**ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)**

# Effecting structural diversity in a series of Co(II)-organic frameworks by the interplay between rigidity of a dicarboxylate and flexibility of bis(tridentate) spanning ligands

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**Table S1.** Selected Bond distances and Bond Angles for **1a, 2a, 3a** and **4a.**

**1a**

**Bond distances (Å)**

| | |
|---|---|
| Co1-O1 | 2.061(3) |
| Co1-O3 | 2.093(3) |
| Co1-O5 | 2.167(3) |
| Co1-N1 | 2.118(4) |
| Co1-N2 | 2.216(4) |
| Co1-N3 | 2.116(4) |

**Bond angles (°)**

| | | | |
|---|---|---|---|
| O1-Co1-O3 | 95.72(13) | N3-Co1-O5 | 86.85(14) |
| O1-Co1-N3 | 97.62(14) | N1-Co1-O5 | 176.03(13) |
| O3-Co1-N3 | 166.25(14) | O1-Co1-N2 | 165.63(14) |
| O1-Co1-N1 | 89.37(14) | O3-Co1-N2 | 89.26(14) |
| O3-Co1-N1 | 86.37(13) | N3-Co1-N2 | 78.58(15) |
| N3-Co1-N1 | 97.11(14) | N1-Co1-N2 | 77.47(15) |
| O1-Co1-O5 | 90.08(13) | O5-Co1-N2 | 103.44(14) |
| O3-Co1-O5 | 89.78(13) | | |

**2a**

**Bond distances (Å)**

| | | | |
|---|---|---|---|
| Co1-O1[1] | 2.130(5) | Co2-O6[1] | 2.125(5) |
| Co1-O2 | 2.044(5) | Co2 -O7 | 2.055(5) |
| Co1-O4[1] | 2.237(5) | Co2-O8[1] | 2.235(5 |
| Co1-N1 | 2.108(6) | Co2-N4 | 2.125(6) |
| Co1-N2 | 2.211(6) | Co2-N5 | 2.208(6) |
| Co1-N3 | 2.087(6) | Co2-N6 | 2.096(6) |

[1]-1+X,+Y,+Z

**Bond angles (°)**

| | | | |
|---|---|---|---|
| O2 -Co1-N3 | 91.27(18) | O7-Co2-N6 | 91.3(2) |
| O2-Co1-N1 | 93.60(17) | O7-Co2-N4 | 92.41(18) |
| N3-Co1-N1 | 156.51(19) | N6-Co2-N4 | 156.6(2) |
| O2-Co1-O1[1] | 107.1(2) | O7-Co2-O6[1] | 107.18(19) |
| N3-Co1-O1[1] | 97.97(18) | N6-Co2-O6[1] | 98.7(2) |
| N1-Co1-O1[1] | 102.52(17) | N4-Co2-O6[1] | 102.20(19) |
| O2-Co1-N2 | 86.69(19) | O7-Co2-N5 | 86.43(19) |
| N3-Co1-N2 | 79.90(18) | N6-Co2-N5 | 79.6(2) |
| N1-Co1-N2 | 77.46(16) | N4-Co2-N5 | 77.66(18) |
| O1[1]-Co1-N2 | 166.18(16) | O6[1]-Co2-N5 | 166.35(15) |
| O2-Co1-O4[1] | 167.23(16) | O7-Co2-O8[1] | 167.33(17) |

| | | | |
|---|---|---|---|
| N3-Co1-O4[1] | 93.19(17) | N6-Co2- O8[1] | 93.33(19) |
| N1-Co1-O4[1] | 87.05(16) | N4-Co2- O8[1] | 87.97(18) |
| O1[1]-Co1-O4[1] | 60.46(17) | O6[1]-Co2- O8[1] | 60.46(18) |
| N2-Co1-O4[1] | 105.88(18) | N5-Co2- O8[1] | 105.99(18) |

[1]-1+x, +y, +z

**3a**

**Bond distances (Å)**

| | |
|---|---|
| Co1-O1 | 2.132(4) |
| Co1-O3 | 2.064(4) |
| Co1-O8 | 2.093(4) |
| Co1-N1 | 2.089(4) |
| Co1-N2 | 2.125(4) |
| Co1-N3 | 2.229(5) |

