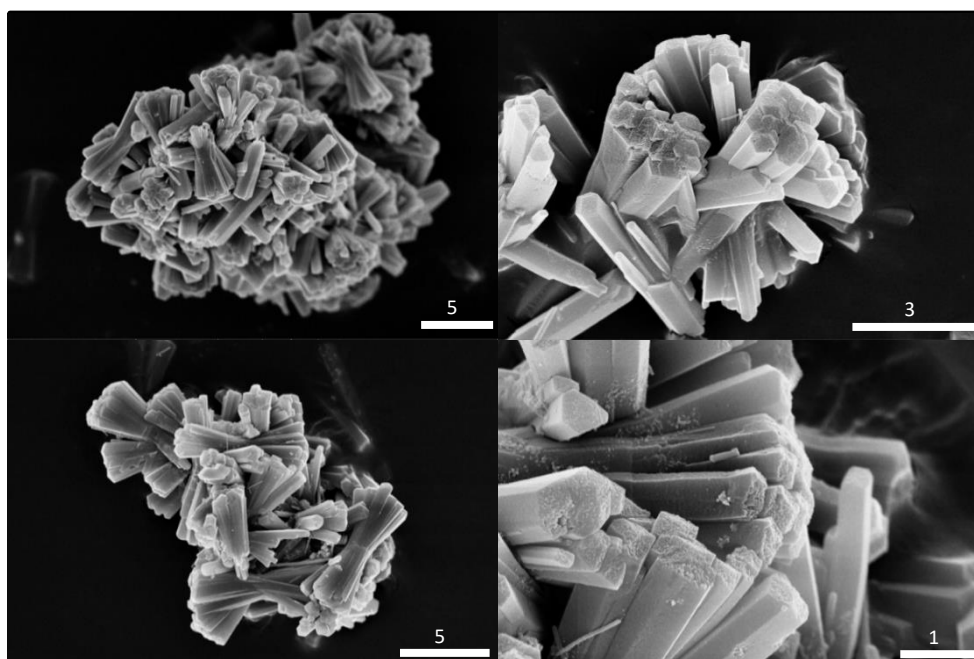


Figure S10. SEM image of MOFs synthesised in MeOH with *L*-Pro (top) and with *D*-Pro (bottom).

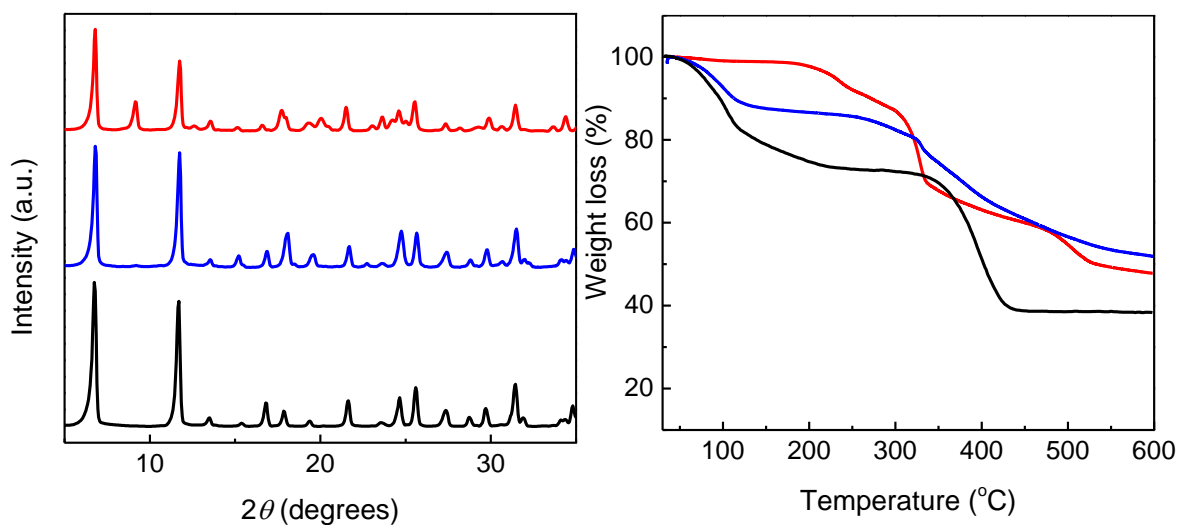


Figure S11. PXRD patterns (left) and TGA curves (right) of non-activated Zn-MOF-74 (black), Zn-MOF-74-*L*-Pro prepared in THF/ac (blue) and in DMF/ac (red). The TGA measurements were carried under inert conditions using a continuous 20 mL/min Ar flow, and a heating ramp of 10K/min.

