

Electronic Supporting Information

Amide Functionalized Metal Organic Frameworks for Diastereoselective Nitroaldol (Henry) Reaction in Aqueous Medium

Anup Paul,^{a*} Anirban Karmakar,^a M. Fátima C. Guedes da Silva,^{a*} Armando J. L. Pombeiro^{a*}

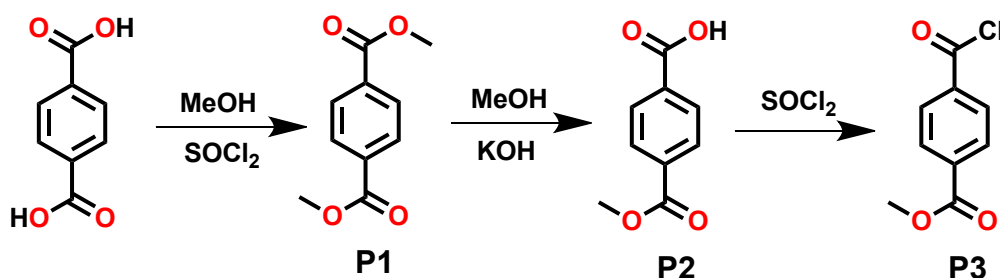
^a*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: kanupual@gmail.com, fatima.guedes@tecnico.ulisboa.pt, pombeiro@tecnico.ulisboa.pt*

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Experimental Section

Synthesis of methyl 4-(chlorocarbonyl)benzoate



Synthesis of P1

Thionyl chloride (10 mL) was added to a methanolic solution (60 mL) of terephthalic acid (H₂DA) (2.0 g, 60.19 mmol) and the suspension was refluxed overnight. The solvent was distilled off and the mixture was extracted with diethyl ether (3×50 mL). It was then dried over sodium sulfate. Rotary evaporated of the solvent gave the diester **P1** as pure colourless solid. Yield: 60 %. ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.08 (s, 4H, H_{Ar}), 3.93 (s, 6H, -OCH₃); ¹³C-NMR (75.45 MHz, CDCl₃, δ ppm): 166.26, 133.88, 129.54, 52.43.

Synthesis of P2

To a methanolic solution of P1 (1 g, 5.16 mmol) was added solid potassium hydroxide (0.290 g, 5.18 mmol) and the reaction mixture was heated to reflux overnight. Removal of the solvent to dryness under reduced pressure in a rotary evaporator afforded a white crystalline material. The

mixture was then dissolved in water, washed several times with dichloromethane, and acidified with conc. HCl to pH 1 upon which a white solid precipitated out. The precipitate thus obtained was dissolved in diethyl ether and dried over magnesium sulfate. Removal of the solvent afforded the desired product **P2** as a white solid. Yield: 82 %. $^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ ppm): 8.06 (s, 4H, H_{Ar}), 3.88 (s, 3H, -O- CH_3); $^{13}\text{C-NMR}$ (75.45 MHz, DMSO- d_6 , δ ppm): 167.13, 165.83, 135.28, 133.22, 129.89, 129.34, 52.61.

Synthesis of **P3**

P2 (1.0 g, 5.56 mmol) and a catalytic amount of N,N-dimethylformide were heated to reflux in thionyl chloride (20 mL) overnight. Then, the thionyl chloride was distilled off and the resulting solid was redissolved in dichloromethane (60 mL), washed several times with water, and dried using anhydrous Na_2SO_4 . Decantation and concentration to dryness under vacuum led to the desired product **P3** as an off white solid. Yield: 91%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.19 (s, 4H, H_{Ar}), 3.99 (s, 3H, -O- CH_3), $^{13}\text{C-NMR}$ (75.45 MHz, CDCl_3 , δ ppm): 168.16, 165.45, 136.62, 135.57, 130.98, 129.33, 52.60.

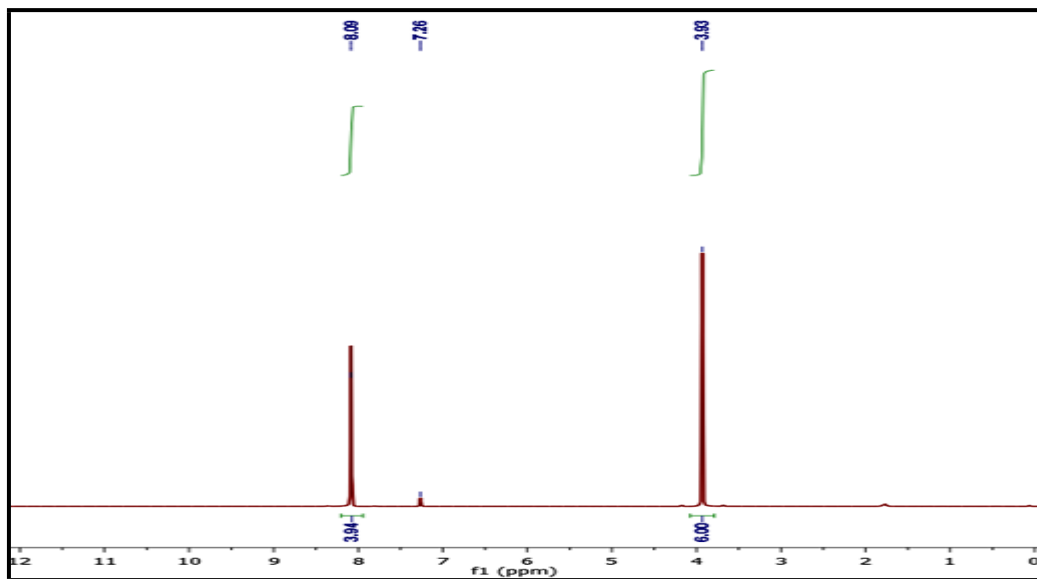


Fig. S1. $^1\text{H NMR}$ of **P1** recorded in CDCl_3 .