**Bond angles (°)**

| | | | |
|---|---|---|---|
| O3-Co1-N1 | 93.21(16) | O8-Co1-O1 | 87.06(16) |
| O3-Co1-O8 | 91.78(16) | N2-Co1-O1 | 85.84(16) |
| N1-Co1-O8 | 86.59(17) | O3-Co1-N3 | 164.73(16) |
| O3-Co1-N2 | 93.30(16) | N1-Co1-N3 | 78.48(16) |
| N1-Co1-N2 | 99.76(18) | O8-Co1-N3 | 100.39(17) |
| O8-Co1-N2 | 171.62(17) | N2-Co1-N3 | 75.77(17) |
| O3-Co1-O1 | 95.32(15) | O1-Co1-N3 | 94.49(15) |
| N1-Co1-O1 | 169.52(16) | | |

**4a**

**Bond distances (Å)**

| | |
|---|---|
| Co1-N1 | 2.2832(18) |
| Co1-N2 | 2.0734(18) |
| Co1-N3 | 2.0565(18) |
| Co1-O1 | 1.9805(15) |
| Co1-O4[1] | 1.9701(16) |

**Bond angles (°)**

| | | | |
|---|---|---|---|
| O4[1]-Co1-O1 | 101.33(7) | N3-Co1-N2 | 110.36(7) |
| O4[1]-Co1-N3 | 94.00(7) | O4[1]-Co1-N1 | 170.90(7) |
| O1-Co1-N3 | 113.95(7) | O1-Co1-N1 | 85.14(7) |
| O4[1]-Co1-N2 | 103.57(7) | N3-Co1-N1 | 77.43(7) |
| O1-Co1-N2 | 126.74(7) | N2-Co1-N1 | 77.03(7) |

[1]-1/2+x, 1/2-y, -1/2+z

**Table S2.** Hydrogen bond parameters for **1a-4a**.

**1a**

| D–H…A | r (D-H) (Å) | r (H…A) (Å) | r (D…A) (Å) | ∠D-H…A (deg) | Symmetry |
|---|---|---|---|---|---|
| O1S--H1SB..O4 | 0.87 | 1.89 | 2.7547 | 171 | 1+x,y,z |
| O5--H19..O4 | 0.87 | 1.86 | 2.6644 | 152 | -x,-1/2+y,1/2-z |
| C7--H4..O4 | 0.99 | 2.44 | 3.3735 | 158 | 1-x,-1/2+y,1/2-z |
| C13--H10..O1S | 0.99 | 2.59 | 3.578 | 175 | x,1/2-y,1/2+z |

**2a**

| D–H…A | r (D-H) (Å) | r (H…A) (Å) | r (D…A) (Å) | ∠D-H…A (deg) | Symmetry |
|---|---|---|---|---|---|
| O(9)--H(9A)..O(6) | 0.85 | 2.09 | 2.8928 | 157 | 2-x,1-y,1-z |
| O(9)--H(9B)..O(10) | 0.85 | 2.03 | 2.7448 | 142 | |
| O(12)--H(12A)..O(9) | 0.82 | 1.99 | 2.7212 | 149 | |
| C(8)--H(4)..O(3) | 0.93 | 2.55 | 3.397 | 152 | -x,2-y,-z |
| C(10)--H(6)..O(8) | 0.93 | 2.27 | 3.1708 | 162 | 1+x,1+y,z |
| C(18)--H(17)..O(5) | 0.93 | 2.59 | 3.3225 | 136 | 1-x,1-y,1-z |
| C(31)--H(26)..O(4) | 0.93 | 2.34 | 3.2188 | 158 | x,-1+y,z |
| C(37)--H(36)..O(3) | 0.97 | 2.59 | 3.4821 | 152 | 1-x,1-y,-z |
| C(39)--H(37)..O(10) | 0.93 | 2.45 | 3.3688 | 170 | 1+x,y,z |