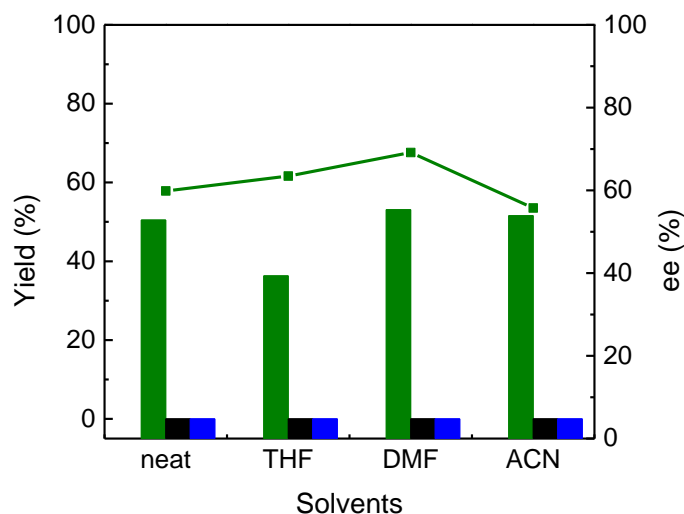


Figure S12. Catalytic results of the asymmetric aldol reaction of pNBA and acetone in different solvents. Reaction conditions: 0.5 mmol *para*-nitro-benzaldehyde, 10 mol % catalyst loading and 5 mL solvent/acetone 4/1 (v/v), 20 h reaction time at room temperature. Green line symbolises the *ee* values obtained when using *L*-Pro as catalyst which were calculated based on chiral HPLC chromatography. The column bars represent the yields when using *L*-Pro (green), MOF-74 (black) or Zn-MOF-74-*L*-Pro (blue) and were calculated based on ^1H NMR spectra.

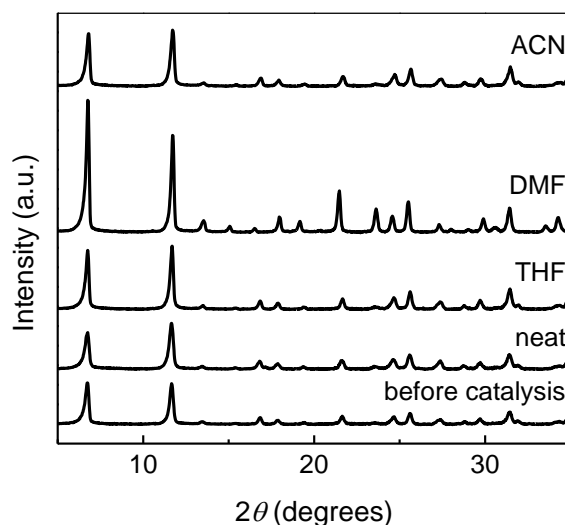


Figure S13. PXRD patterns of Zn-MOF-74-*L*-Pro catalysts before and after testing in the aldol reaction.

