Electronic Supplementary Information

Effect of flexible chain length of the dimetal subunit on the formation of 1D coordination polymer to molecular rectangle

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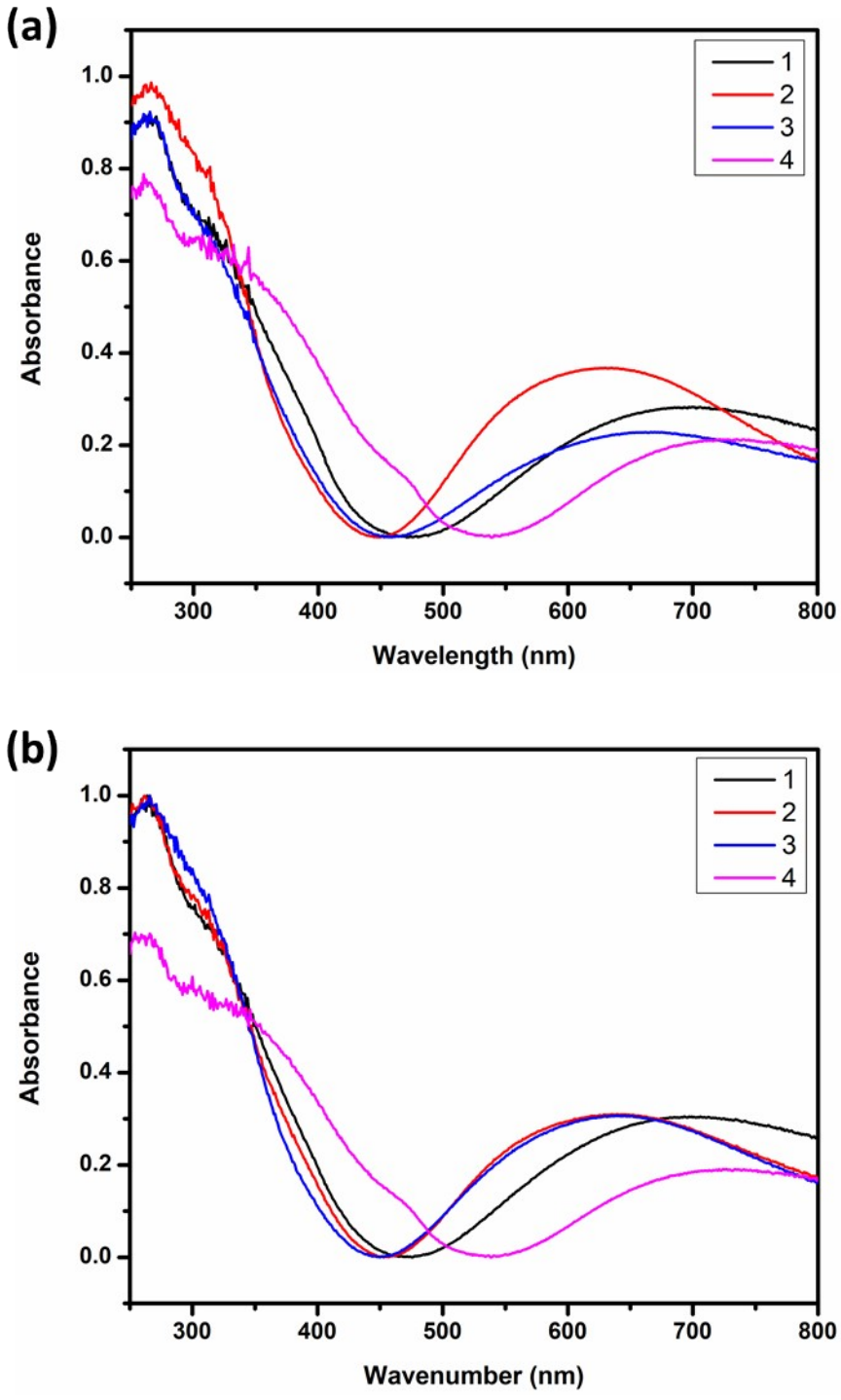

Fig S1. Solid-state diffuse reflectance spectra of (a) as-synthesized **1**-**4**, and (b) solid crystals of **1**-**4** isolated from their respective solution in 1:1 H_2O/CH_3CN. λ_{max} (nm) for the d-d transition**:** 693 for **1**; 623 for **2**; 654 for **3** and 732 for **4**.

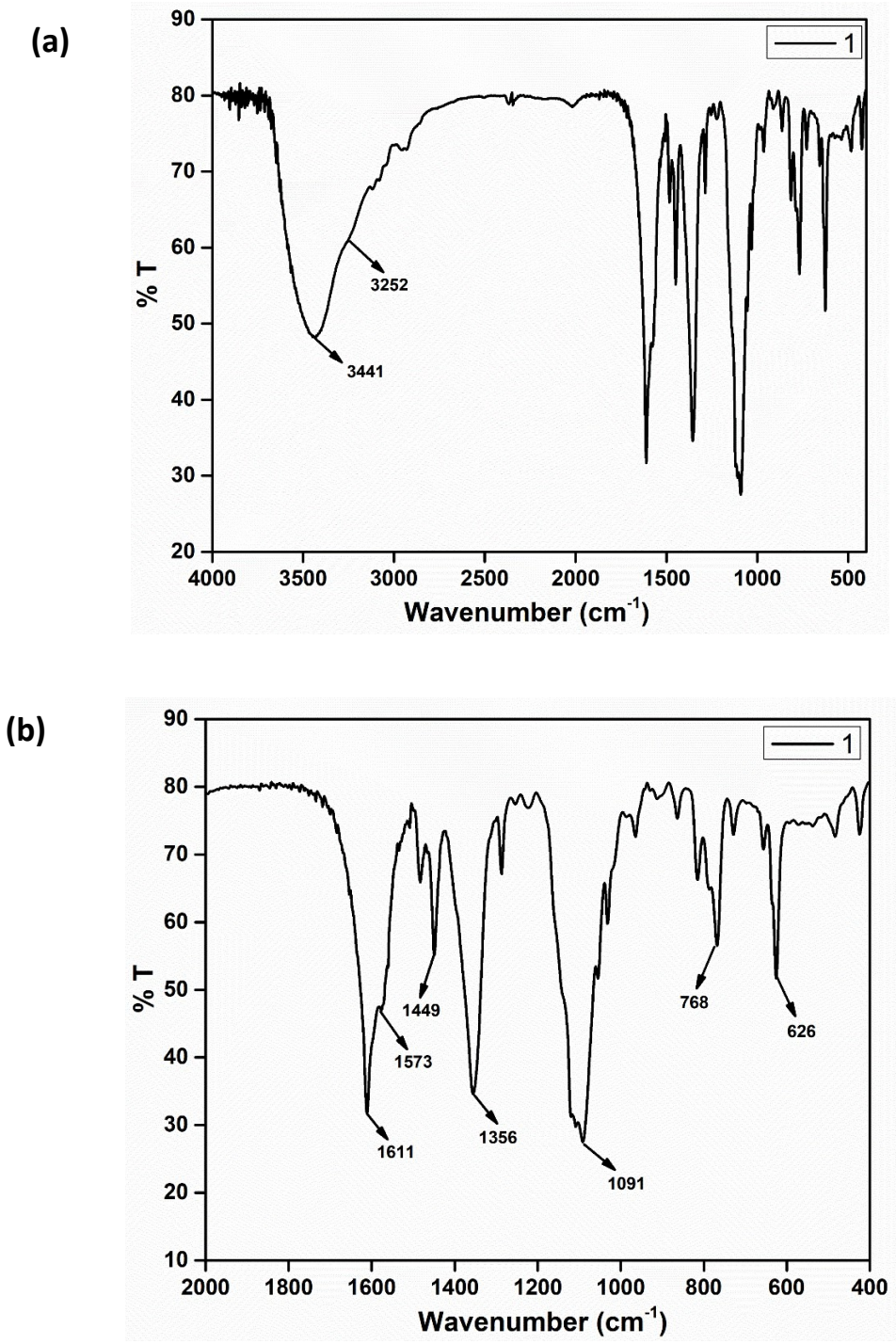

Fig. S2 (a) Full and (b) expanded region in FTIR spectrum of **1**.

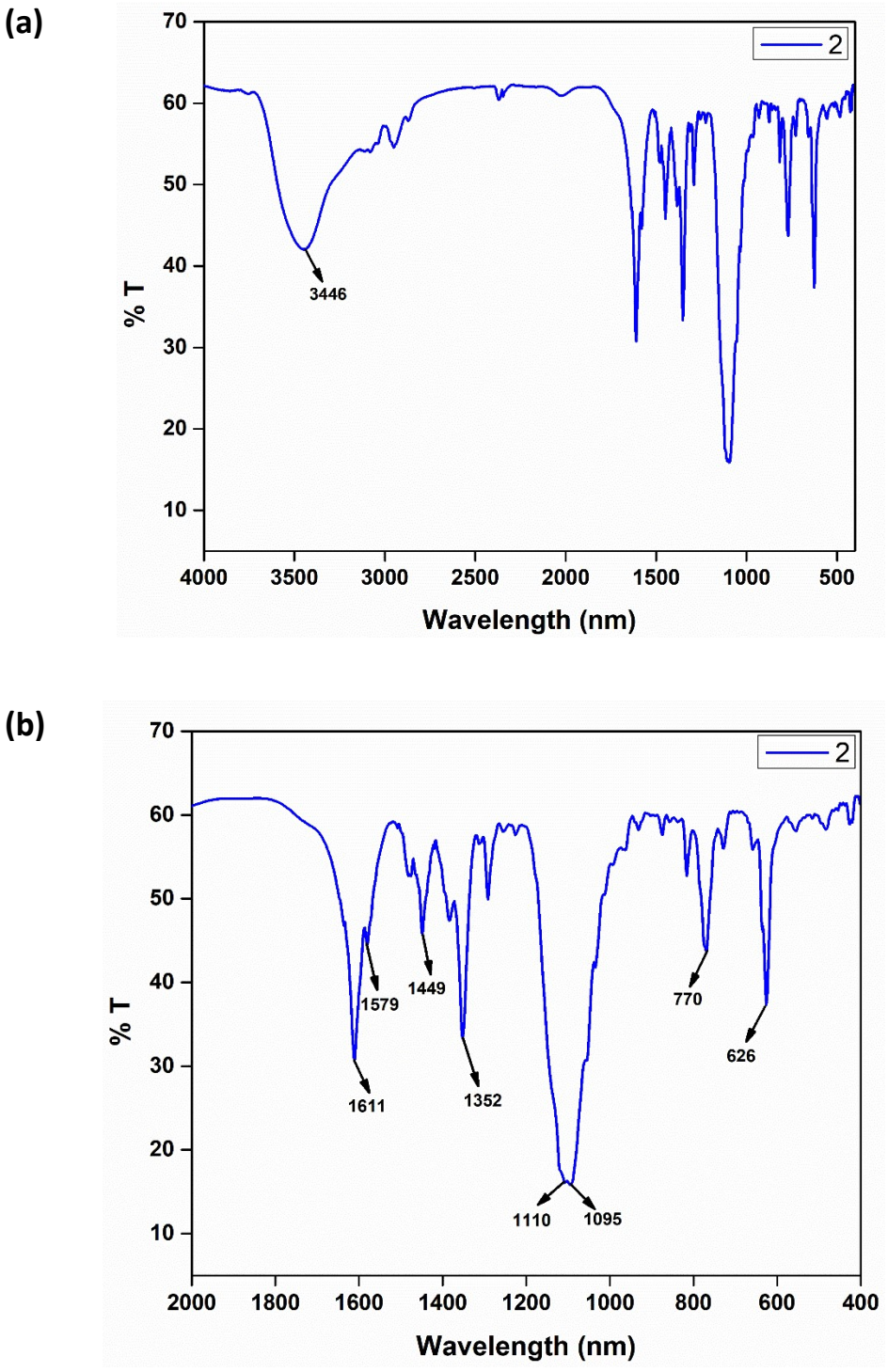

Fig. S3 (a) Full and (b) expanded region in FTIR spectrum of **2**.

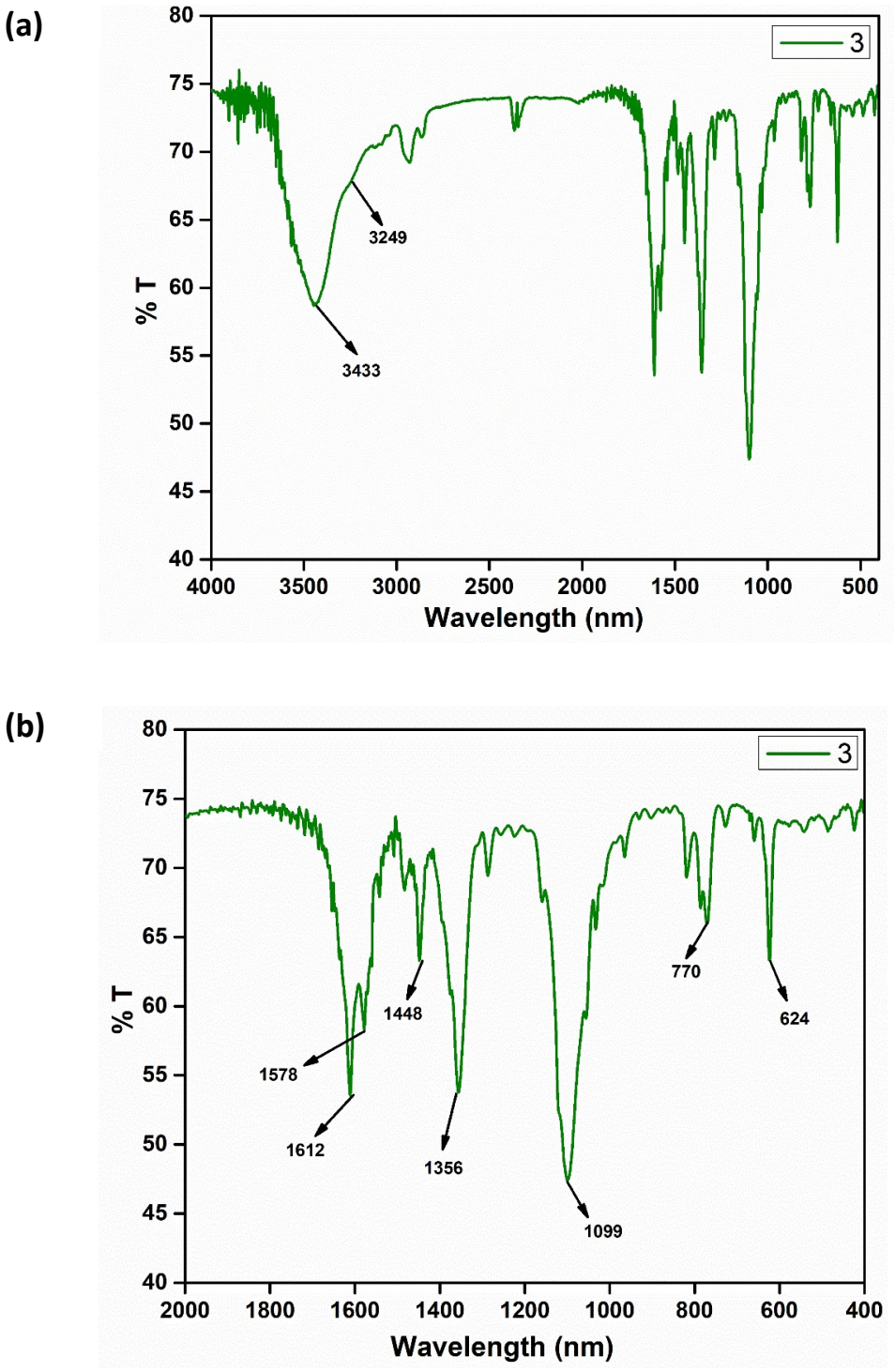

Fig. S4 (a) Full and (b) expanded region in FTIR spectrum of **3**.