**3a**

| D–H…A | r (D-H) (Å) | r (H…A) (Å) | r (D…A) (Å) | ∠D-H…A (deg) | Symmetry |
|---|---|---|---|---|---|
| O1S--H1SA..O4 | 0.85 | 2.01 | 2.8087 | 157 | -x,1-y,1-z |
| O1--H1B..O2 | 0.86 | 1.89 | 2.6739 | 152 | |
| O6--H6..O1S | 0.82 | 2.25 | 2.8933 | 135 | 1-x,1-y,1-z |
| C20--H20..O4 | 0.93 | 2.55 | 3.4266 | 157 | 1+x,y,z |
| C22--H22..O1 | 0.93 | 2.39 | 3.2994 | 167 | x,1/2-y,1/2+z |

**4a**

| D–H…A | r (D-H) (Å) | r (H…A) (Å) | r (D…A) (Å) | ∠D-H…A (deg) | Symmetry |
|---|---|---|---|---|---|
| C(7)--H(6)..O(1) | 0.93 | 2.4 | 3.2022 | 144 | 1/2+x,1/2-y,1/2+z |
| C(21)--H(11)..O(2) | 0.93 | 2.44 | 3.3335 | 161 | -1/2+x,1/2-y,1/2+z |
| C(22)--H(12)..O(3) | 0.93 | 2.32 | 3.1598 | 149 | |
| C(11)--H(13)..O(3) | 0.97 | 2.55 | 3.4478 | 154 | 1/2-x,-1/2+y,3/2-z |
| C(15)--H(17)..O(2) | 0.93 | 2.44 | 3.2441 | 144 | 1/2-x,-1/2+y,1/2-z |