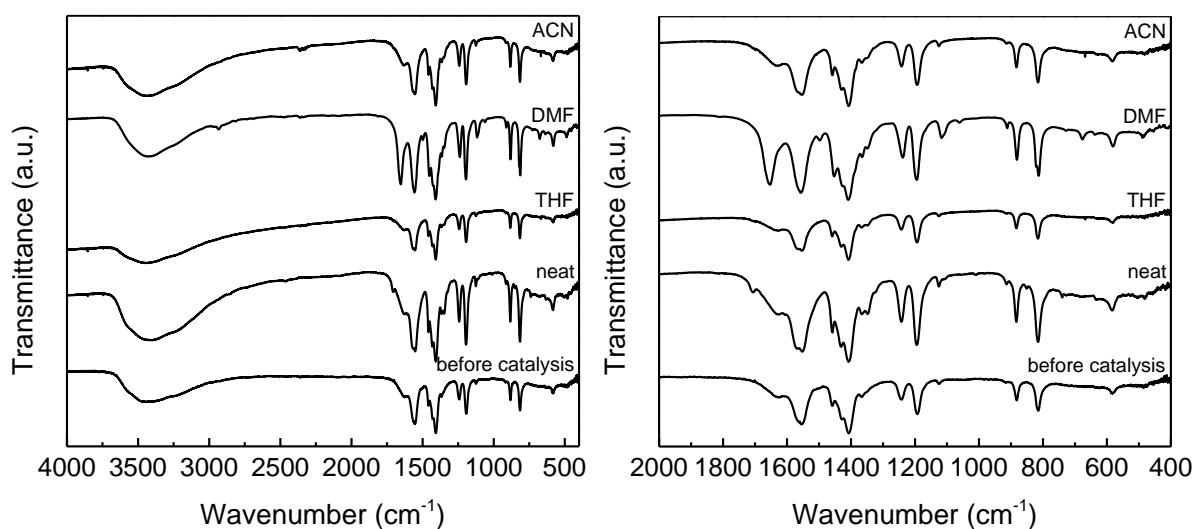


Figure S14. FTIR spectra of the Zn-MOF-74-L-Pro catalyst before and after testing in the aldol reaction (left) and FTIR with zoom in on the fingerprint region (right).

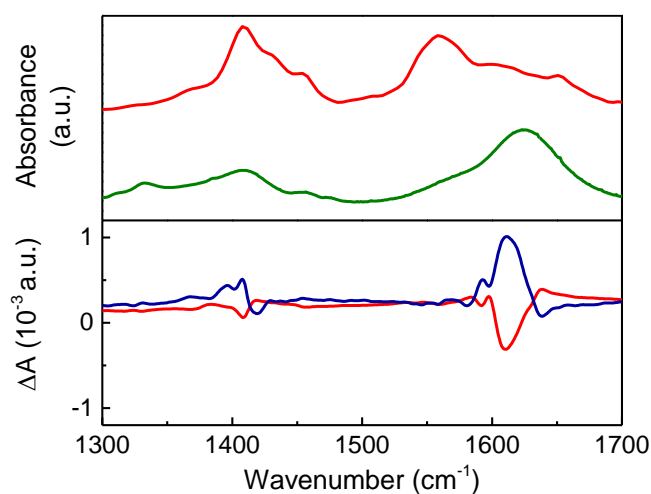


Figure S15. FTIR spectra of *L*-Pro (green), MOFs synthesised with *L*-Pro in DMF (red) (top) and raw VCD spectra of MOFs synthesised in DMF with *L*-Pro (red) and with *D*-Pro (blue) (bottom).

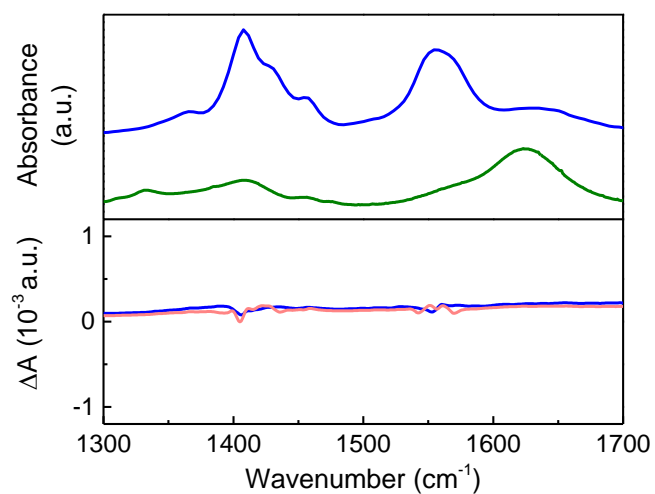


Figure S16. FTIR spectra of *L*-Pro (green), MOFs synthesised with *L*-Pro in MeOH (blue) (top) and raw VCD spectra of MOFs synthesised in MeOH with *L*-Pro (blue) and with *D*-Pro (red) (bottom).