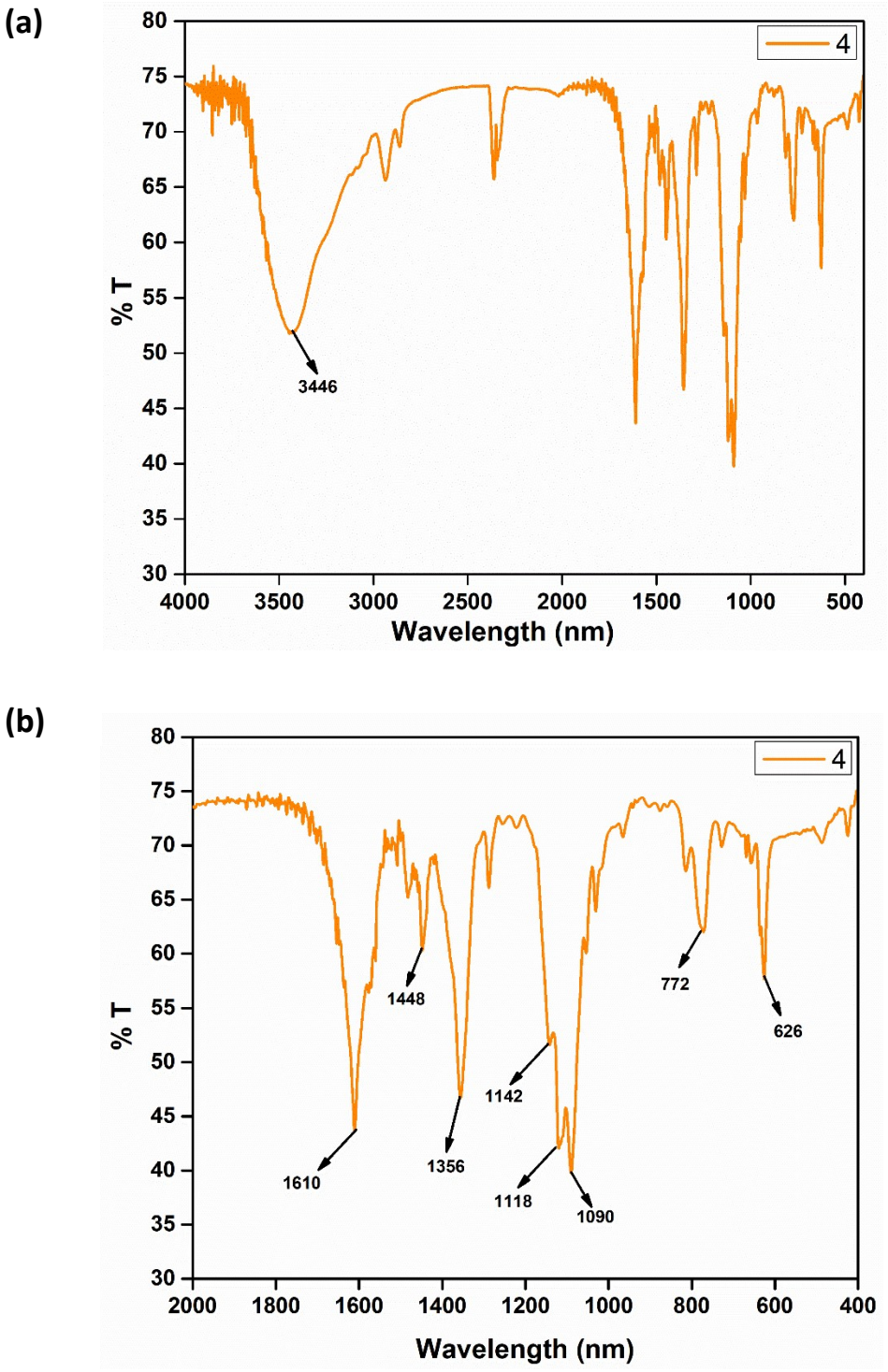

Fig. S5 (a) Full and (b) expanded region in FTIR spectrum of **4**.

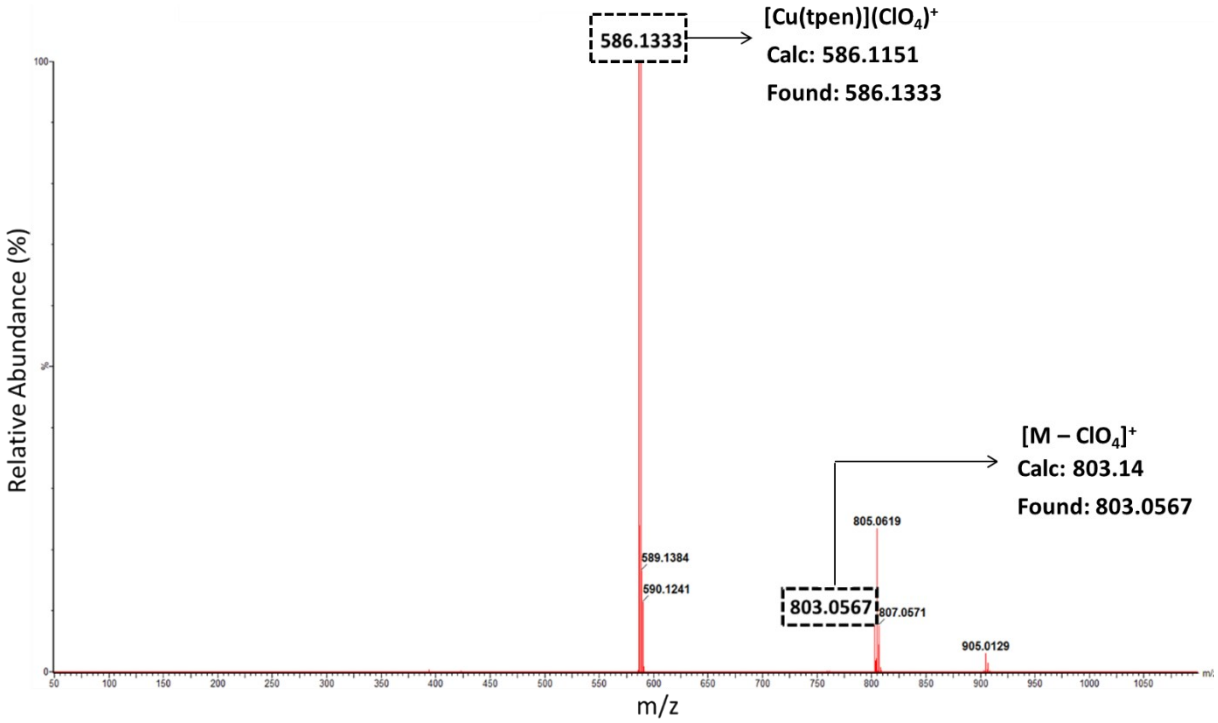

Fig. S6 ESI mass spectrum of **1** in H_2O.

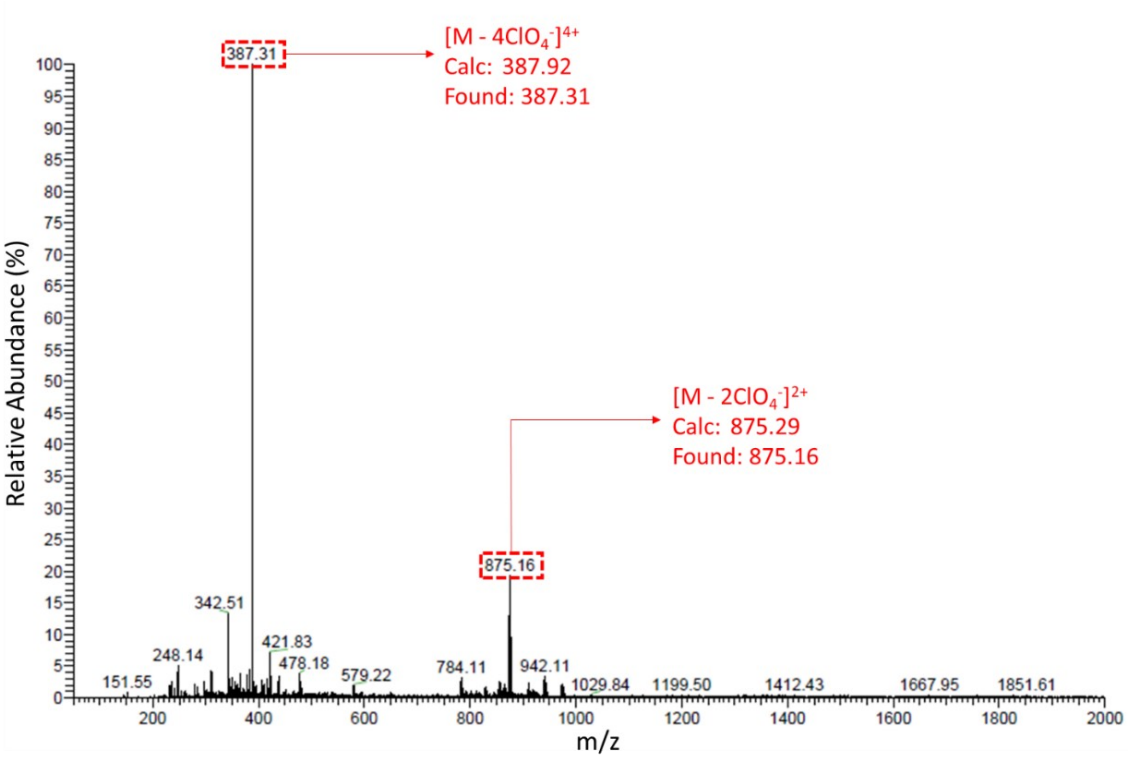

Fig. S7 ESI mass spectrum of **4** in H_2O/CH_3CN.

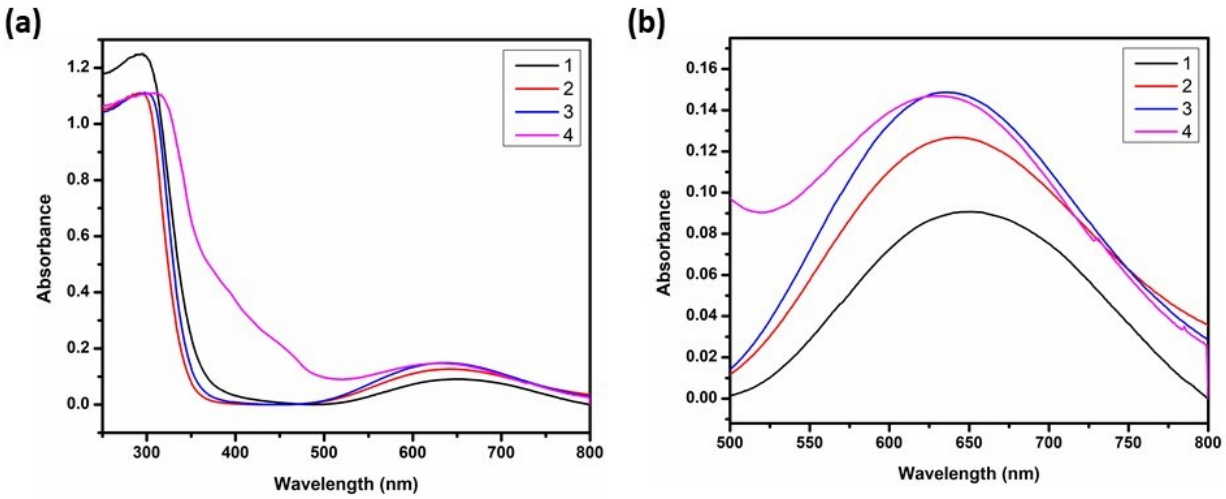

Fig. 8 UV-vis spectra of **1**-**4** in a 1:1 H_2O and CH_3CN solution: (a) full and (b) expanded visible region.

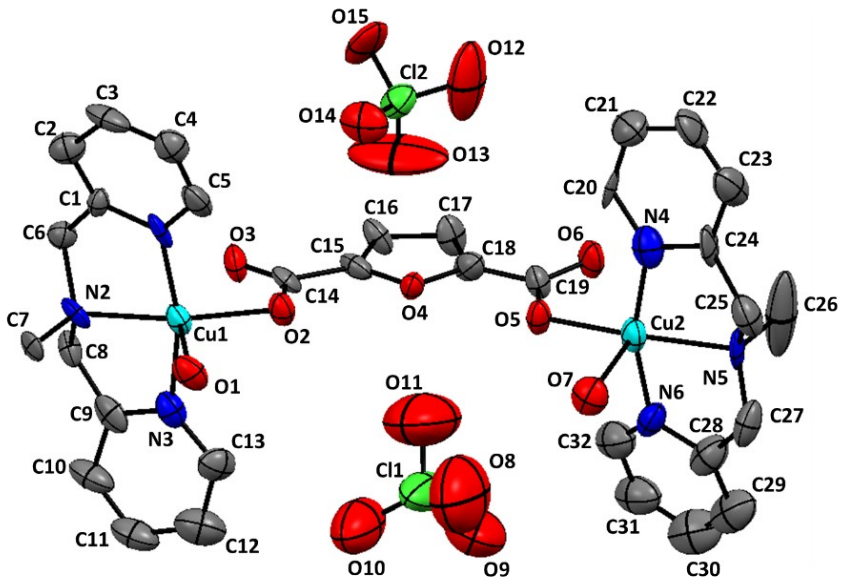

Fig. S9 ORTEP view of **1** describing coordination environment around the Cu(II) centers.

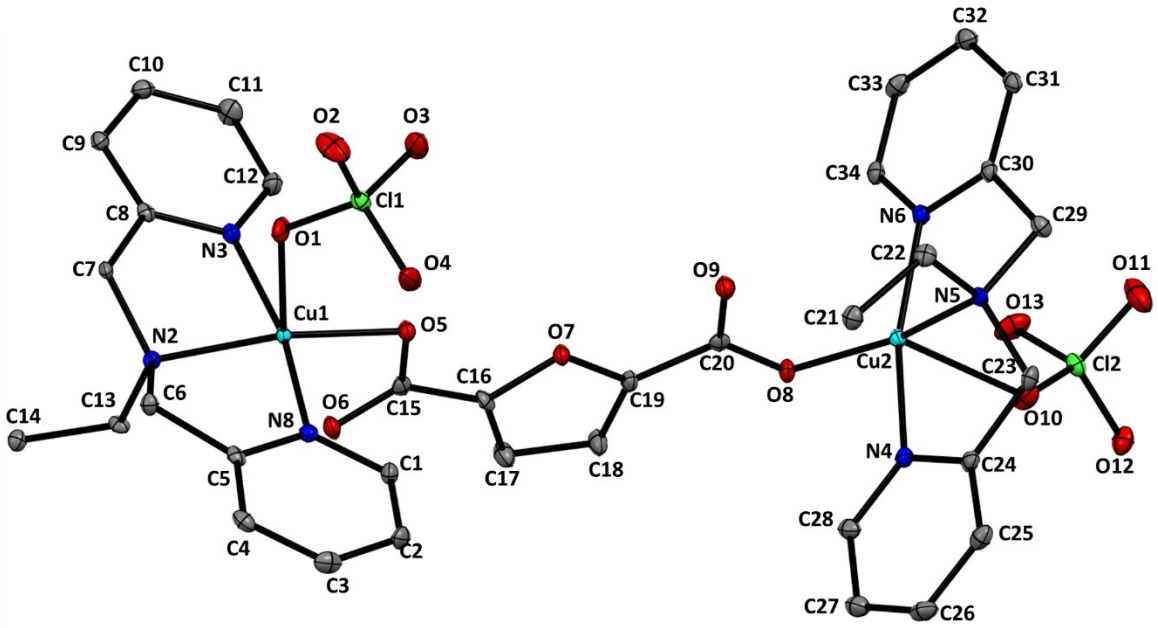

Fig. S10 ORTEP view of **2**.

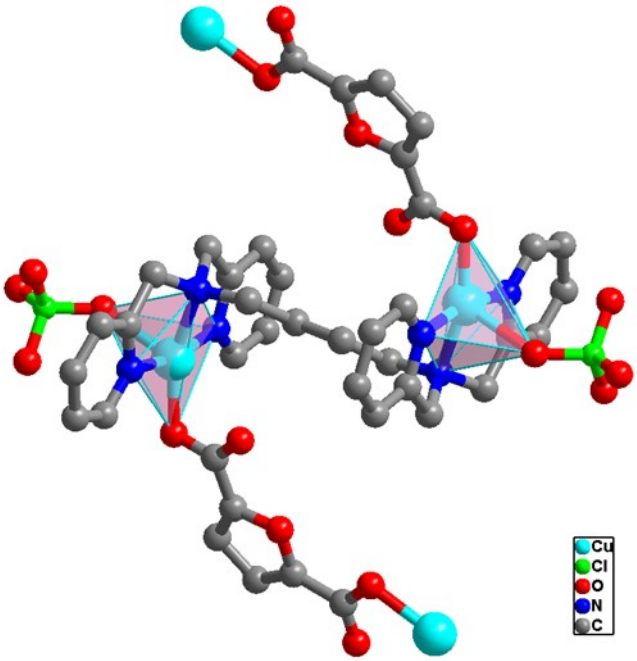

Fig. S11 Coordination environment around Cu(II) centers in **2**.

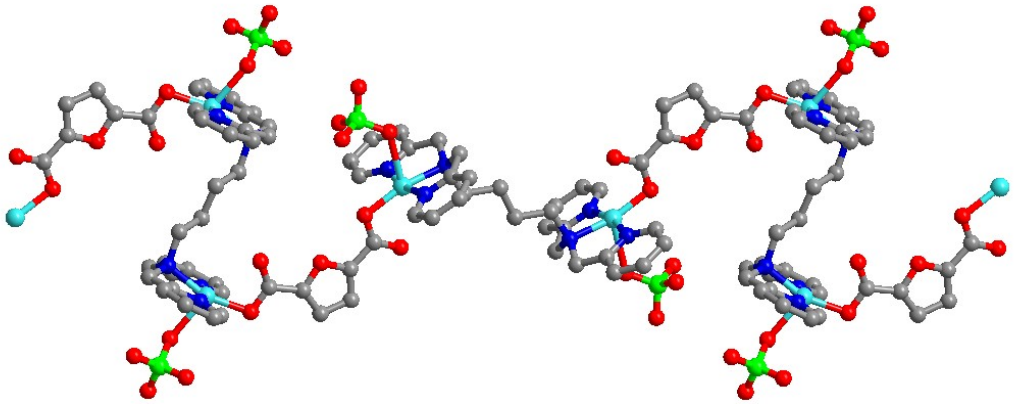

Fig. S12 Perspective view of a 1D coordination polymer of **2**.