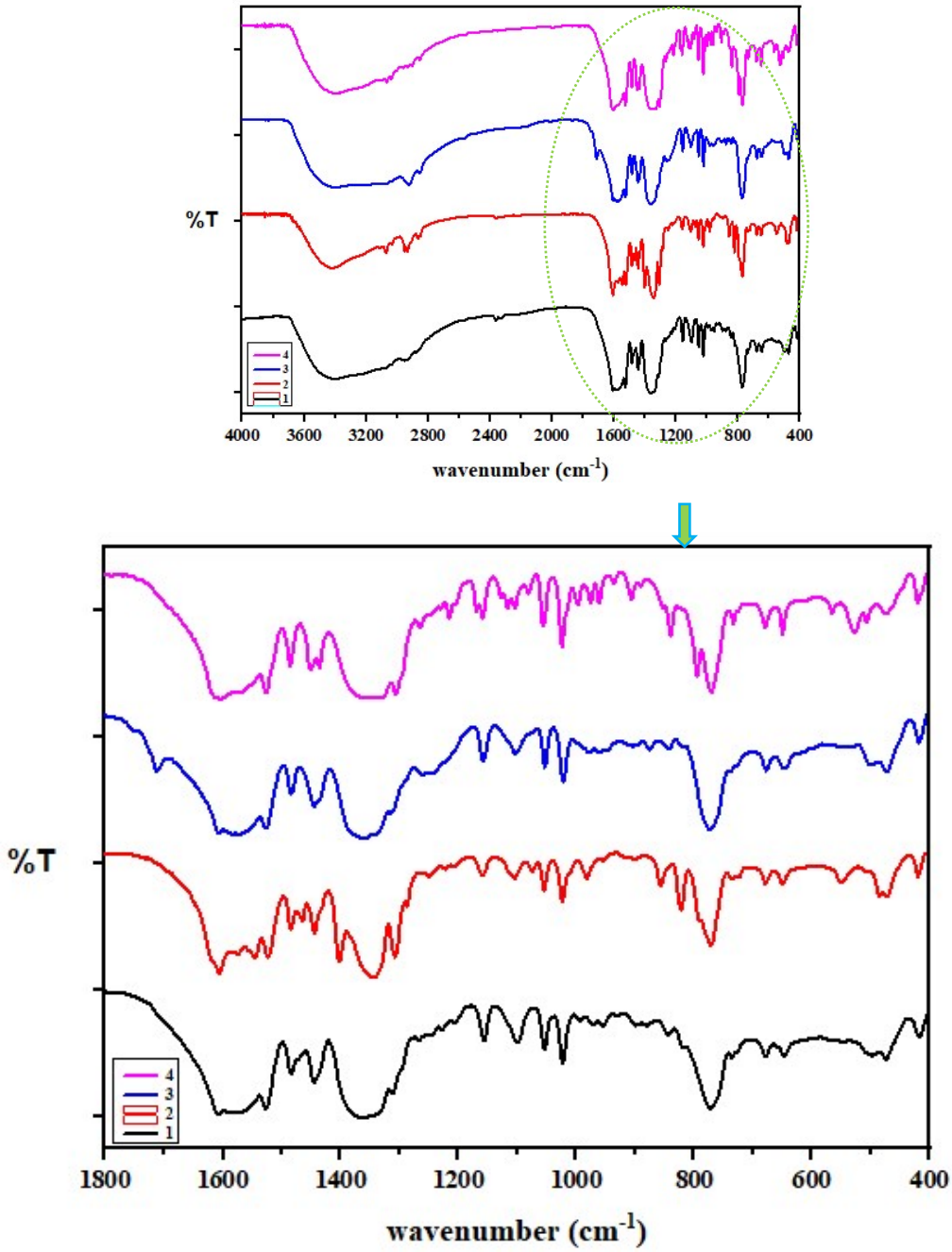


**Fig. S1** FTIR spectra of **1-4**.

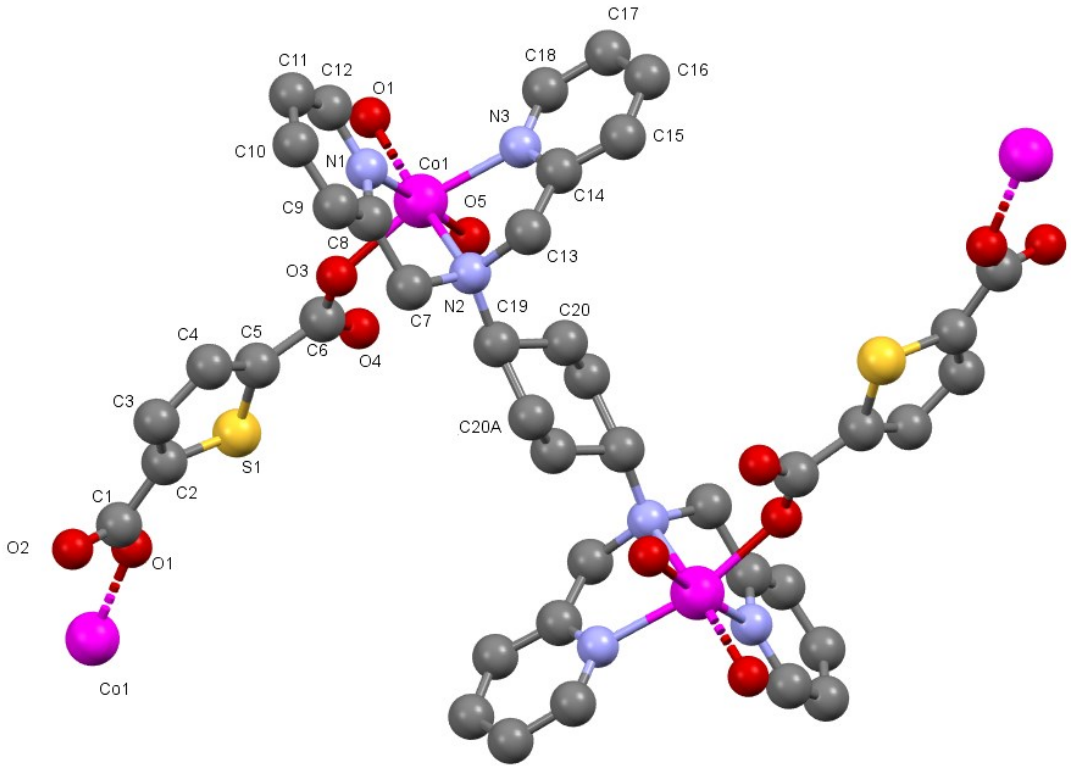


**Fig. S2** A labelled diagram for the structure of **1a**. One half of the molecule is in the asymmetric unit and relates to the other half by symmetry. Two middle carbons in the $(CH_2)_4$ spacer are disordered over two positions.