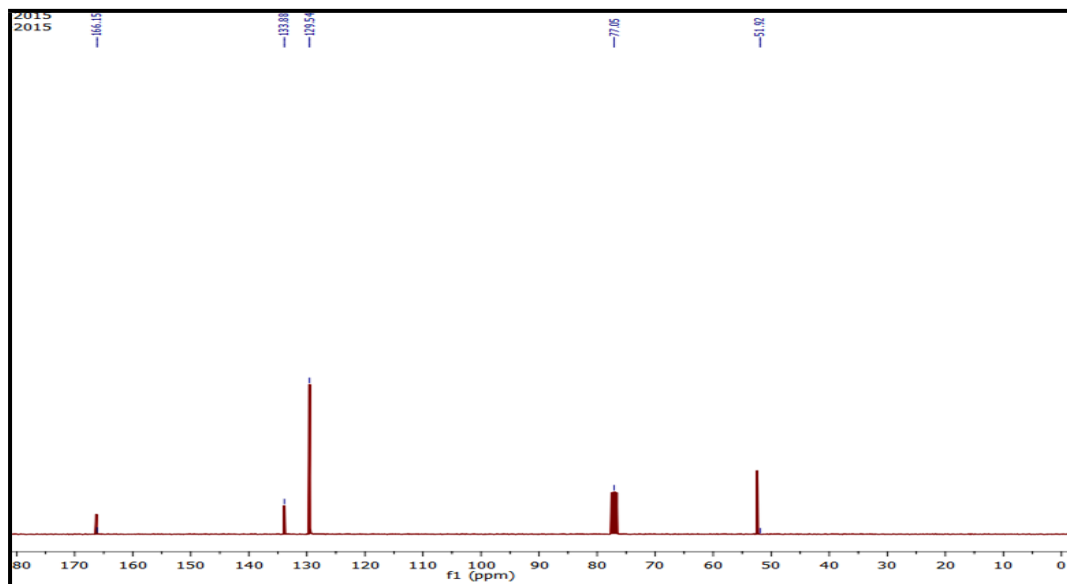


Fig. S2. ^{13}C NMR of **P1** recorded in CDCl_3 .

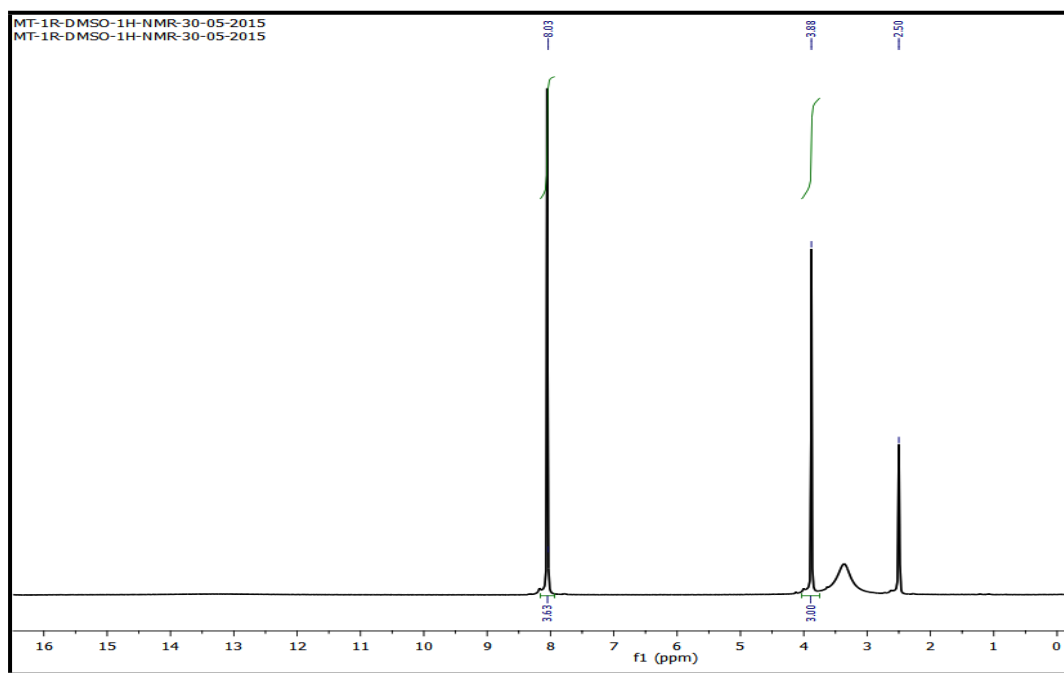


Fig. S3. ^1H NMR of **P2** recorded in DMSO-d_6 .

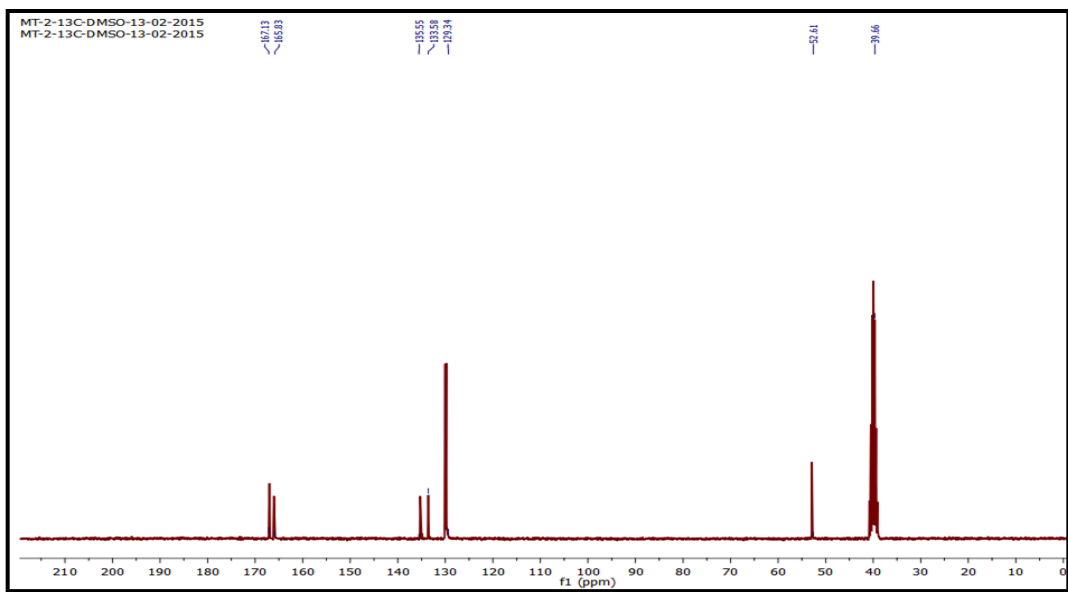


Fig. S4. ^{13}C NMR of **P2** recorded in DMSO-d_6 .