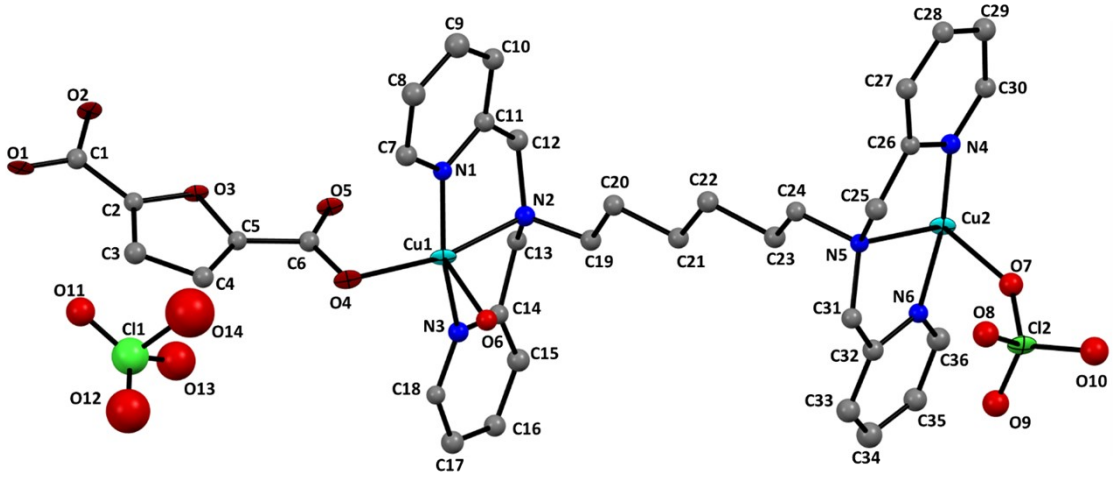

Fig. S13 ORTEP view of **3** describing the coordination environment around the Cu(II) centers.

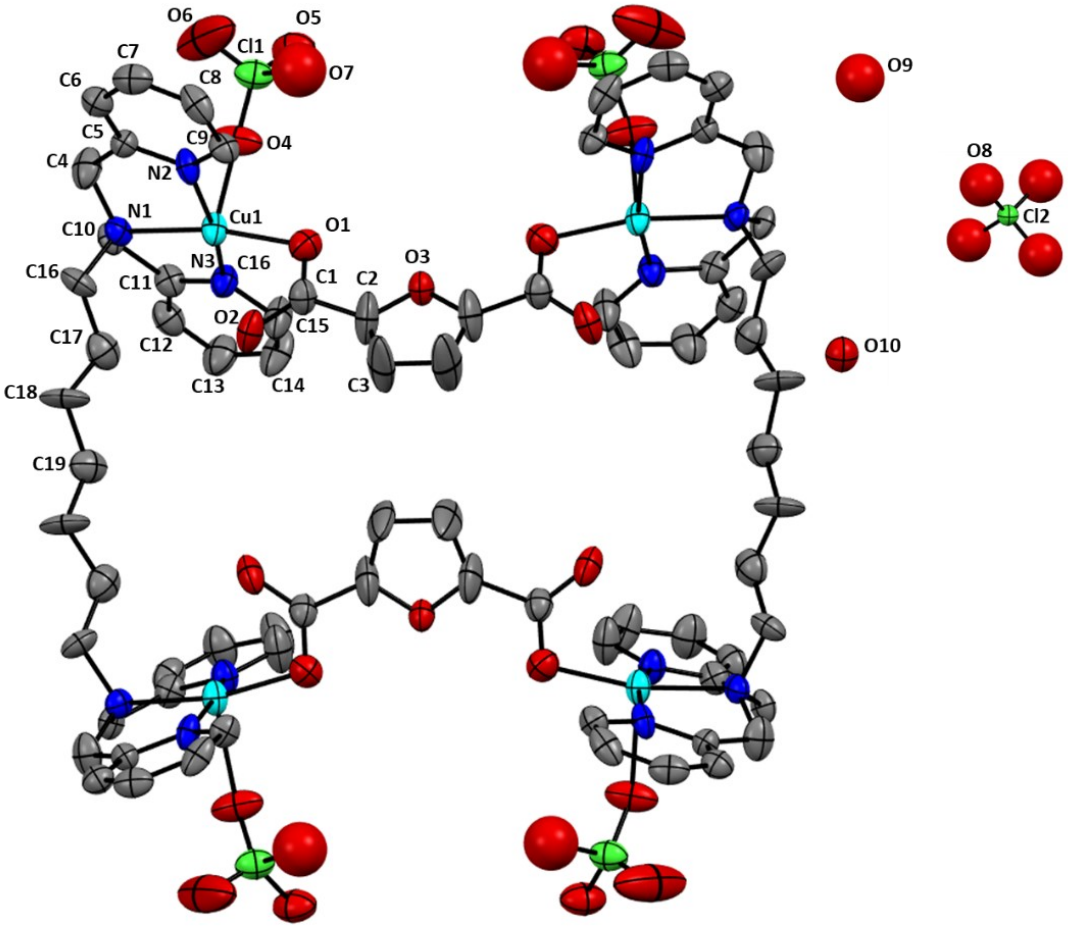

Fig. S14 ORTEP view of **4** where one-fourth of the molecule is in the asymmetric unit.

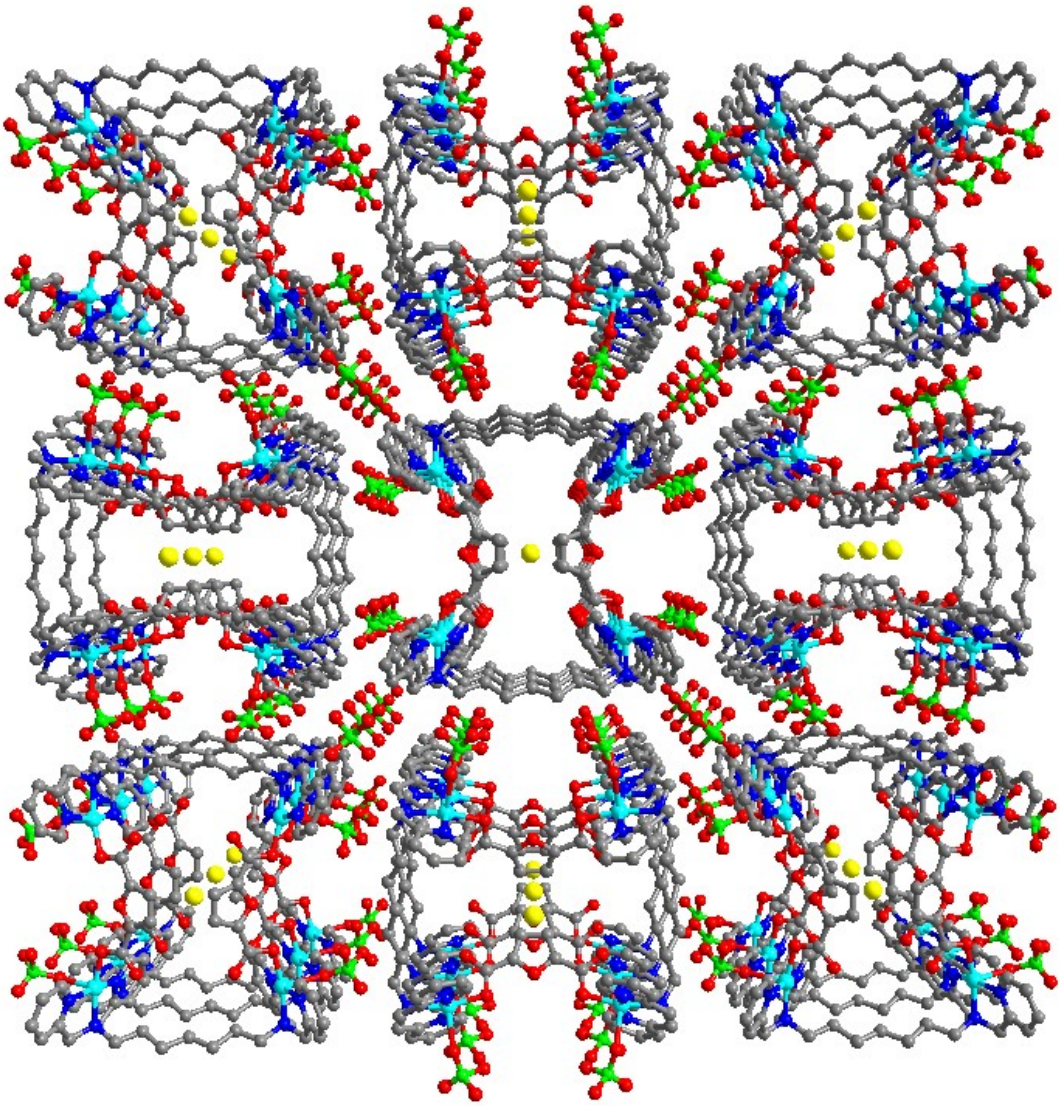

Fig. S15 Packing diagram of molecular rectangles in **4**. (Color codes: carbon, grey; oxygen, red; nitrogen, blue; copper, cyan; sodium, yellow).

Catalysis study of **1**-**4**

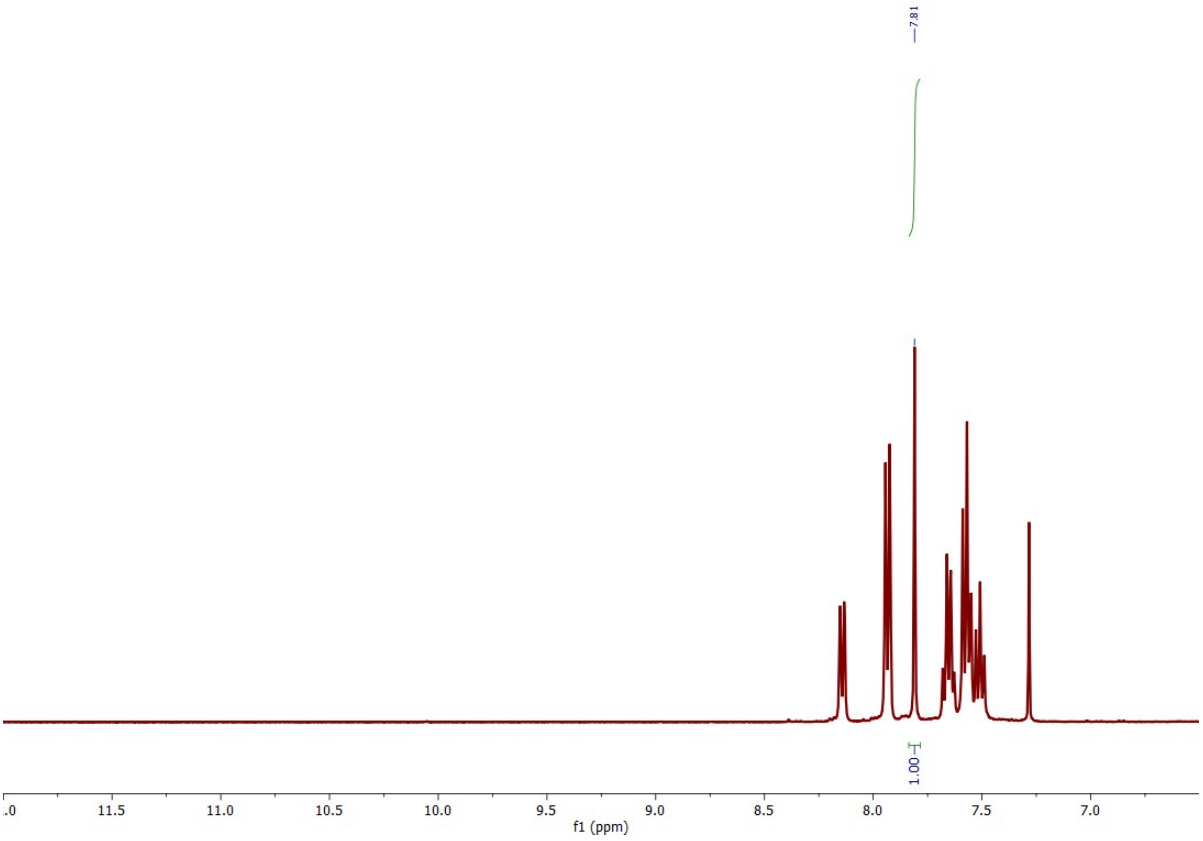

Fig. S16 Example of integration in the ^{1}H NMR spectrum for the determination of catalysis reaction product (Table 3, Entry 1).

Calculation of the Conversion (%) in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by 1a

Total amount of compounds at the end: Unreacted bezaldehyde (10.01 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(benzylidene)malononitrile = (1/1) * 100 = 100%.

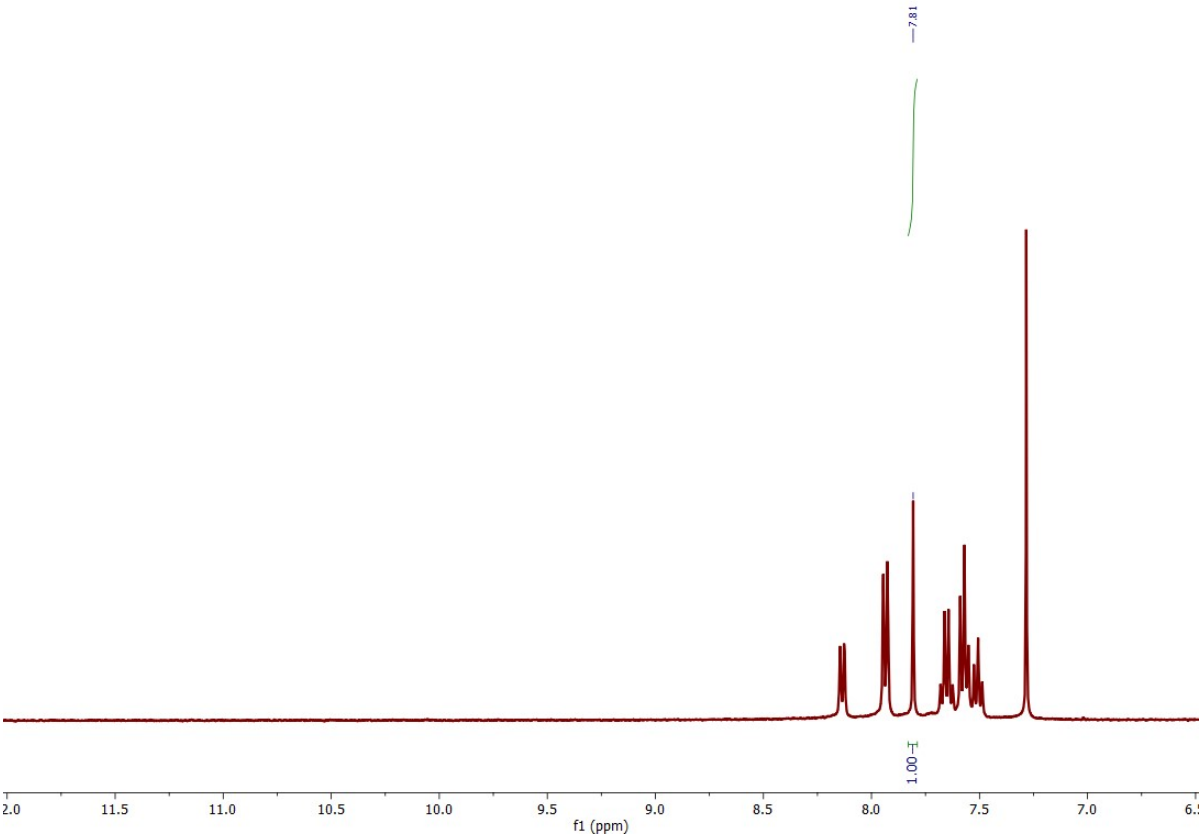

Fig. S17 Example of integration in the ^{1}H NMR spectrum for the determination of catalysis reaction product (Table 3, Entry 3).

Calculation of the Conversion (%) in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by 2a

Total amount of compounds at the end: Unreacted bezaldehyde (10.01 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(benzylidene)malononitrile = (1/1) * 100 = 100%.

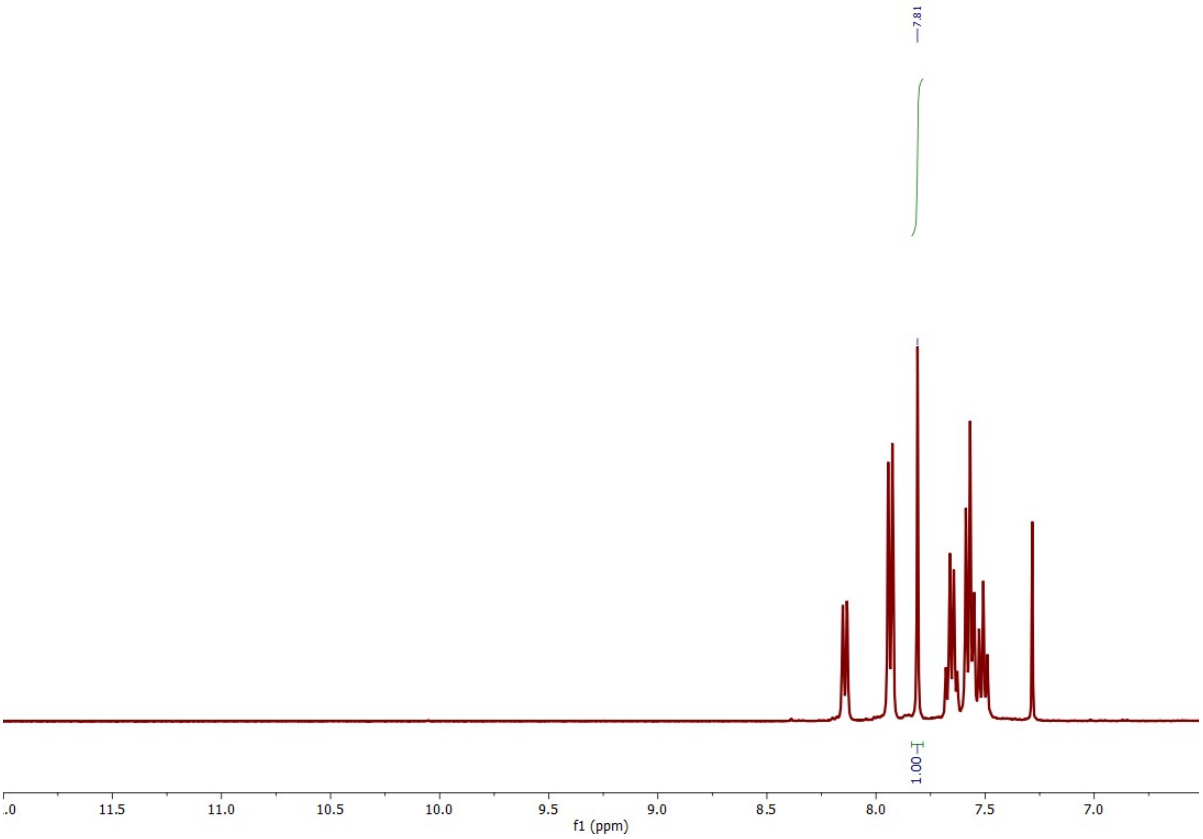

Fig. S18 Example of integration in the ^{1}H NMR spectrum for the determination of catalysis reaction product (Table 3, Entry 6).