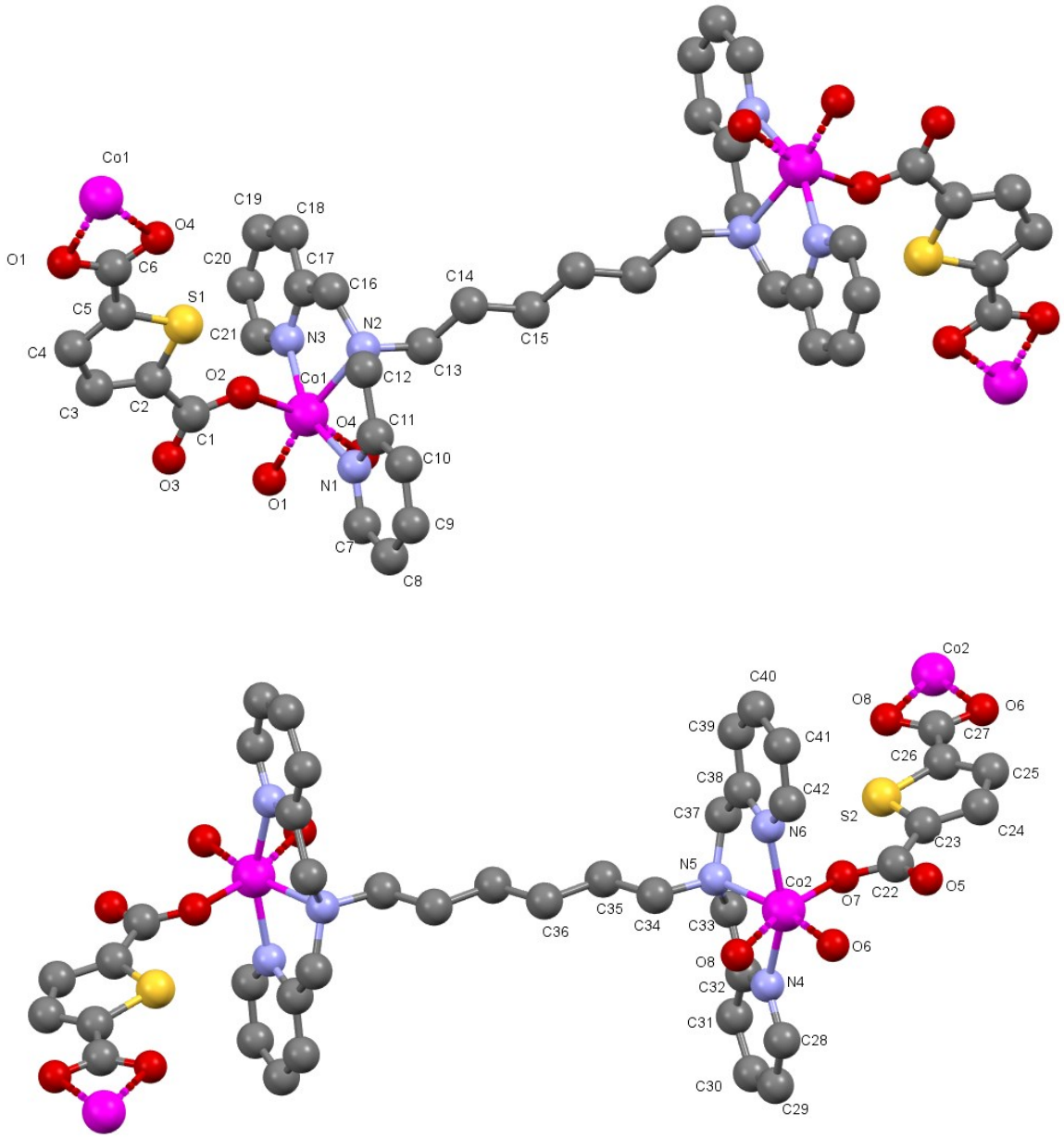


**Fig. S3** A labelled diagram for the two indepedent molecules of **2a**. There are two indepent molecules in the asymmetric unit. In both cases, one half of the molecule is in the asymmetric unit and relates to the other half by symmetry.