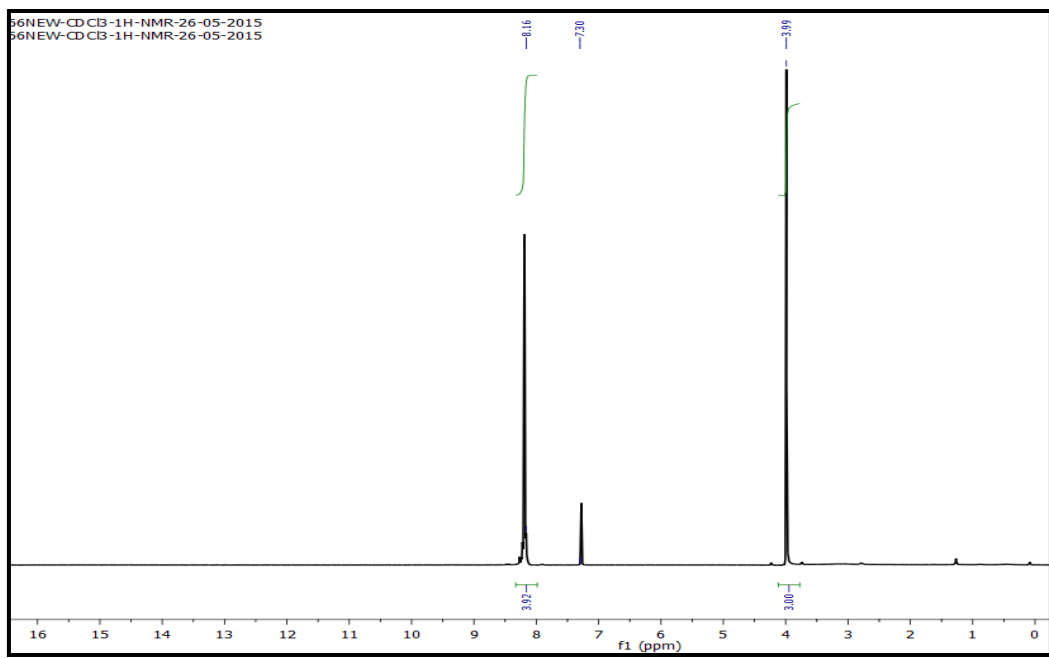


Fig. S5. ^1H NMR of **P3** recorded in CDCl_3 .

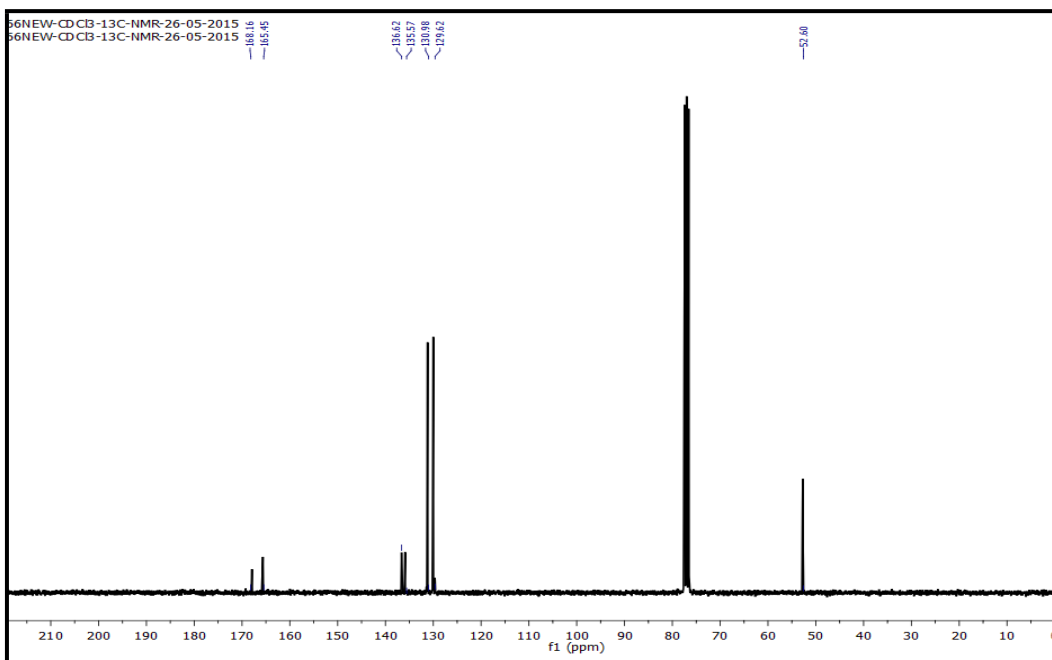


Fig. S6. ^{13}C NMR of **P3** recorded in CDCl_3 .