Calculation of the Conversion (%) in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by 3a

Total amount of compounds at the end: Unreacted bezaldehyde (10.01 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(benzylidene)malononitrile = (1/1) * 100 = 100%.

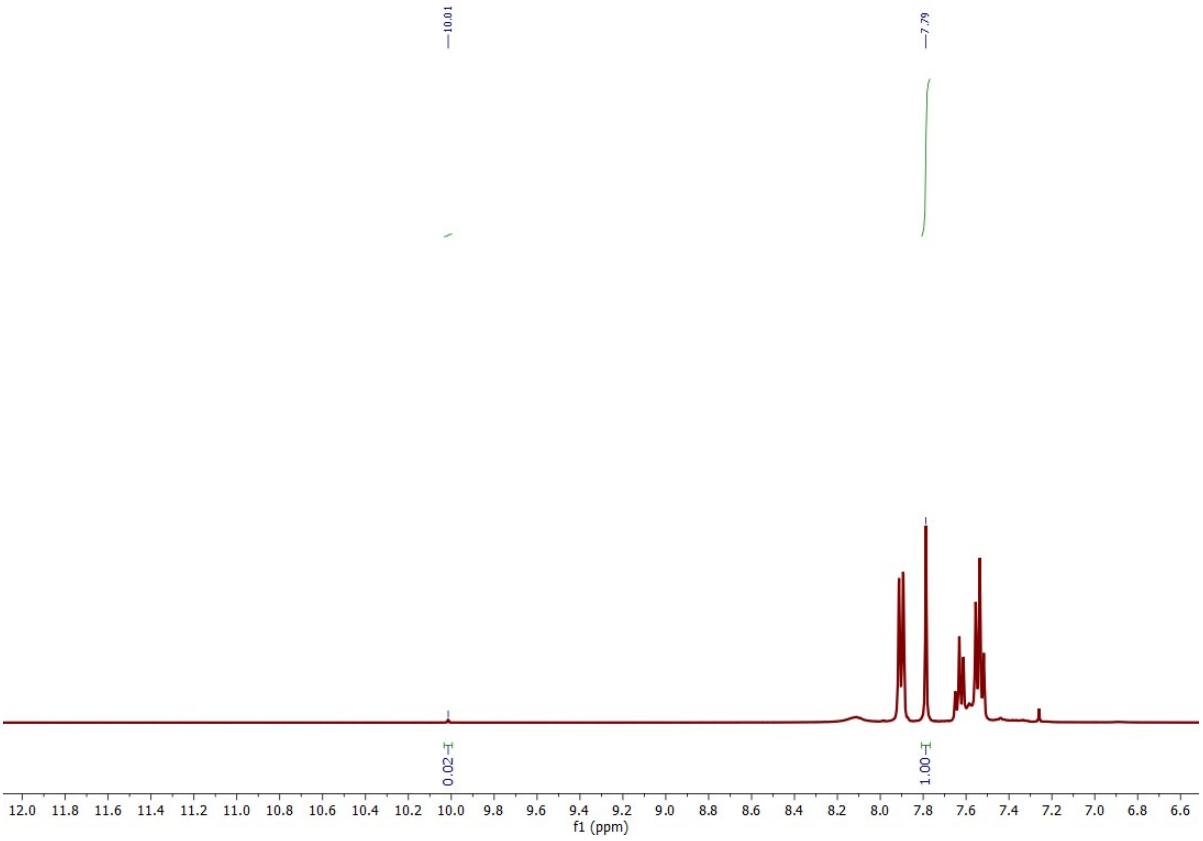

Fig. S19 Example of integration in the ^{1}H NMR spectrum for the determination of catalysis reaction product (Table 3, Entry 8).

Calculation of the Conversion (%) in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by 4a

Total amount of compounds at the end: Unreacted benzaldehyde (10.01 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0.02 + 1.00 = 1.02

Conversion (%) of 2-(benzylidene)malononitrile = (1/1.02) * 100 = 98%.

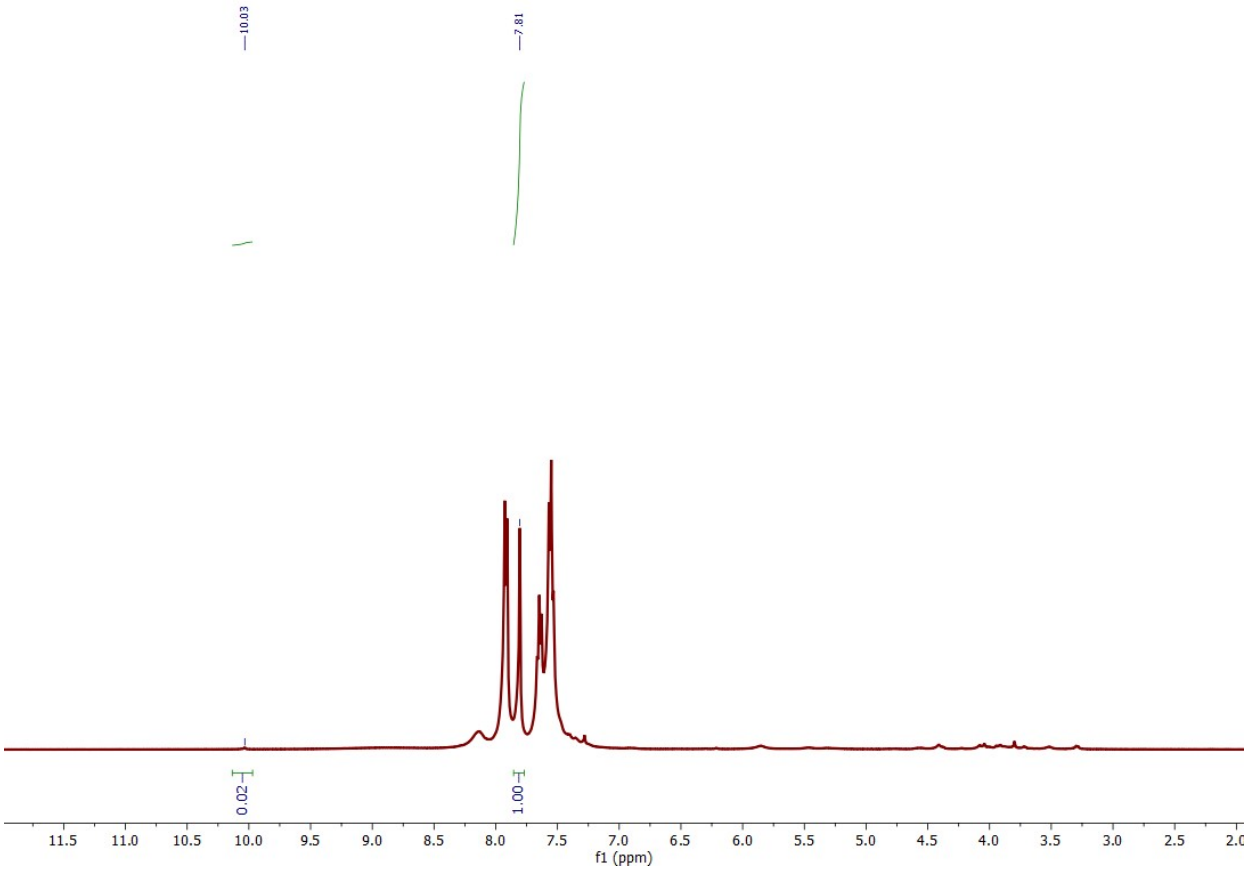

Fig. S20 Example of integration in the ^{1}H NMR spectrum for the determination of catalysis reaction product (Table 3, Entry 10).

Calculation of the Conversion (%) in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by un-activated 2

Total amount of compounds at the end: Unreacted bezaldehyde (10.03 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0.02 + 1.00 = 1.02

Conversion (%) of 2-(benzylidene)malononitrile = (1/1.02) * 100 = 98%.

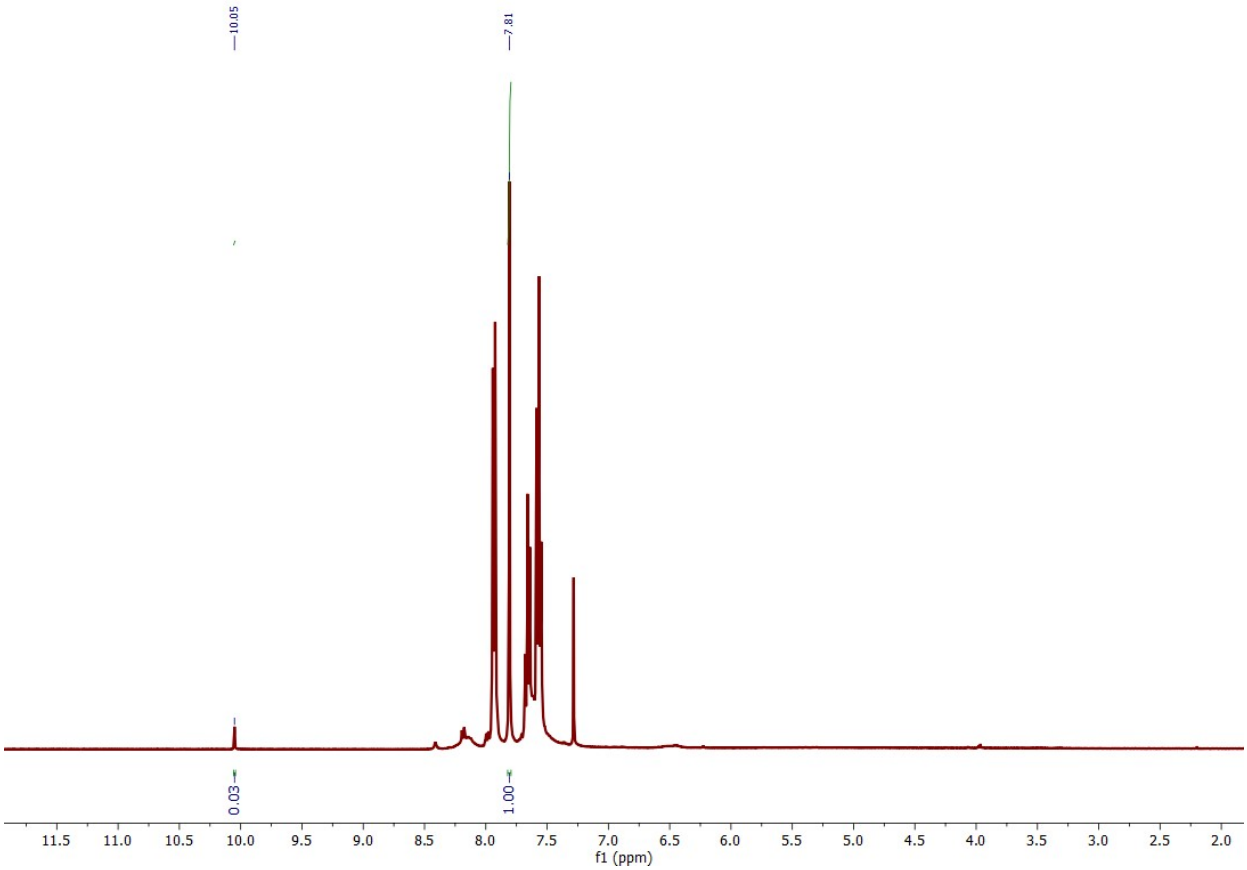

Fig. S21 Example of integration in the ^{1}H NMR spectrum for the determination of catalysis reaction product (Table 3, Entry 11).

Calculation of the Conversion (%) in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by un-activated 4

Total amount of compounds at the end: Unreacted bezaldehyde (10.05 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0.03 + 1.00 = 1.03

Conversion (%) of 2-(benzylidene)malononitrile = (1/1.03) * 100 = 97%.

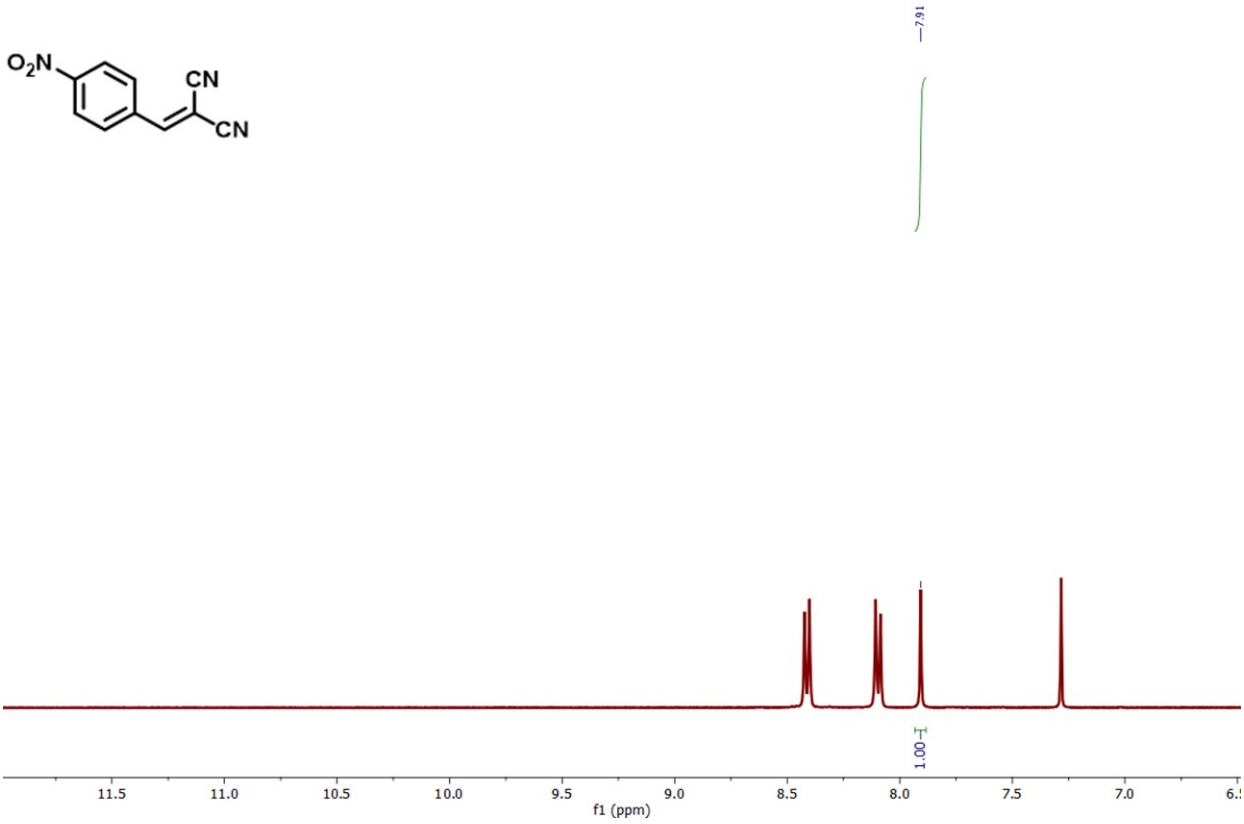

Fig. S22 ^{1}H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-nitrobenzaldehyde with malononitrile catalyzed by 2a (Table 4, entry 1)

Total amount of compounds at the end: Unreacted 4-nitrobezaldehyde (10.01 ppm) + 2-(4-nitrobenzylidene)malononitrile (7.91 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(4-nitrobenzylidene)malononitrile = (1/1) * 100 = 100%.