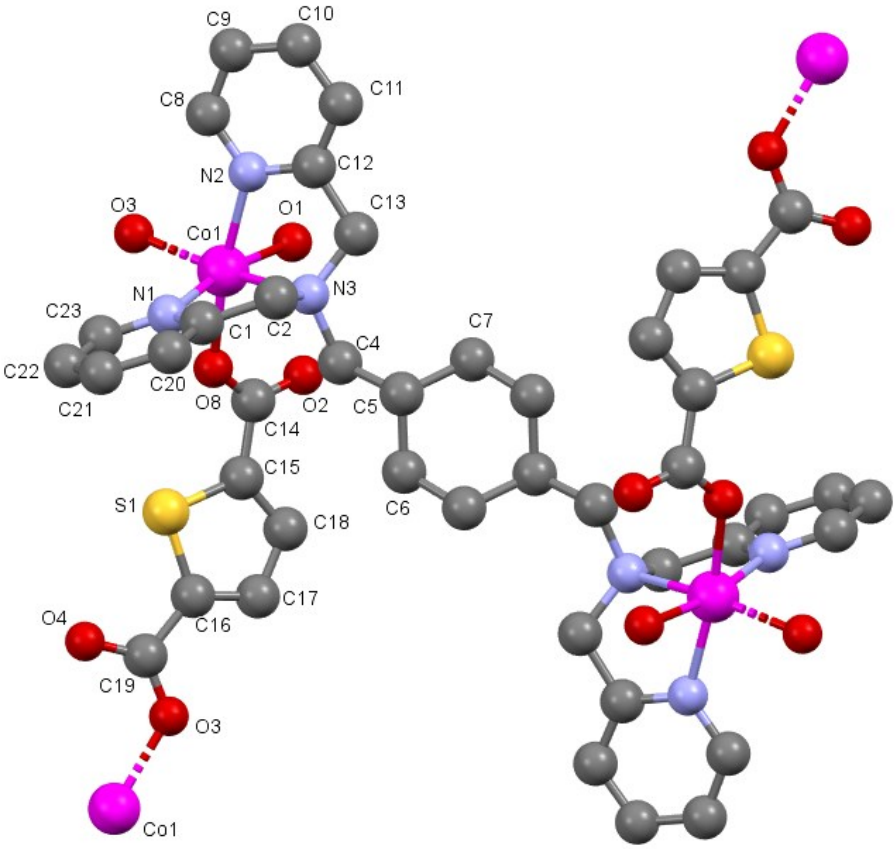


**Fig. S4** A labelled diagram for the structure of **3a**. One half of the molecule is in the asymmetric unit and relates to the other half by symmetry.