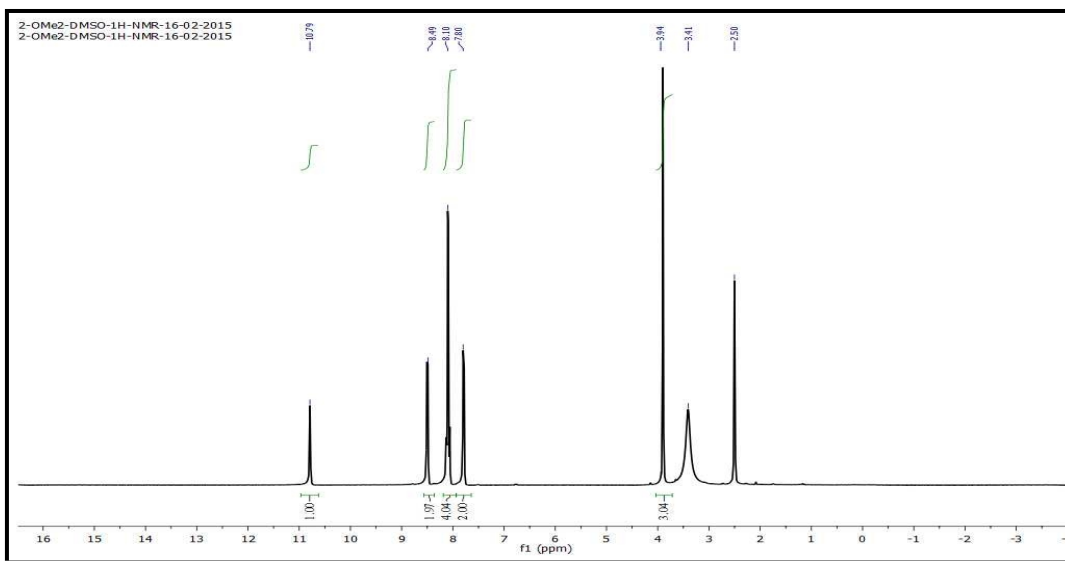


Fig. S7. ^1H NMR of **MeL** recorded in DMSO-d_6 .

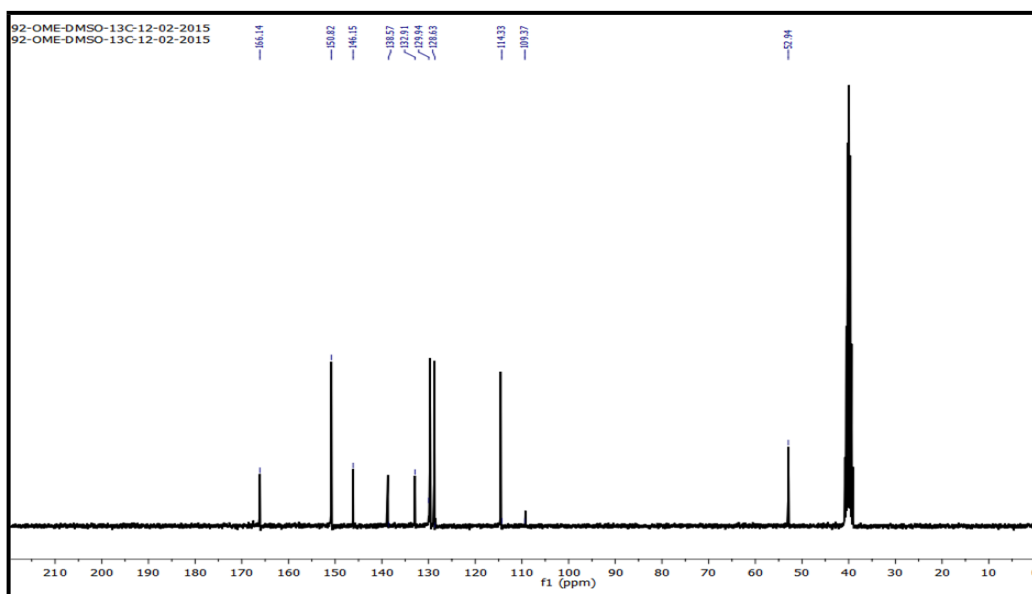


Fig. S8. ^{13}C NMR of MeL recorded in DMSO-d_6 .

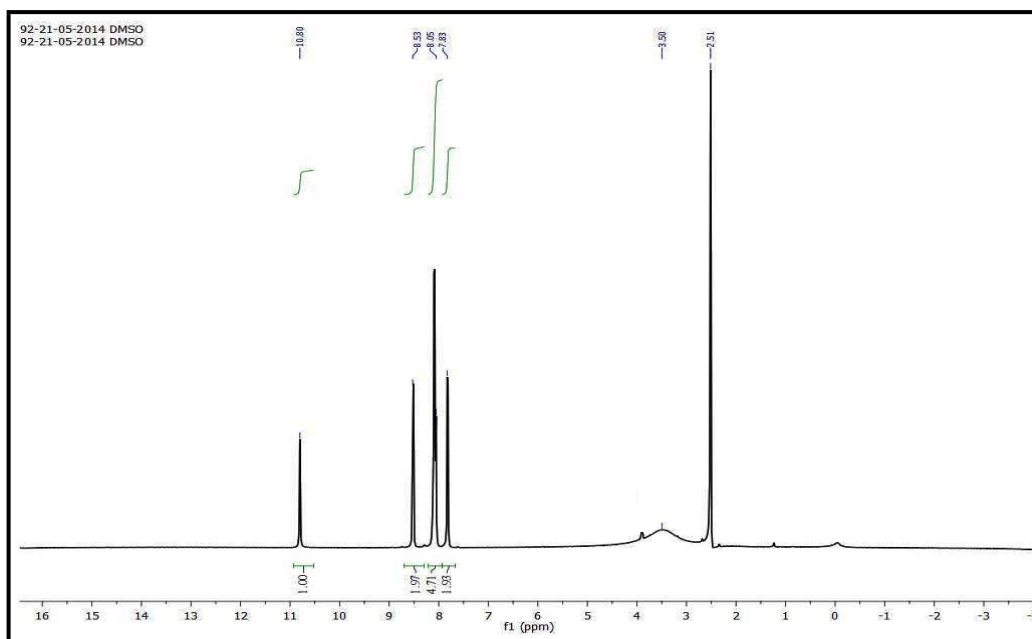


Fig. S9. ^1H NMR of HL recorded in DMSO-d_6 .