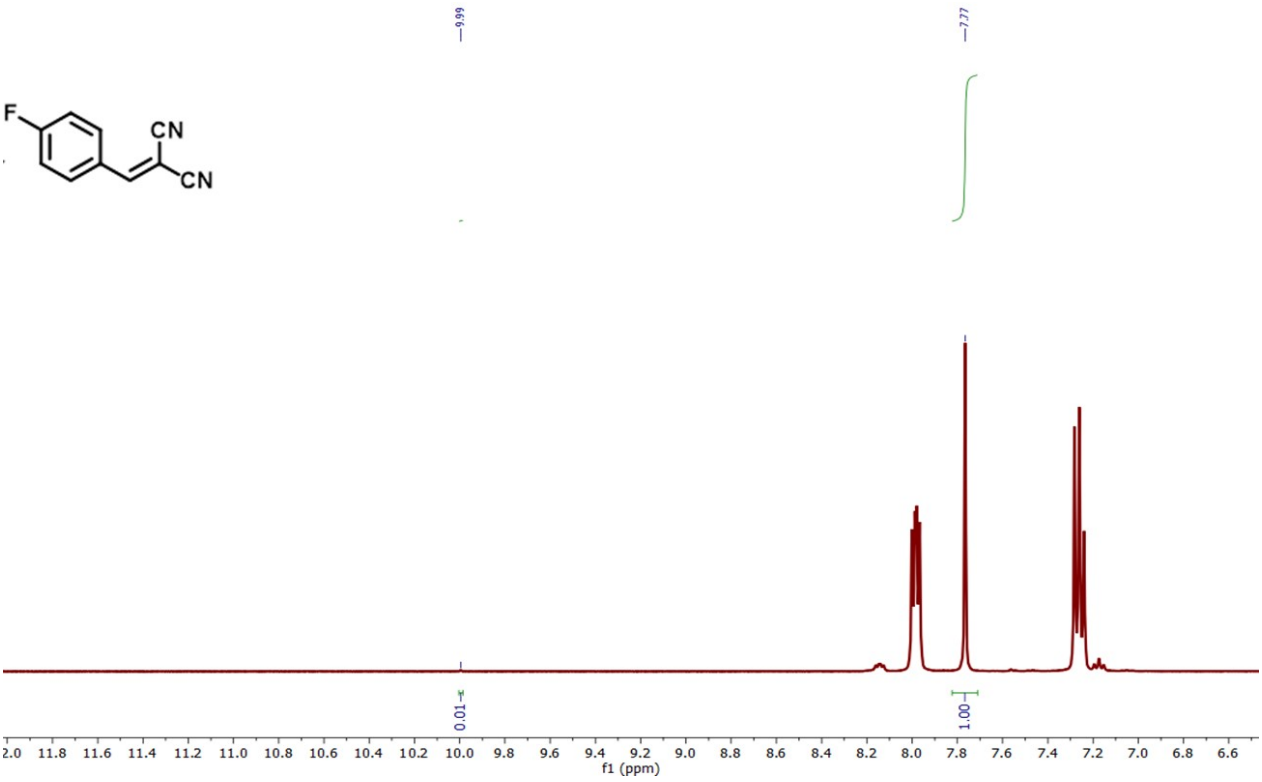

Fig. S23 ^{1}H NMR spectrum of 2-(4-fluorobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-fluorobenzaldehyde with malononitrile catalyzed by 2a (Table 4, entry 2)

Total amount of compounds at the end: Unreacted 4-fluorobezaldehyde (9.99 ppm) + 2-(4-fluorobenzylidene)malononitrile (7.77 ppm) = 0.01 + 1.00 = 1.01

Conversion (%) of 2-(4-fluorobenzylidene)malononitrile = (1/1.01) * 100 = 99%.

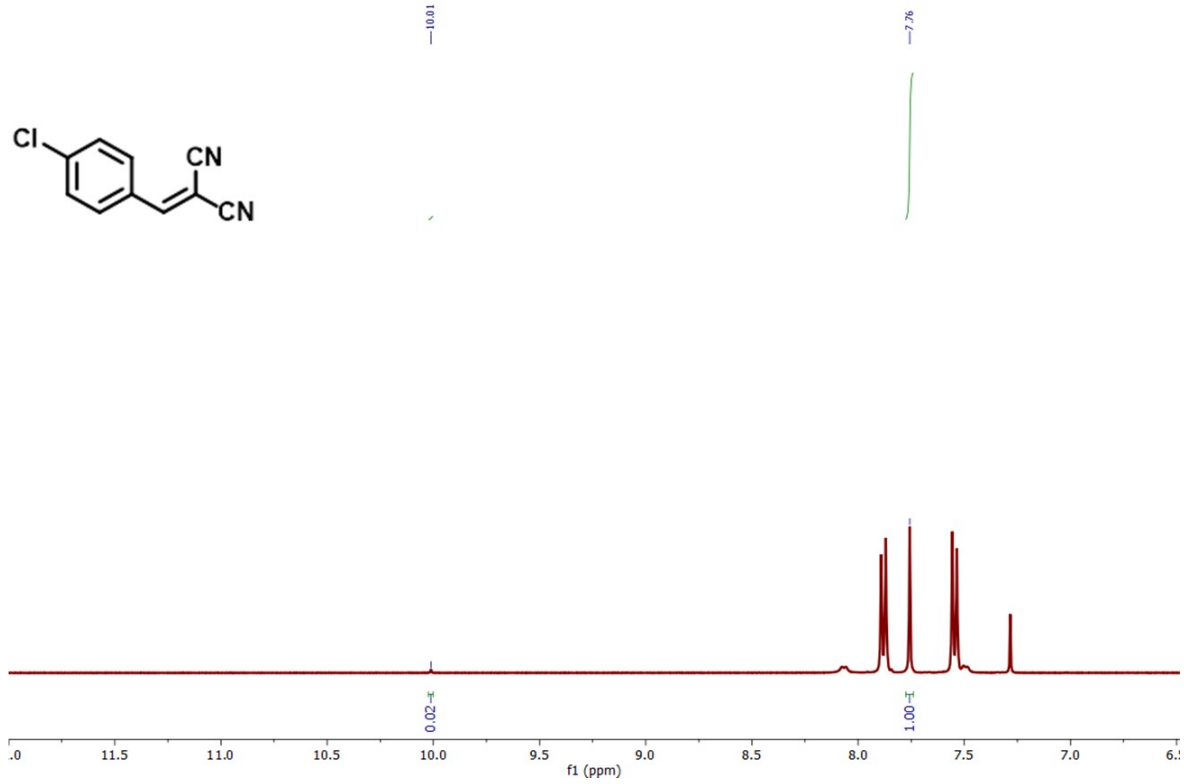

Fig. S24 ^{1}H NMR spectrum of 2-(4-chlororobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-chlorobenzaldehyde with malononitrile catalyzed by 2a (Table 4, entry 3)

Total amount of compounds at the end: Unreacted 4-chlorobezaldehyde (10.01 ppm) + 2-(4-chlorobenzylidene)malononitrile (7.76 ppm) = 0.02 + 1.00 = 1.02

Conversion (%) of 2-(4-chlorobenzylidene)malononitrile = (1/1.01) * 100 = 98%.

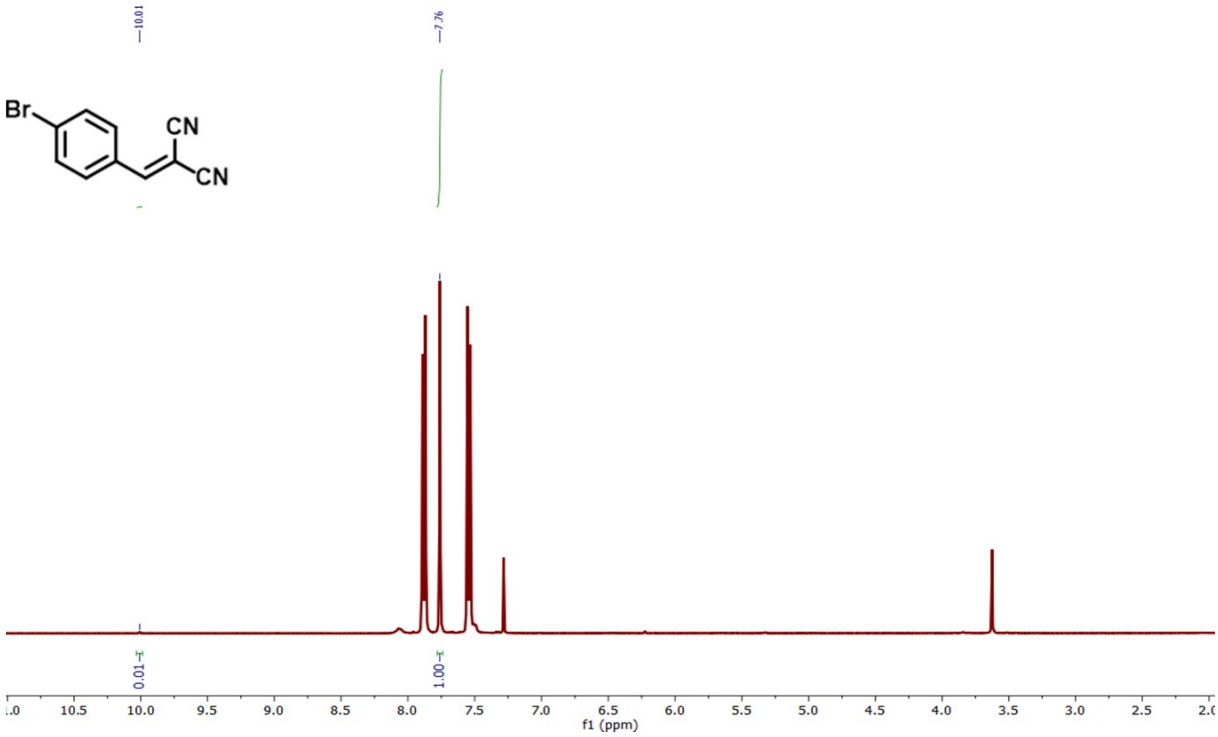

Fig. S25 ^{1}H NMR spectrum of 2-(4-bromobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-bromobenzaldehyde with malononitrile catalyzed by 2a (Table 4, entry 4)

Total amount of compounds at the end: Unreacted 4-bromobezaldehyde (10.01 ppm) + 2-(4-bromobenzylidene)malononitrile (7.76 ppm) = 0.01 + 1.00 = 1.01

Conversion (%) of 2-(4-bromobenzylidene)malononitrile = (1/1.01) * 100 = 99%.

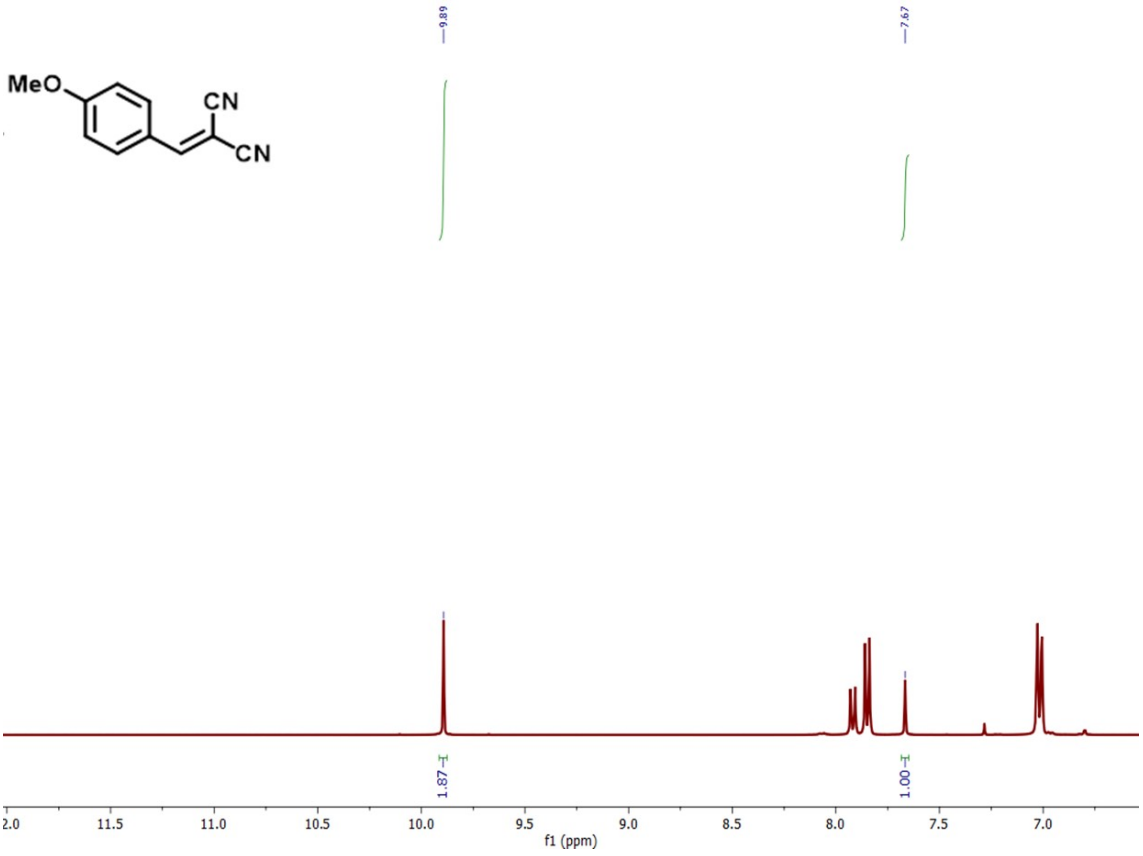

Fig. S26 ^{1}H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-methoxybenzaldehyde with malononitrile catalyzed by 2a (Table 4, entry 5)

Total amount of compounds at the end: Unreacted 4-methoxybezaldehyde (9.89 ppm) + 2-(4-methoxybenzylidene)malononitrile (7.67 ppm) = 1.87 + 1.00 = 2.87

Conversion (%) of 2-(4-methoxybenzylidene)malononitrile = (1/2.87) * 100 = 35%.

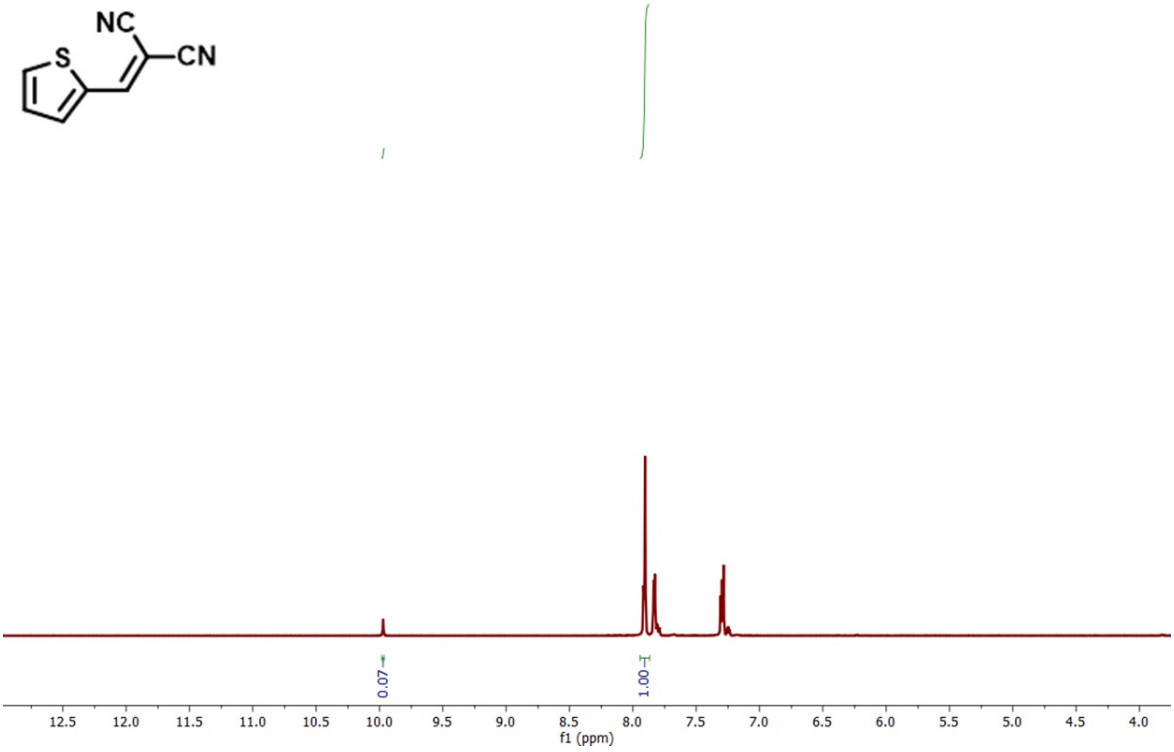

Fig. S27 ^{1}H NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of thiophene-2-carboxaldehyde with malononitrile catalyzed by 2a (Table 4, entry 6)

Total amount of compounds at the end: Unreacted thiophene-2-carboxaldehyde (9.9 ppm) + 2-(thiophen-2-ylmethylene)malononitrile (7.8 ppm) = 0.07 + 1.00 = 1.07

Conversion (%) of 2-(thiophen-2-ylmethylene)malononitrile = (1/1.07) * 100 = 93%.

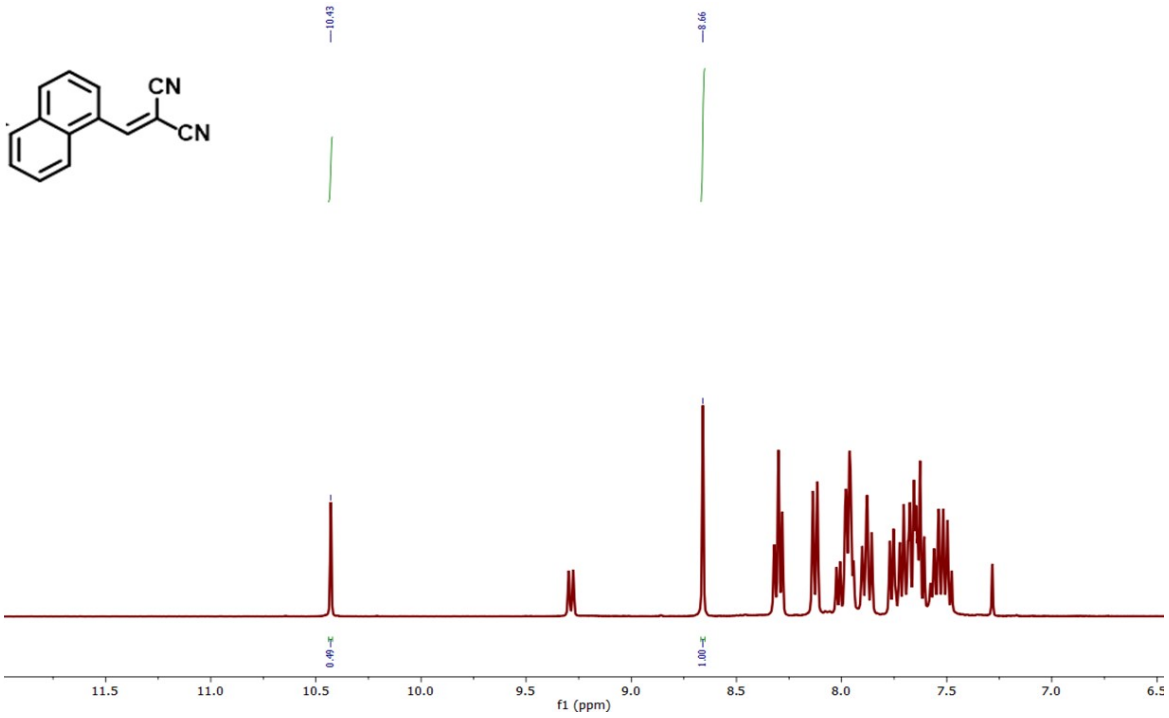

Fig. S28 ^{1}H NMR spectrum of 2-(naphthalen-1-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of naphthalene-2-carboxaldehyde with malononitrile catalyzed by 2a (Table 4, entry 7)

Total amount of compounds at the end: Unreacted naphthaldehyde (10.43 ppm) + 2-(naphthalen-1-ylmethylene)malononitrile (8.66 ppm) = 0.49 + 1.00 = 1.49

Conversion (%) of 2-(naphthalen-1-ylmethylene)malononitrile = (1/1.49) * 100 = 67%.