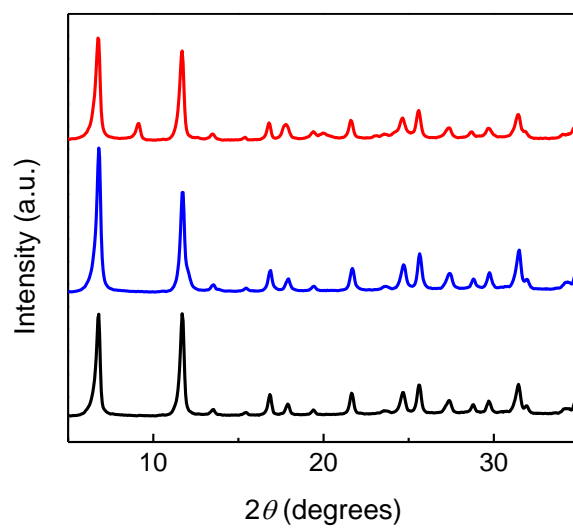


Figure S17. PXRD patterns of Zn-MOF-74 (black), Zn-MOF-74-*L*-Pro synthesised in MeOH (blue) and in DMF (red) after nitrogen adsorption studies.

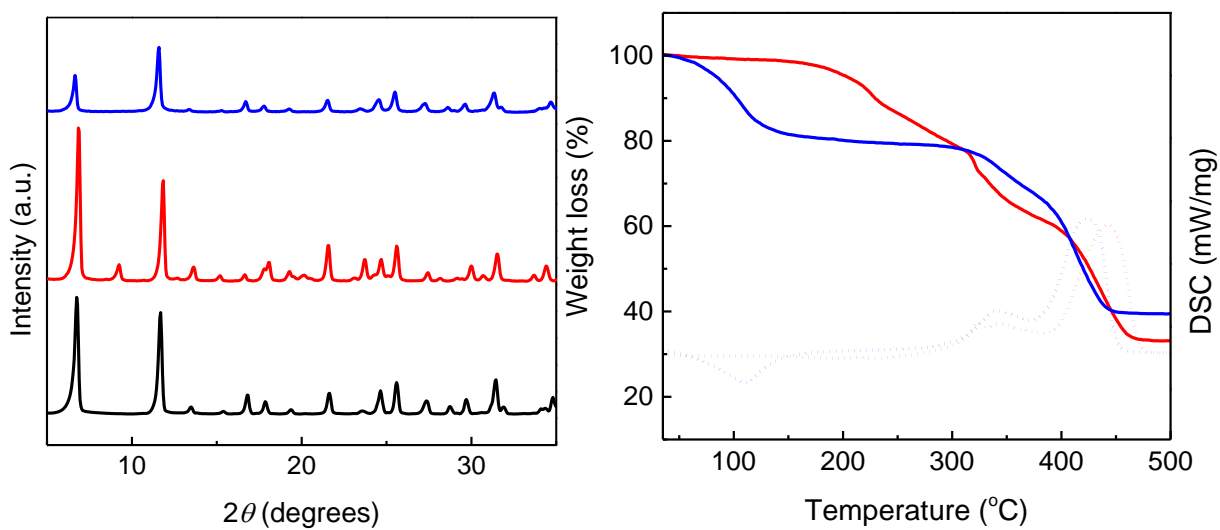


Figure S18. PXRD patterns (left) and TGA-DSC (right) of Zn-MOF-74 (black), Zn-MOF-74-*L-Pro* synthesised in MeOH (blue) and in DMF (red) using a molar ratio of 1:2 *L-Pro* to Zn-MOF-74. The TGA-DSC analysis was performed with a heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$ and 20 mLmin^{-1} flow of Ar.