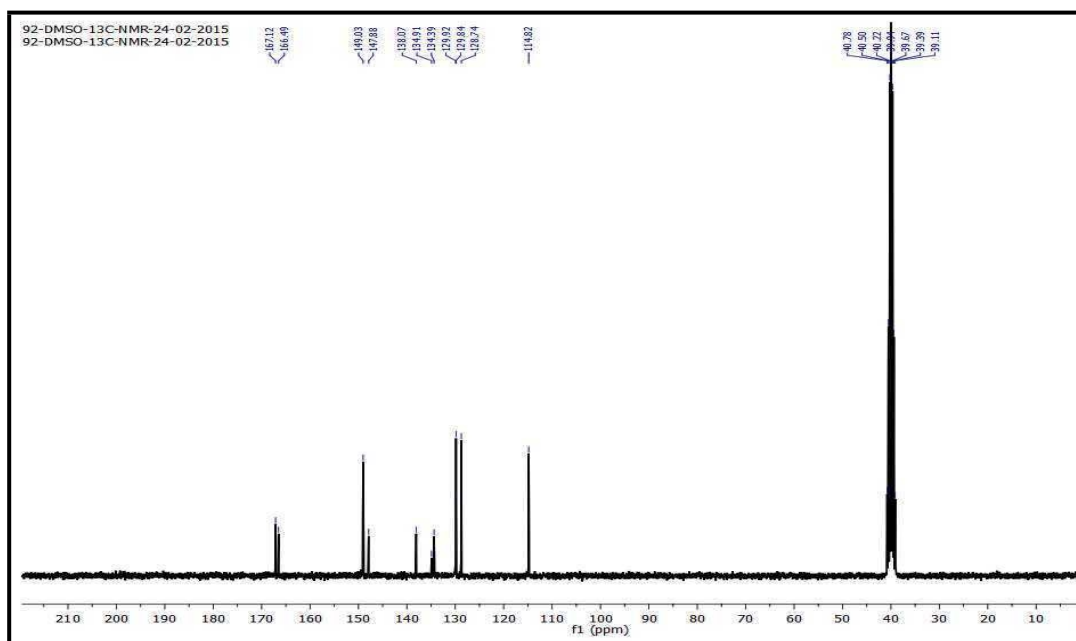


Fig. S10. ^{13}C NMR of **HL** recorded in DMSO-d_6 .

Thermogravimetric analyses

In order to get an insight into the thermal stability and structural variation of frameworks **1** and **2** as a function of temperature, thermogravimetric analysis (TGA) was carried out under dinitrogen in the 30-700 $^{\circ}\text{C}$ range at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ (Fig. S11). Compound **1** with a 2D net exhibits the loss of two non-coordinated DMF molecules at 89-343 $^{\circ}\text{C}$ with an observed weight loss of 15.4 % (calculated = 15.8 %). Above 350 $^{\circ}\text{C}$, the polymeric structure disintegrates leading to the formation of ZnO (Fig. S11).

The TGA analysis of framework **2** (Fig. S11) exhibits a weight loss of 35.8 % (calculated = 36.2 %) in the 75-325 $^{\circ}\text{C}$ temperature range, corresponding to the loss of four DMF and one water molecules. After this, the remaining material decomposes gradually leading to the formation of CuO.

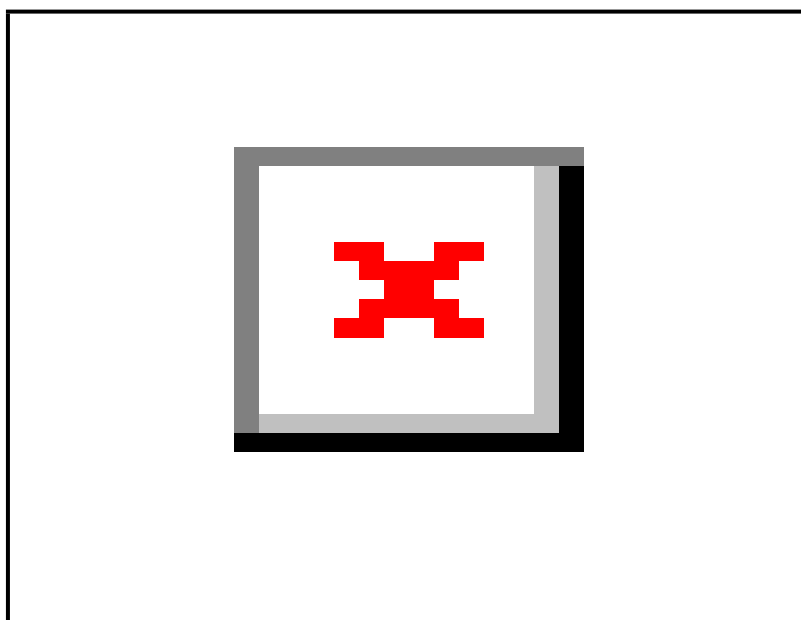


Fig S11. Thermogravimetric curves for 1 and 2.