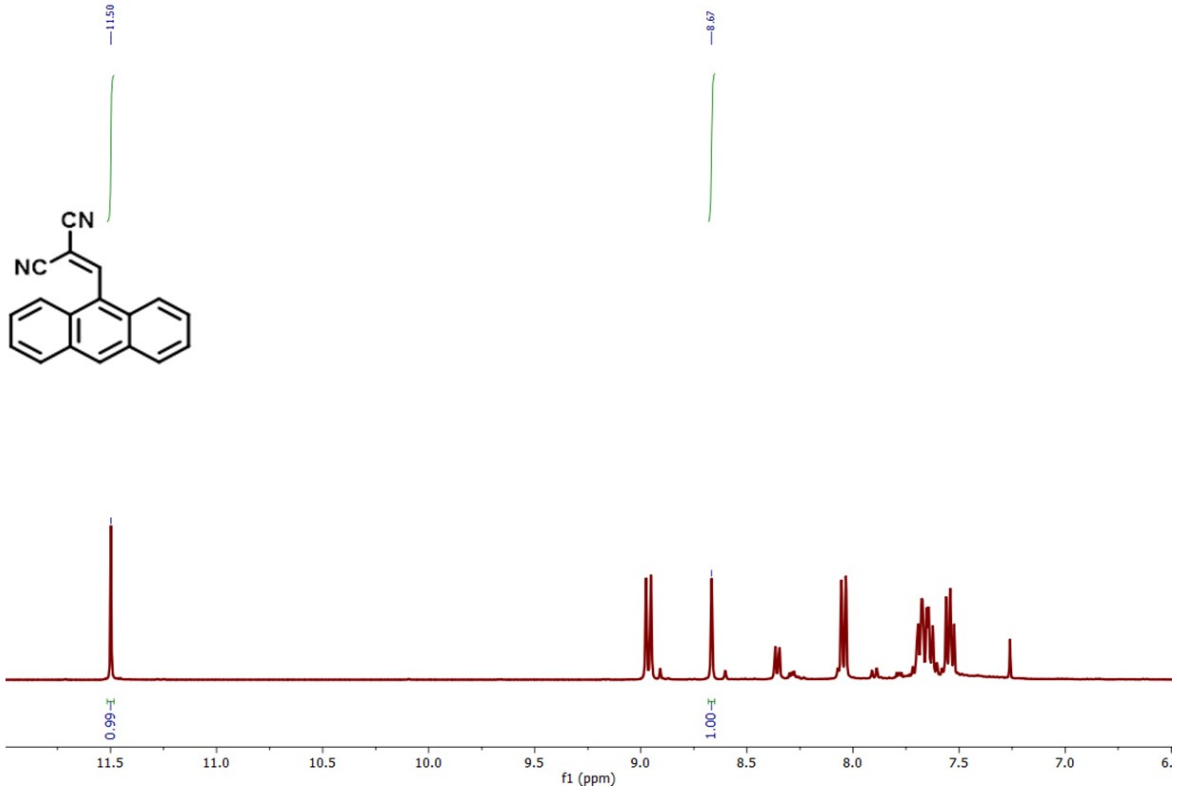

Fig. S29 ^{1}H NMR spectrum of 2-(anthracen-9-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 9-anthracene-carboxaldehyde with malononitrile catalyzed by 2a (Table 4, entry 8)

Total amount of compounds at the end: Unreacted naphthaldehyde (11.50 ppm) + 2-(anthracen-9-ylmethylene)malononitrile (8.67 ppm) = 0.99 + 1.00 = 1.99

Conversion (%) of 2-(anthracen-9-ylmethylene)malononitrile = (1/1.99) * 100 = 50%.

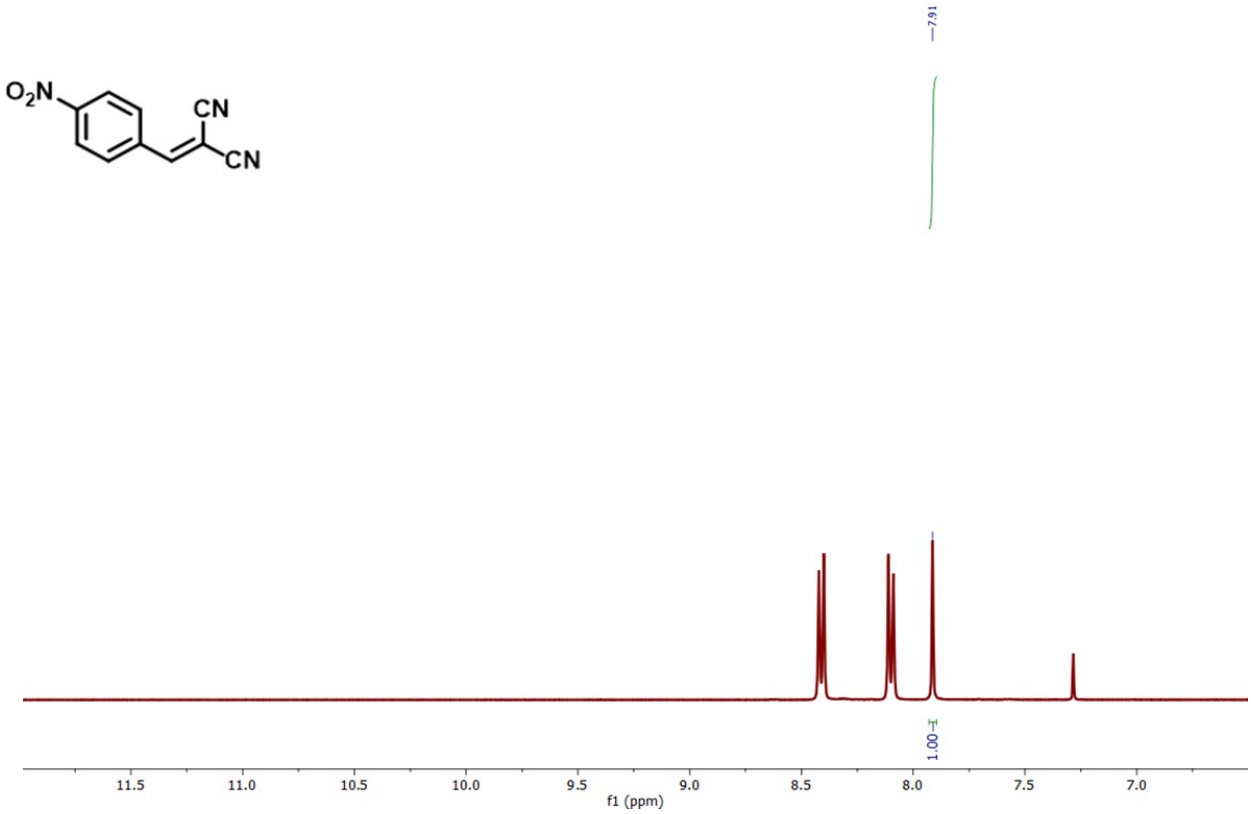

Fig. S30 ^{1}H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-nitrobenzaldehyde with malononitrile catalyzed by 4a (Table 4, entry 1)

Total amount of compounds at the end: Unreacted 4-nitrobezaldehyde (10.01 ppm) + 2-(4-nitrobenzylidene)malononitrile (7.91 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(4-nitrobenzylidene)malononitrile = (1/1) * 100 = 100%.

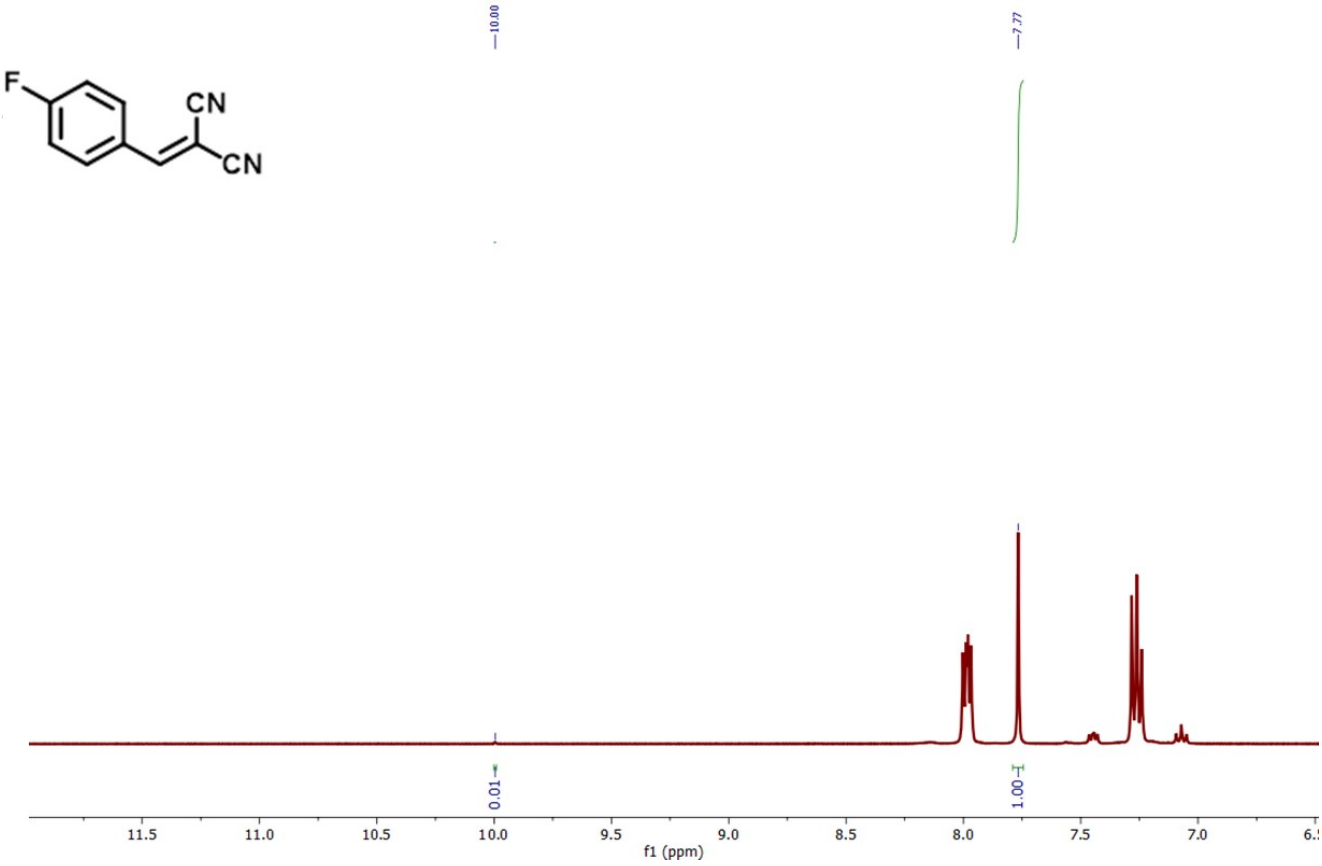

Fig. S31 ^{1}H NMR spectrum of 2-(4-fluorobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-fluorobenzaldehyde with malononitrile catalyzed by 4a (Table 4, entry 2)

Total amount of compounds at the end: Unreacted 4-fluorobezaldehyde (10 ppm) + 2-(4-fluorobenzylidene)malononitrile (7.77 ppm) = 0.01 + 1.00 = 1.01

Conversion (%) of 2-(4-fluorobenzylidene)malononitrile = (1/1.01) * 100 = 99%.

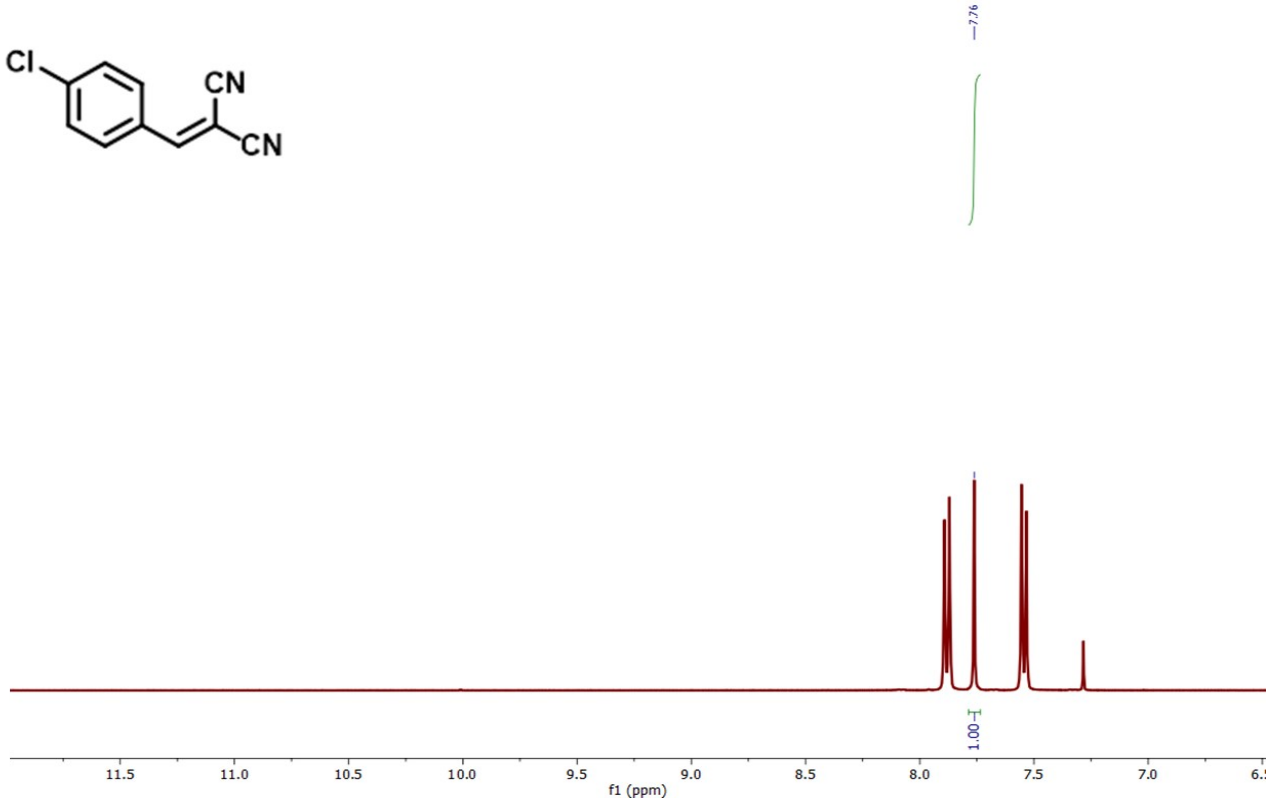

Fig. S32 ^{1}H NMR spectrum of 2-(4-chlororobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-chlorobenzaldehyde with malononitrile catalyzed by 4a (Table 4, entry 3)

Total amount of compounds at the end: Unreacted 4-chlorobezaldehyde (10.01 ppm) + 2-(4-chlorobenzylidene)malononitrile (7.76 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(4-chlorobenzylidene)malononitrile = (1/1) * 100 = 100%.

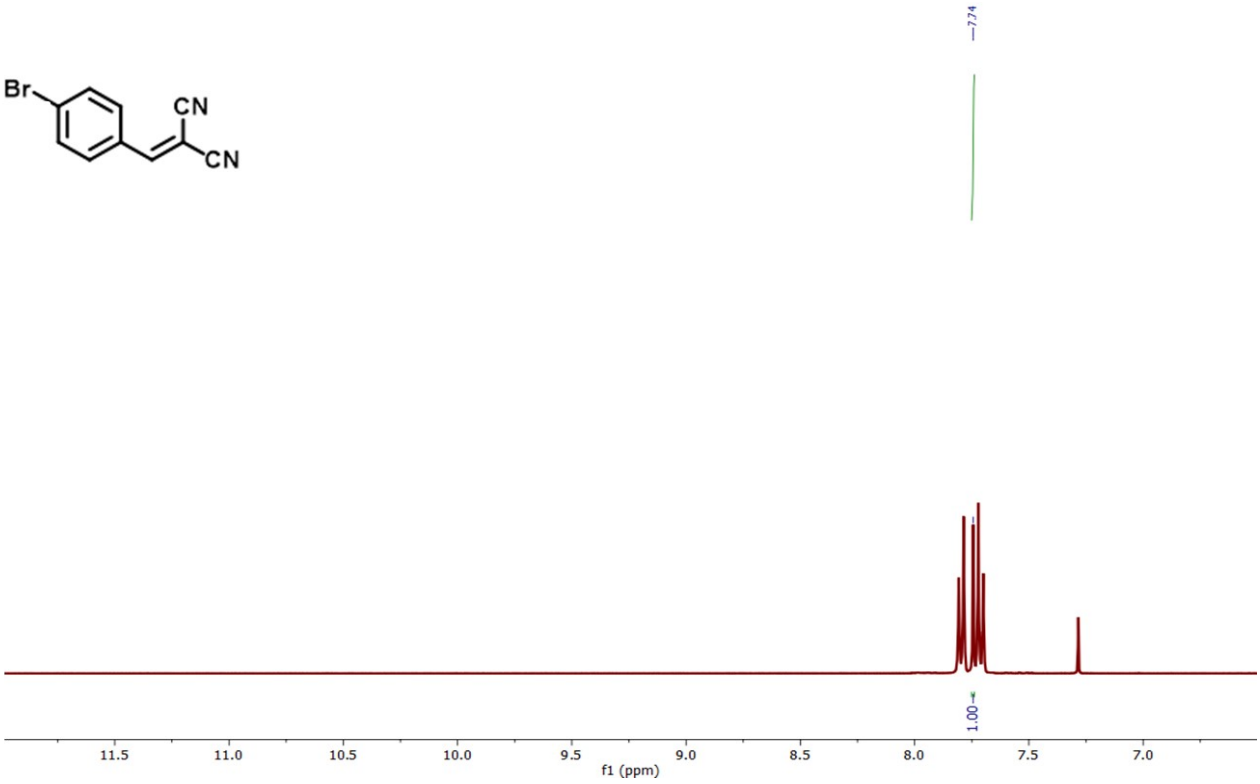

Fig. S33 ^{1}H NMR spectrum of 2-(4-bromobenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-bromobenzaldehyde with malononitrile catalyzed by 4a (Table 4, entry 4)

Total amount of compounds at the end: Unreacted 4-bromobezaldehyde (10.01 ppm) + 2-(4-bromobenzylidene)malononitrile (7.74 ppm) = 0 + 1.00 = 1

Conversion (%) of 2-(4-bromobenzylidene)malononitrile = (1/1) * 100 = 100%.

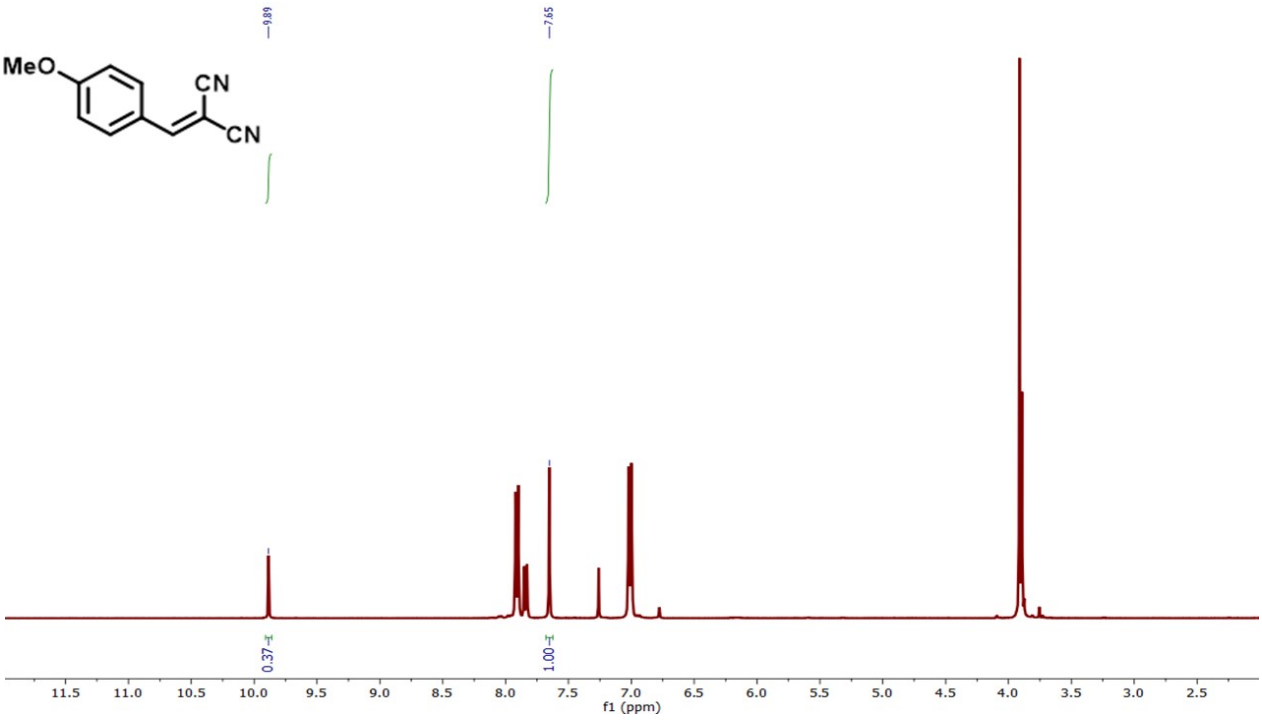

Fig. S34 ^{1}H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 4-methoxybenzaldehyde with malononitrile catalyzed by 4a (Table 4, entry 5)

Total amount of compounds at the end: Unreacted 4-methoxybezaldehyde (9.89 ppm) + 2-(4-methoxybenzylidene)malononitrile (7.65 ppm) = 0.37 + 1.00 = 1.37

Conversion (%) of 2-(4-methoxybenzylidene)malononitrile = (1/1.37) * 100 = 73%.

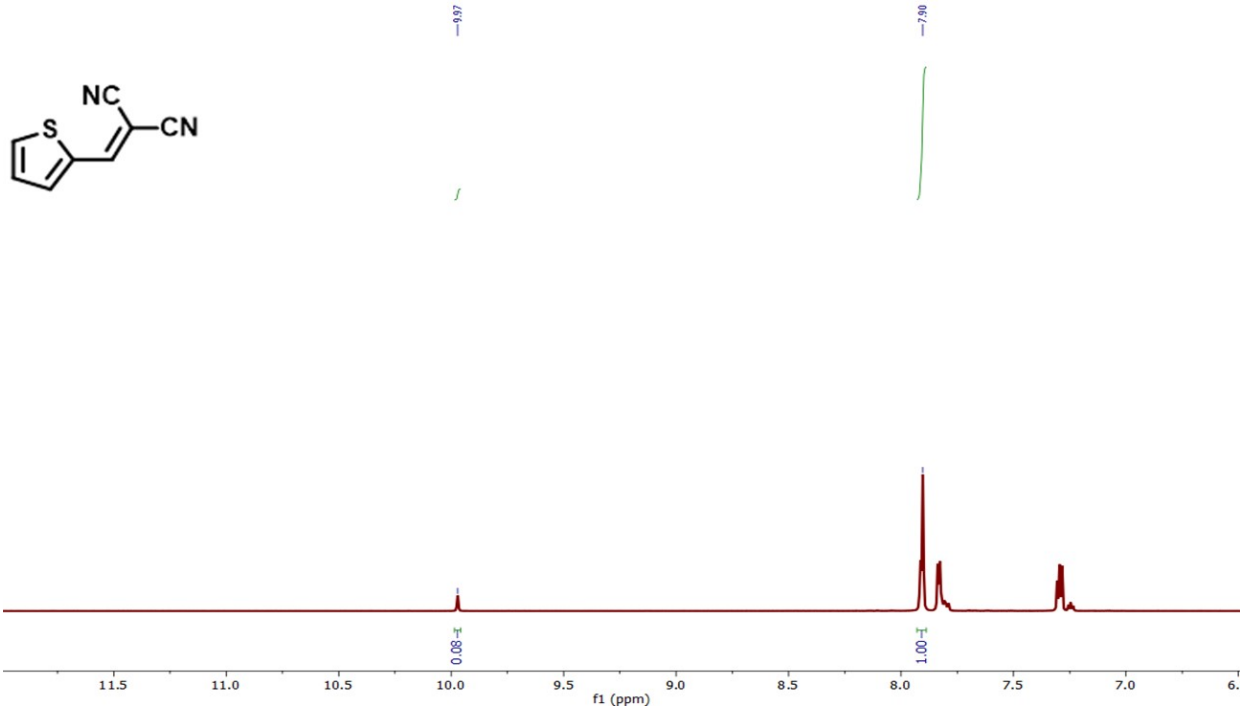

Fig. S35 ^{1}H NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of thiophene-2-carboxaldehyde with malononitrile catalyzed by 4a (Table 4, entry 6)

Total amount of compounds at the end: Unreacted thiophene-2-carboxaldehyde (9.97 ppm) + 2-(thiophen-2-ylmethylene)malononitrile (7.9 ppm) = 0.08 + 1.00 = 1.08

Conversion (%) of 2-(thiophen-2-ylmethylene)malononitrile = (1/1.08) * 100 = 92%.

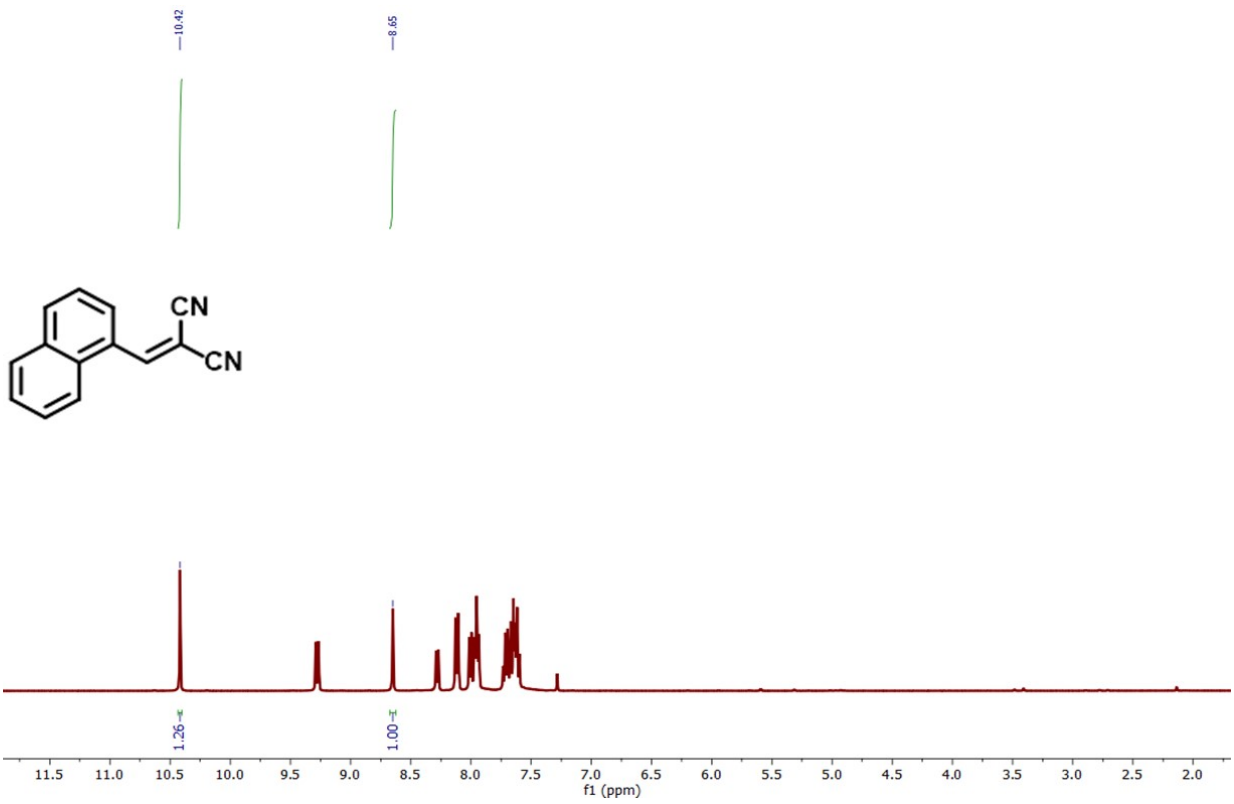

Fig. S36 ^{1}H NMR spectrum of 2-(naphthalen-1-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of naphthalene-2-carboxaldehyde with malononitrile catalyzed by 4a (Table 4, entry 7)

Total amount of compounds at the end: Unreacted naphthaldehyde (10.42 ppm) + 2-(naphthalen-1-ylmethylene)malononitrile (8.65 ppm) = 1.26 + 1.00 = 2.26

Conversion (%) of 2-(naphthalen-1-ylmethylene)malononitrile = (1/2.26) * 100 = 44%.

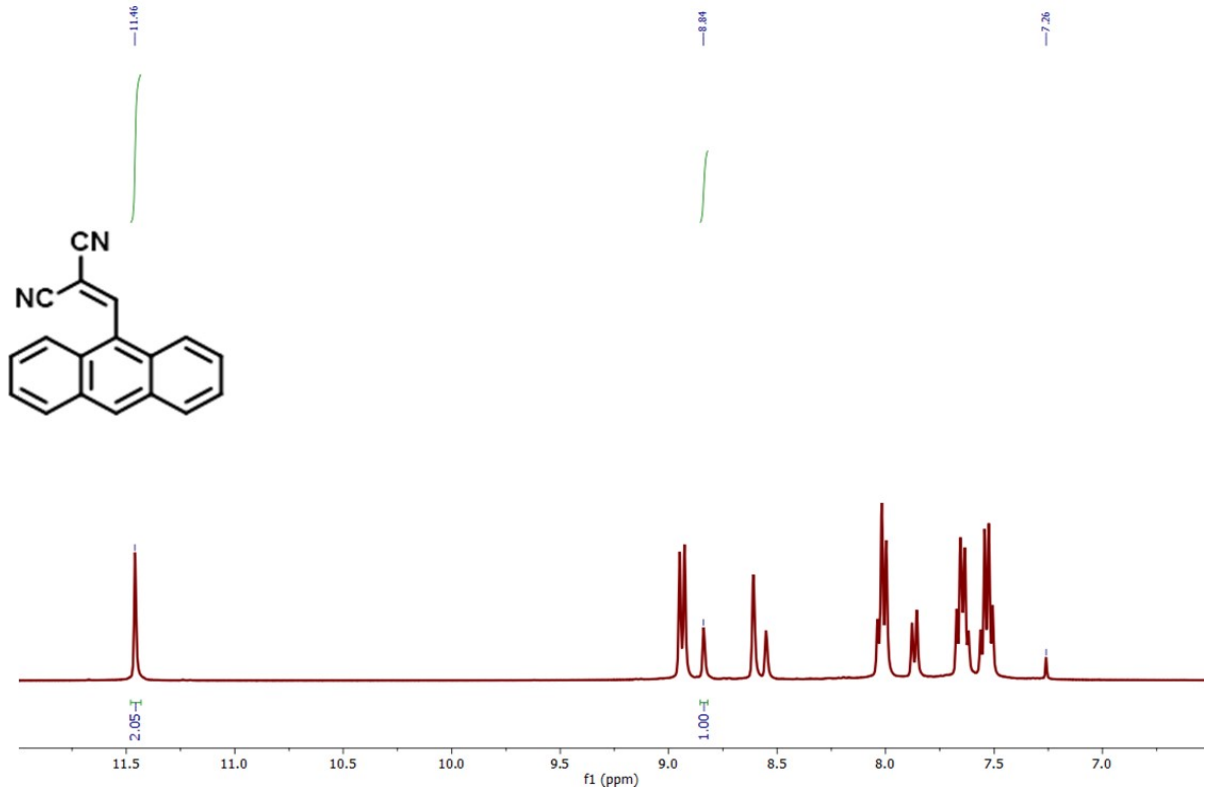

Fig. S37 ^{1}H NMR spectrum of 2-(anthracen-9-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 9-anthracene-carboxaldehyde with malononitrile catalyzed by 4a (Table 4, entry 8)

Total amount of compounds at the end: Unreacted naphthaldehyde (11.46 ppm) + 2-(anthracen-9-ylmethylene)malononitrile (8.84 ppm) = 2.05 + 1.00 = 3.05

Conversion (%) of 2-(anthracen-9-ylmethylene)malononitrile = (1/3.05) * 100 = 33%.