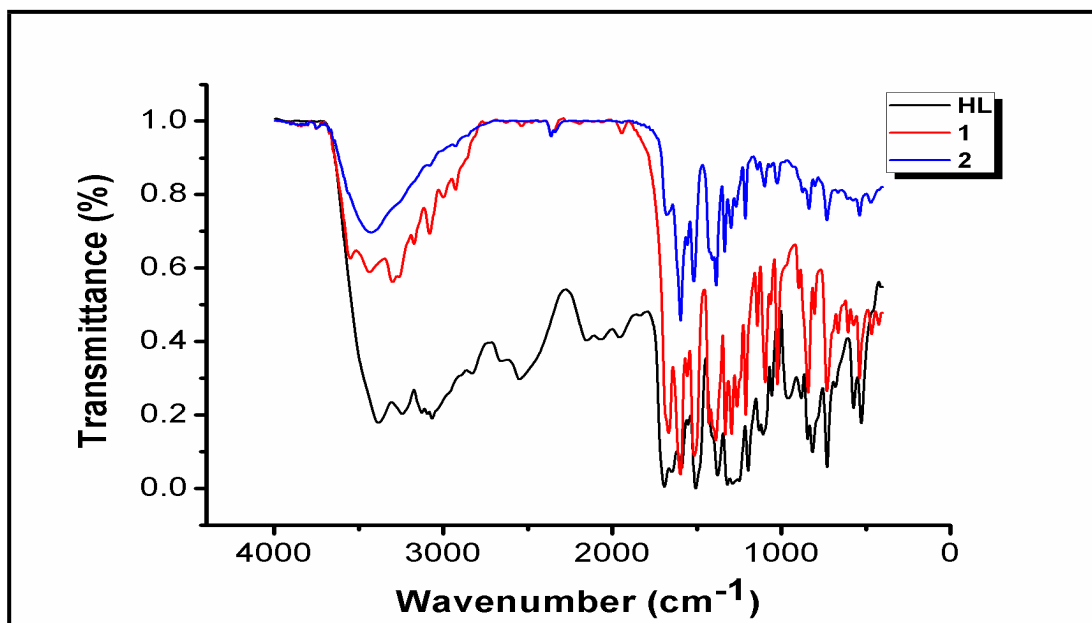


Fig. S12. FT-IR spectra of HL, 1 and 2.

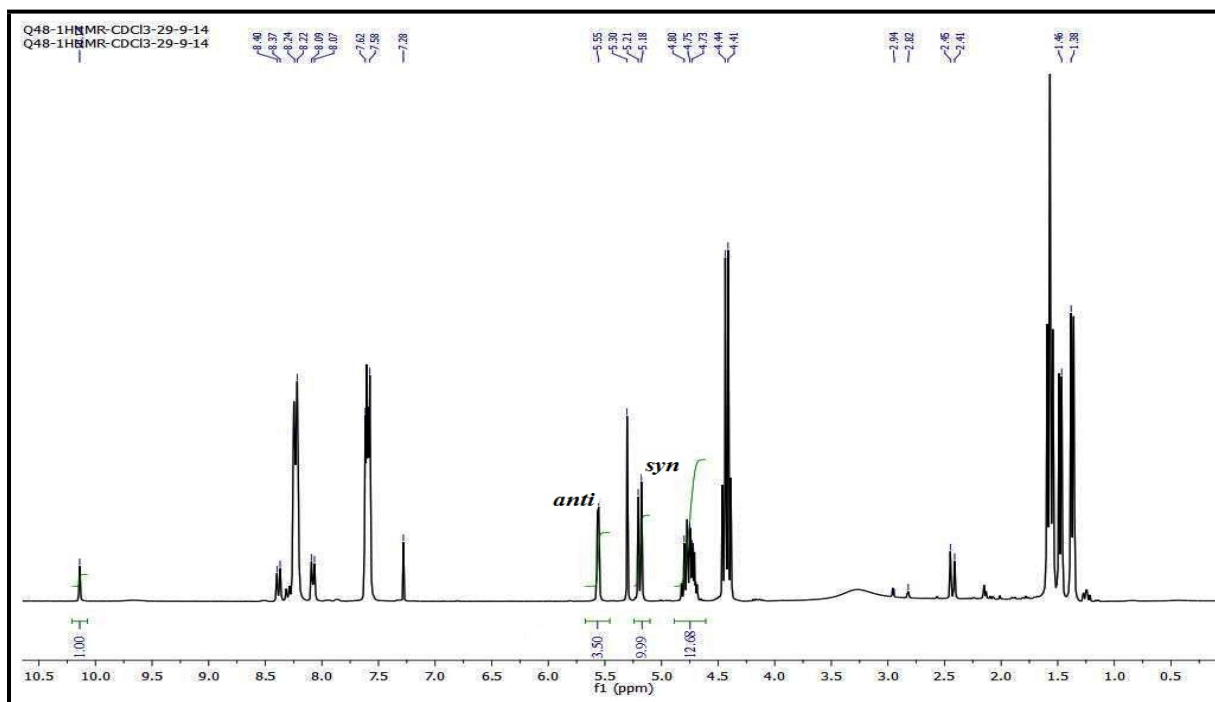


Fig. S13. Example of integration in the ^1H -NMR spectrum for the determination of Henry reaction products (Table 1, entry 5).

Calculation of the yield and selectivity for complex 1 in the Henry reaction:

Yield:

Total amount of compounds

$$p\text{-nitrobenzaldehyde} + \text{anti} + \text{syn} = 1 + 3.50 + 9.99 = 14.49$$

$$\text{Percentage of the unreacted aldehyde: } (1/14.49) \times 100 = 7\%$$

$$\text{Yield of } \beta\text{-nitroalkanols} = 100 - 7 = 93\%$$

$$\text{Yield of } \textit{syn} = (9.99/14.49) \times 100 = 69\%$$

$$\text{Yield of } \textit{anti} = (3.5/14.49) \times 100 = 24\%$$

Selectivity:

$$(\textit{syn} + \textit{anti}) = 69 + 24 = 93 \text{ (100\%).}$$

$$\text{Selectivity of } \textit{syn} = (69/93) \times 100 = 74\%$$

$$\text{Selectivity of } \textit{anti} = (24/93) \times 100 = 26\%$$

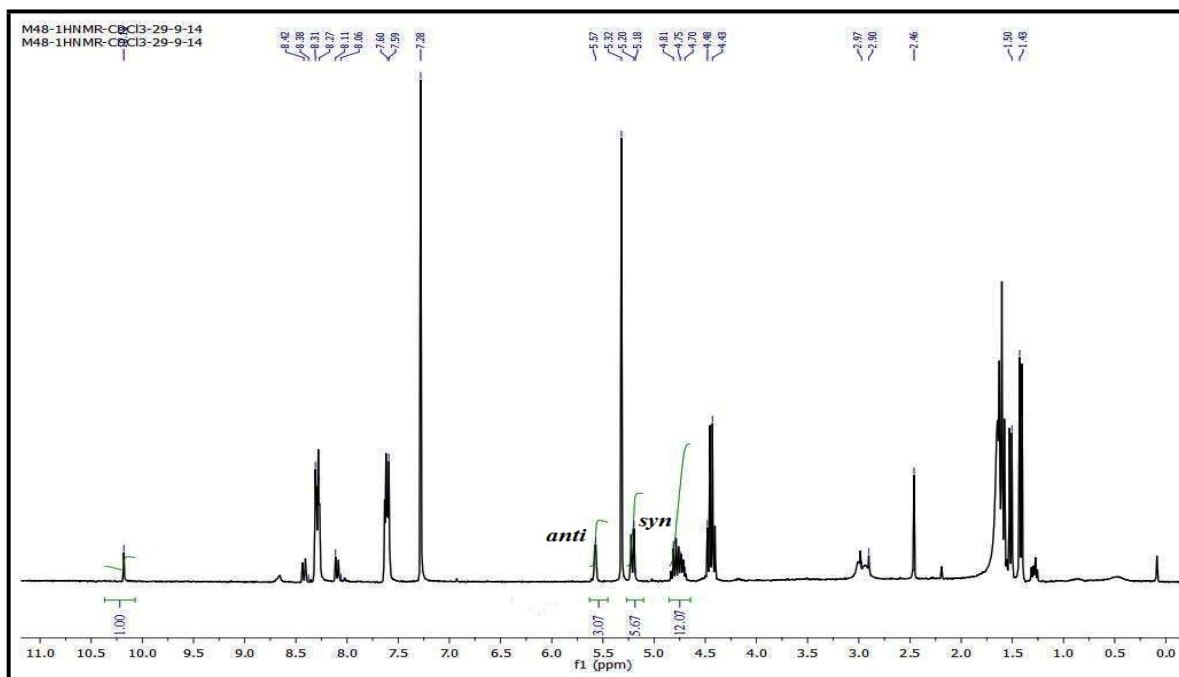


Fig. S14. Example of integration in the ^1H -NMR spectrum for the determination of Henry reaction products (Table 1, entry 5).

Calculation of the yield and selectivity for complex 2 in the Henry reaction:

Yield:

Total amount of compounds:

$$\text{p-nitrobenzaldehyde} + \text{anti} + \text{syn} = 1 + 3.07 + 5.67 = 9.74$$

$$\text{Percentage of the unreacted aldehyde: } (1/9.74) \times 100 = 10\%$$

$$\text{Yield of } \beta\text{-nitroalkanols} = 100 - 10 = 90\%$$

$$\text{Yield of } \textit{syn} = (5.67/9.74) \times 100 = 58\%$$

$$\text{Yield of } \textit{anti} = (3.07/9.74) \times 100 = 31\%$$

Selectivity:

$$(\textit{syn} + \textit{anti}) = 58 + 31 = 89 \text{ (100\%).}$$

$$\text{Selectivity of } \textit{syn} = (58 / 89) \times 100 = 65\%$$

$$\text{Selectivity of } \textit{anti} = (31/89) \times 100 = 35\%$$

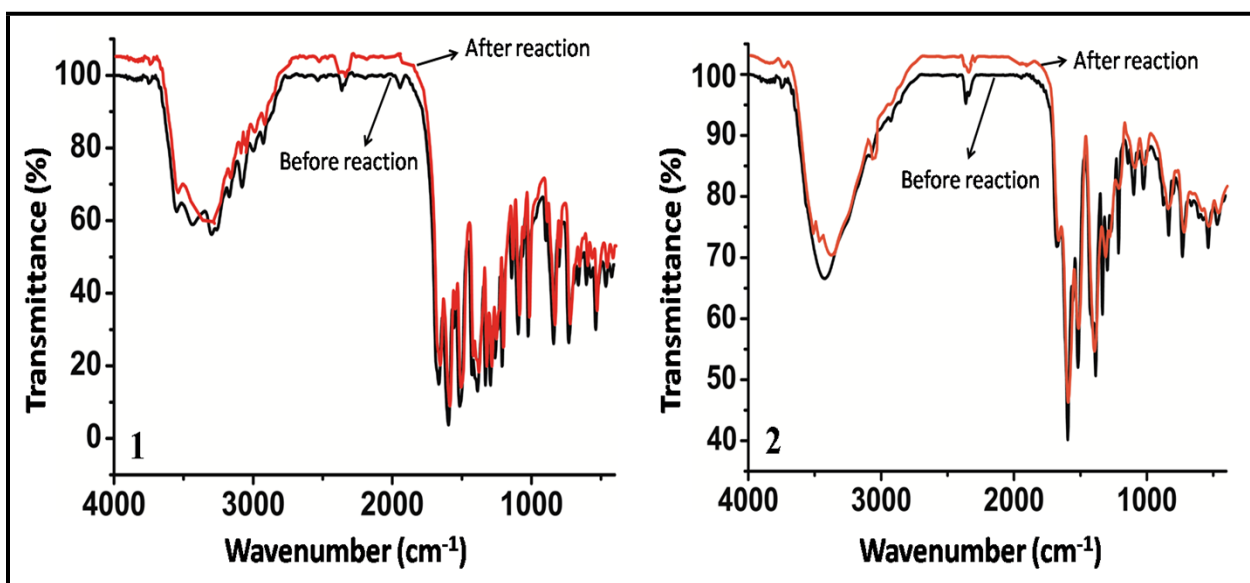


Fig. S15. FT-IR spectra of **1** and **2** recorded before and after the catalytic reaction.