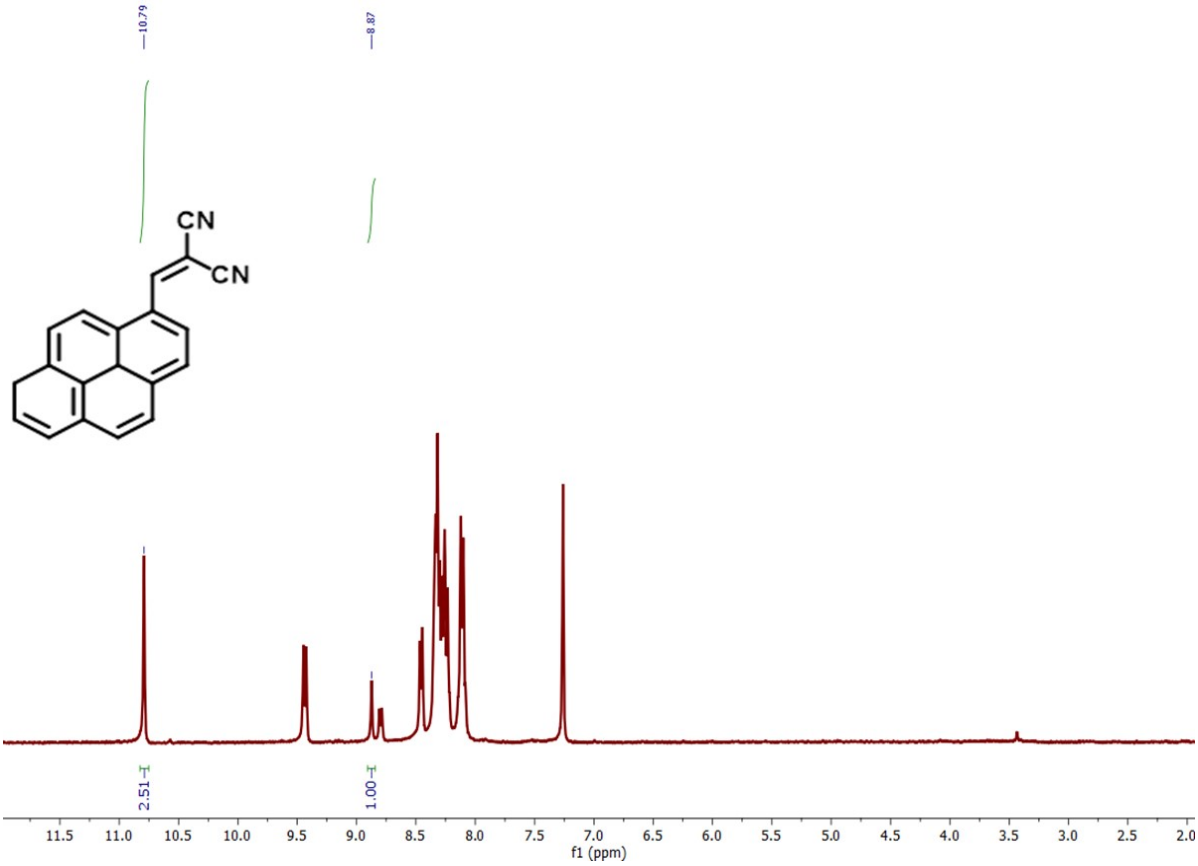

Fig. S38 ^{1}H NMR spectrum of 2-(pyren-1-ylmethylene)malononitrile in $CDCl_3$.

Calculation of the conversion (%) in the Knoevenagel condensation reaction of 1-pyrene-carboxaldehyde with malononitrile catalyzed by 4a (Table 4, entry 9)

Total amount of compounds at the end: Unreacted naphthaldehyde (10.79 ppm) + 2-(pyren-1-ylmethylene)malononitrile (8.87 ppm) = 2.51 + 1.00 = 3.51

Conversion (%) of 2-(pyren-1-ylmethylene)malononitrile = (1/3.51) * 100 = 28%.

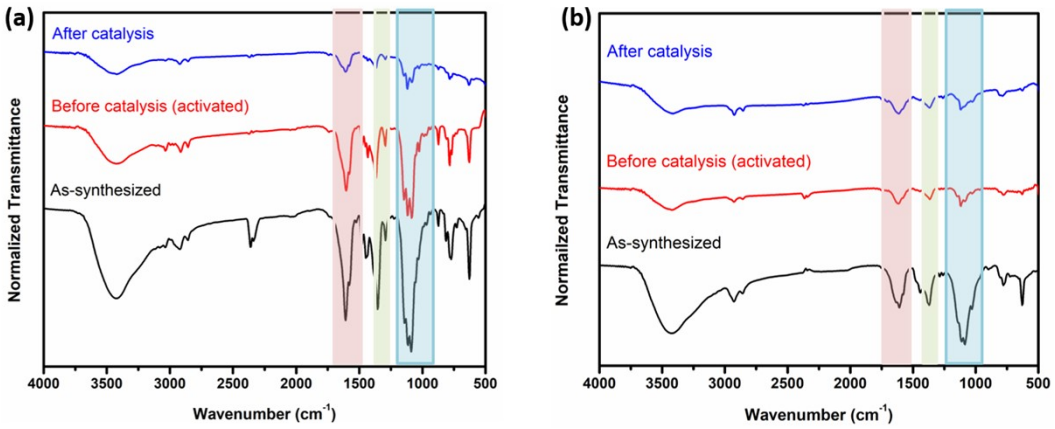

Fig. S39 Comparison of FTIR spectra of (a) **2** and (b) **4** [as-synthesized, before and after catalysis].

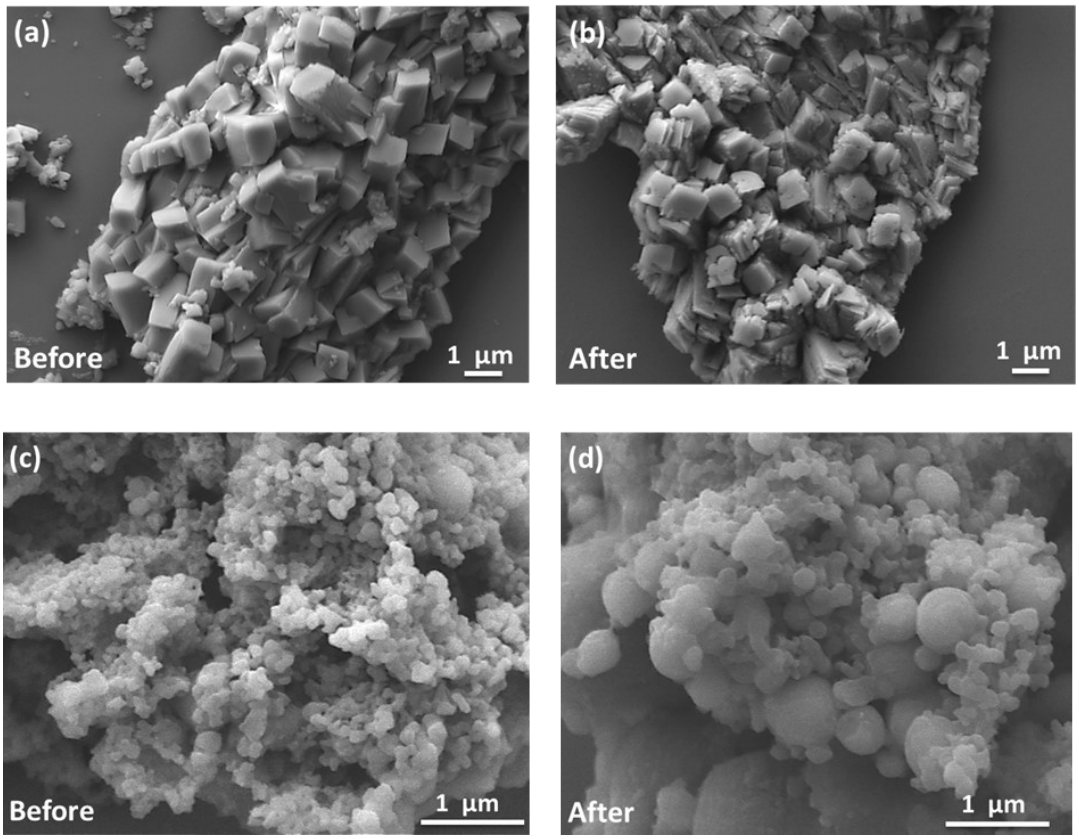

Fig. S40 FESEM images of **2** and **4** before (a,c) and after (b,d) catalysis, respectively.

Table S1 Selected bond lengths (Å) and angles (°) for **1**.

Bond distances (Å)

Cu1-N1	1.964(10)	Cu1-N3	1.991(10)
Cu1-O2	1.995(8)	Cu1-N2	2.045(10)
Cu1-O1	2.313(8)	Cu2-O5	1.949(8)
Cu2-N6	1.994(11)	Cu2-N4	1.999(11)
Cu2-N5	2.045(9)	Cu2-O7	2.244(8)

Bond angles (°)

N1-Cu1-N3	165.2(4)	N1-Cu1-O2	97.6(3)
N3-Cu1-O2	97.0(4)	N1-Cu1-N2	83.5(4)
N3-Cu1-N2	81.9(4)	O2-Cu1-N2	159.9(3)
N1-Cu1-O1	89.2(3)	N3-Cu1-O1	93.1(4)
O2-Cu1-O1	90.9(3)	N2-Cu1-O1	109.2(3)
O5-Cu2-N6	98.3(4)	O5-Cu2-N4	97.7(4)
N6-Cu2-N4	161.6(4)	O5-Cu2-N5	172.7(3)
N6-Cu2-N5	80.1(5)	N4-Cu2-N5	83.0(5)
O5-Cu2-O7	88.8(3)	N6-Cu2-O7	93.9(3)
N4-Cu2-O7	95.6(3)	N5-Cu2-O7	98.5(4)

Table S2 Hydrogen Bonding Parameters for **1**.

D⋯H⋯A	**r(D⋯H) (Å)**	**r(H⋯A) (Å)**	**r(D⋯A) (Å)**	**∠D⋯H⋯A (deg)**
O1⋯H1A⋯O12	0.86	2.28	3.0781(13)	154.00
C6⋯H6B⋯O15	0.99	2.39	3.3471(14)	162.00
C7⋯H7C⋯O15	0.99	2.49	3.4661(15)	171.00
C10⋯H10⋯O8	0.95	2.40	3.2827(14)	155.00
C16⋯H16⋯O3	0.95	2.36	3.1915(14)	145.00

Calculation for Determining the Number of Solvent Molecules Squeezed Out for the Refinement of SCXRD Structure of 1:

A solvent mask was calculated and 376 electrons were found in a volume of 1016\%A^3^ in **1** voids per unit cell. This is consistent with the presence of 1[CH3OH], 1[8H2O] per Asymmetric Unit, which account for 392 electrons per unit cell.

Table S3 Selected bond lengths (Å) and angles (°) for **2**.

Bond distances (Å)

Cu1-N3	1.965(3)	Cu1-N8	1.972(3)
Cu1-O5	1.985(3)	Cu1-N2	2.031(3)
Cu1-O1	2.487(3)	Cu2-N6	1.971(3)
Cu2-O8	1.976(3)	Cu2-N4	1.989(3)
Cu2-N5	2.035(3)	Cu2-O10	2.353(3)

Bond angles (°)

N3-Cu1-N8	165.81(14)	N3-Cu1-O5	97.10(13)
N8-Cu1-O5	96.74(12)	N3-Cu1-N2	83.47(13)
N8-Cu1-N2	83.79(13)	O5-Cu1-N2	166.74(12)
N3-Cu1-O1	85.99(12)	N8-Cu1-O1	86.73(12)
O5-Cu1-O1	108.17(10)	N2-Cu1-O1	85.08(11)
N6-Cu2-O8	100.83(13)	N6-Cu2-N4	165.18(14)
O8-Cu2-N4	93.96(13)	N6-Cu2-N5	83.18(13)
O8-Cu2-N5	160.46(12)	N4-Cu2-N5	83.13(13)
N6-Cu2-O10	91.73(12)	O8-Cu2-O10	109.50(11)
N4-Cu2-O10	82.47(12)	N5-Cu2-O10	89.34(12)

Table S4 Hydrogen Bonding Parameters for **2**.

D⋯H⋯A	r(D⋯H) (Å)	r(H⋯A) (Å)	r(D⋯A) (Å)	∠D⋯H⋯A (deg)
O14⋯H14C⋯O5	0.85	2.18	3.018 (4)	170.00
O14⋯H14D⋯O9	0.85	2.13	2.964 (4)	169.00
C2⋯H2⋯O5	0.95	2.57	3.486 (6)	162.00
C6⋯H6A⋯O11	0.99	2.51	3.335 (6)	140.00
C7⋯H7A⋯O2	0.99	2.51	3.412(5)	151.00
C7⋯H7B⋯O12	0.99	2.54	3.453(5)	153.00
C10⋯H10⋯O6	0.95	2.48	3.208 (5)	133.00
C13⋯H13B⋯O13	0.99	2.41	3.194 (5)	136.00
C18⋯H18⋯O15	0.95	2.53	3.332(7)	142.00
C21⋯H21B⋯O9	0.99	2.42	3.220 (5)	137.00
C23⋯H23A⋯O14	0.99	2.37	3.345 (5)	170.00
C23⋯H23B⋯O3	0.99	2.55	3.207 (5)	123.00
C26⋯H26⋯O9	0.95	2.58	3.175 (5)	121.00
C29⋯H29A⋯O11	0.99	2.55	3.327 (5)	136.00
C29⋯H29A⋯O3	0.99	2.58	3.197 (5)	121.00
C31⋯H31⋯O2	0.95	2.59	3.322(5)	135.00
C34⋯H34⋯O6	0.95	2.40	3.182 (5)	139.00
C34⋯H35A⋯O14	0.98	2.26	3.032 (14)	135.00
C35⋯H35C⋯O4	0.98	2.23	3.100 (15)	148.00

Table S5 Selected bond lengths (Å) and angles (°) for **3**.

Bond distances (Å)

Cu01-N1	1.952(10)	Cu01-O4	1.984(9)
Cu01-N3	1.985(10)	Cu01-N2	2.048(10)
Cu01-O6	2.251(9)	Cu02-N6	1.953(10)
Cu02-O2	1.968(8)	Cu02-N4	1.968(10)
Cu02-N5	2.025(9)	Cu02-O7	2.502(10)

Bond angles (°)

N1-Cu01-O4	94.7(4)	N1-Cu01-N3	165.9(4)
O4-Cu01-N3	96.6(4)	N1-Cu01-N2	83.9(4)
O4-Cu01-N2	159.9(4)	N3-Cu01-N2	82.6(4)
N1-Cu01-O6	96.7(4)	O4-Cu01-O6	94.6(3)
N3-Cu01-O6	90.8(4)	N2-Cu01-O6	105.4(4)
N6-Cu02-O2	96.2(4)	N6-Cu02-N4	166.6(4)
O2-Cu02-N4	97.2(4)	N6-Cu02-N5	83.3(4)
O2-Cu02-N5	176.8(4)	N4-Cu02-N5	83.4(4)
N6-Cu02-O7	90.7(4)	O2-Cu02-O7	95.1(3)
N4-Cu02-O7	86.5(4)	N5-Cu02-O7	88.1(3)

Table S6 Selected bond lengths (Å) and angles (°) for **4**.

Bond distances (Å)

Cu1-N3	1.959(16)	Cu1-N2	1.975(16)
Cu1-O1	1.978(14)	Cu1-N1	1.987(13)
Cu1-O4	2.358(14)	Cl1-O6	1.25(2)

Bond angles (°)

N3-Cu1-N2	166.6(7)	N3-Cu1-O1	95.1(6)
N2-Cu1-O1	97.2(6)	N3-Cu1-N1	84.4(6)
N2-Cu1-N1	84.7(6)	O1-Cu1-N1	167.2(6)
N3-Cu1-O4	82.0(6)	N2-Cu1-O4	90.8(6)
O1-Cu1-O4	99.1(7)	N1-Cu1-O4	93.5(7)

Table S7 Comparison of the catalytic activity of various MOCNs in the Knoevenagel condensation reaction of an aldehyde and malononitrile

Catalyst	Cat. amount	Time (h)	Solvent	Temp (˚C)	Yield (%)	Ref.[a]
$\{[Cu_2(tpbn)_2(fdc)(ClO_4)_2]\cdot H_2O\cdot 2CH_3CH_2OH\}_n$ (**2**)	3 mol%	2	CH_3OH	r.t.	100	This work
$[Cu_4(tphpn)_2(fdc)_2(ClO_4)_4]\cdot 4H_2O\cdot NaClO_4$ (**4**)	2 mol%	2	CH_3OH	r.t.	98	This work
Zn-CBS	5 mol%	3	CH_3OH	r.t.	82	46
ZIF-9	5 mol%	4	Toluene	r.t.	99	48
$[Zn(Lz)(H_2O)_2]_n\cdot n(NMF)$	3 mol%	6	THF	r.t.	97	49
$[Cd(4\text{-}btapa)_2(NO_3)_2]\cdot 6H_2O\cdot 2DMF$	5 mol%	12	Benzene	r.t.	98	50
$\{[Ni_4(\mu_6\text{-}MTB)_2(\mu_2\text{-}H_2O)_4(H_2O)_4]\cdot 10DMF\cdot 11H_2O\}_n$	3 mol%	6	p-Xylene	r.t.	78	51
$[PbLx_2]\cdot 2DMF\cdot 6H_2O$	3 mol%	24	CH_3CN	r.t.	78	52
$[Zn(\kappa N\text{–}H_3Ly)(H_2O)_3]\cdot 3H_2O$	3 mol%	12	THF	r.t.	89	53
Tb.DCBA	10 (wt%)	6	CH_2Cl_2	r.t.	>99	54
NUC-27	0.03 mmol	1	C_2H_5OH	60	99	55
$[Zn(TIC4R)(HCOO)](HCOO)\cdot 0.5DMF\cdot 1.5H_2O$	0.01 mmol	0.66	-	60	>99	56
$\{[Cd(bpp)(L)(H_2O)]\cdot DMF\}_n$	3 mol%	1	CH_3OH	30	80	57
NUC-21	0.03 mmol	1	-	70	99	58
$\{[Cd_2(2\text{-}bpbg)(fum)_2(H_2O)_2]\cdot 8.5H_2O\}_n$	2 mol%	1	CH_3OH	27	100	59
V-Zn-MOF	1 mol%	1	-	60	>99	60
$[Mn_2(bpta)_2(L1)_2(H_2O)_2]$	5 mol%	1.66	Water	30	98	61
$[Co_2(tdc)_2(tpxn)]\cdot(H_2O)_6\}_n$	2 mol%	1	CH_3OH	30	96	62
SPUZ-1	1 mol%	0.5	-	60	99.9	63
JNU-402-NH_2	0.06 mmol	1	-	80	>99	64

[a]The reference numbers are as appeared in the paper