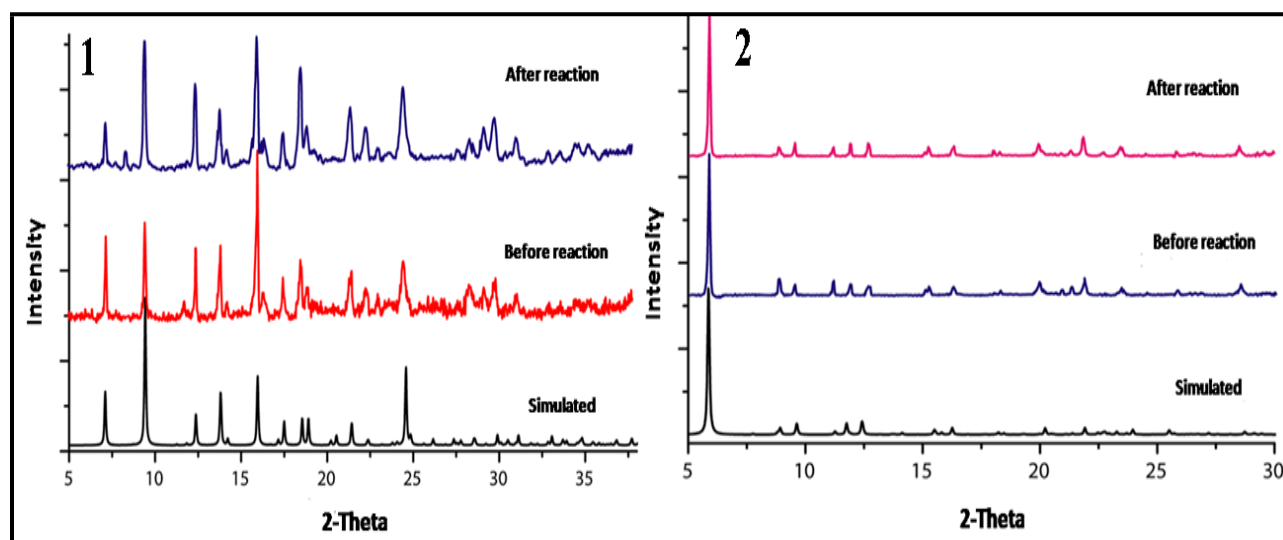


Fig. S16. Powder XRD of **1** and **2** recorded before and after the catalytic reaction.

Table S1: Hydrogen bond geometry (Å, °) in compounds **1** and **2**.

Compound	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	<D-H...A(°)	Symmetry
1	N4-H4N...O20	0.84	2.20(6)	2.985(8)	157.0	-x+1, y+1/2, -z+1
	N6-H6N...O21	0.83	2.17(6)	2.980(9)	164.0	-
	C11-H11...O10	0.93	2.46	3.069(7)	122.9	-
	C12-H12...O20	0.93	2.37	3.144(9)	140.1	-x+1, y+1/2, -z+1
	C23-H23...O12	0.93	2.24	2.801(8)	118.2	-
	C32-H32...O21	0.93	2.36	3.142(10)	141.5	-
	C56-H56...O23	0.93	2.27	2.848(8)	119.6	-
	C60-H60...O9	0.93	2.45	3.058(8)	123.4	-
2	C9-H9...O2	0.95	2.47	3.041(7)	118.1	-x+1, -y+1, -z+1
	C10-H10...O6	0.95	2.26	2.841(7)	118.5	-x+3/2, y+1/2, -z+3/2
	C12-H12...O8	0.95	2.50	3.276(7)	138.8	x+1/2, -y+3/2, z+1/2
	C13-H13...O1	0.95	2.37	2.887(6)	113.7	-
	C24-H24...O1	0.95	2.45	2.937(6)	111.6	-x+3/2, y+1/2, -z+1/2
	C24-H24...O4	0.95	2.51	3.230(7)	132.5	x-1/2, -y+3/2, z-1/2
	C26-H26...O5	0.95	2.26	2.851(7)	119.8	-

Table S2: Selected bond distances (Å) and angles (°) for compounds **1** and **2**.

	Bond distances		Bond angles		Bond angles
1					
Zn1-O1	2.031(3)	<N5-Zn1-O2	104.78(18)	<O22-Zn2-N3	104.12(18)
Zn1-O2	2.019(4)	<N5-Zn1-O1	104.13(16)	<O22-Zn2-O3	89.12(17)
Zn2-O3	2.034(3)	<O2-Zn1-O1	88.99(16)	<N3-Zn2-O3	103.86(15)

Zn1-04	2.044(3)	<N5-Zn1-04	96.65(15)	<O22-Zn2-05	89.63(15)
Zn1-09	2.080(4)	<O2-Zn1-04	89.38(15)	<N3-Zn2-05	97.82(15)
Zn1-N5	2.010(4)	<O1-Zn1-04	158.87(15)	<O3-Zn2-05	157.91(16)
Zn2-05	2.044(3)	<N5-Zn1-09	96.7(2)	<O22-Zn2-010	158.14(15)
Zn2-010	2.084(4)	<O2-Zn1-09	158.42(15)	<N3-Zn2-010	97.72(19)
Zn2-022	2.026(4)	<O1-Zn1-09	87.40(16)	<O3-Zn2-010	86.47(17)
Zn2-N3	2.025(5)	<O4-Zn1-09	86.42(17)	<O5-Zn2-010	86.53(16)
Zn1-Zn2	2.9936(5)				
2					
Cu1-N1	2.004(4)	<O1-Cu1-03	157.35(16)	<O1-Cu1-02	116.82(15)
Cu1-N3	2.020(4)	<O1-Cu1-N1	88.00(16)	<O3-Cu1-02	85.66(14)
Cu1-01	1.961(3)	<O3-Cu1-N1	90.83(16)	<N1-Cu1-02	86.54(16)
Cu1-02	2.342(4)	<O1-Cu1-N3	91.84(16)	<N3-Cu1-02	90.42(16)
Cu1-03	1.967(3)	<O3-Cu1-N3	90.67 (17)		
		<N1-Cu1-N3	176.50(18)		