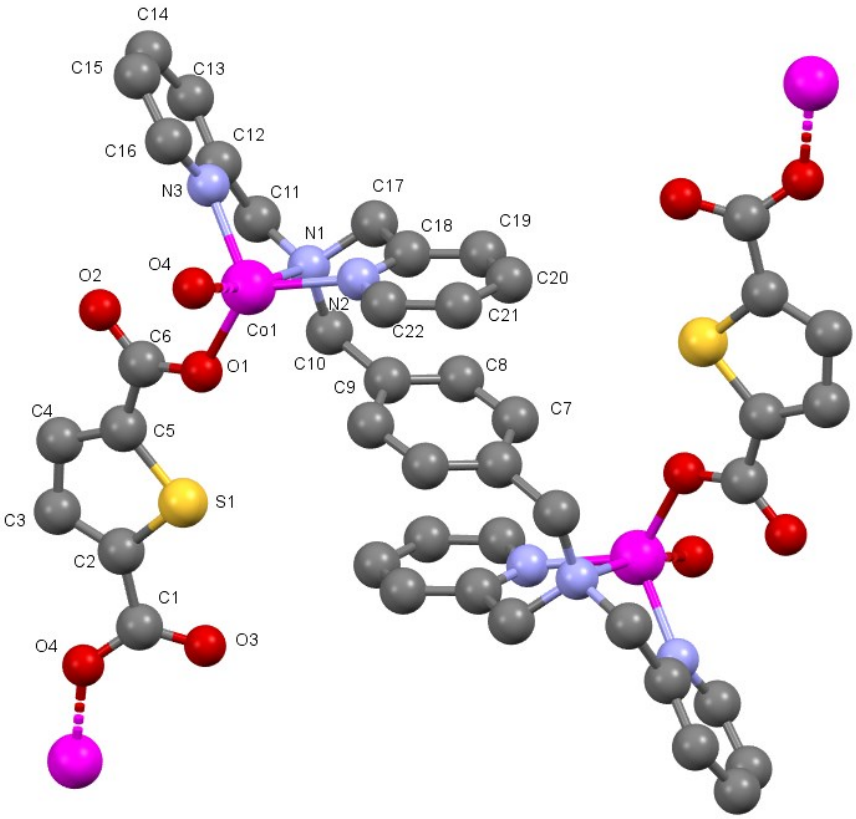


**Fig. S5** A labelled diagram for the structure of **4a**. One half of the molecule is in the asymmetric unit and relates to the other half by symmetry.

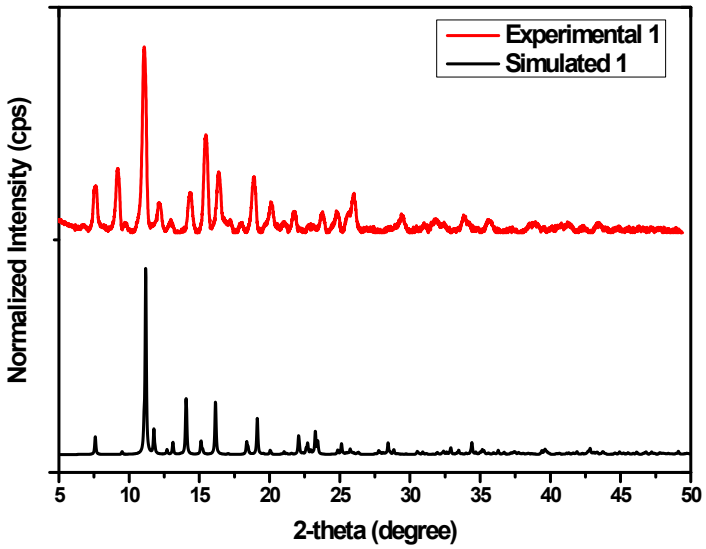


**Fig. S6** PXRD patterns of the as-synthesized **1a** compared to the corresponding simulated powder patterns obtained from single crystal structures.

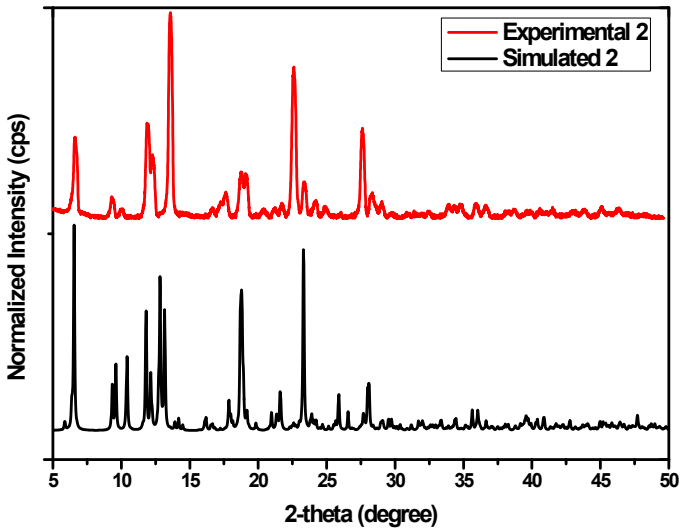


**Fig. S7** PXRD patterns of the as-synthesized **2a** compared to the corresponding simulated powder patterns obtained from single crystal structures.

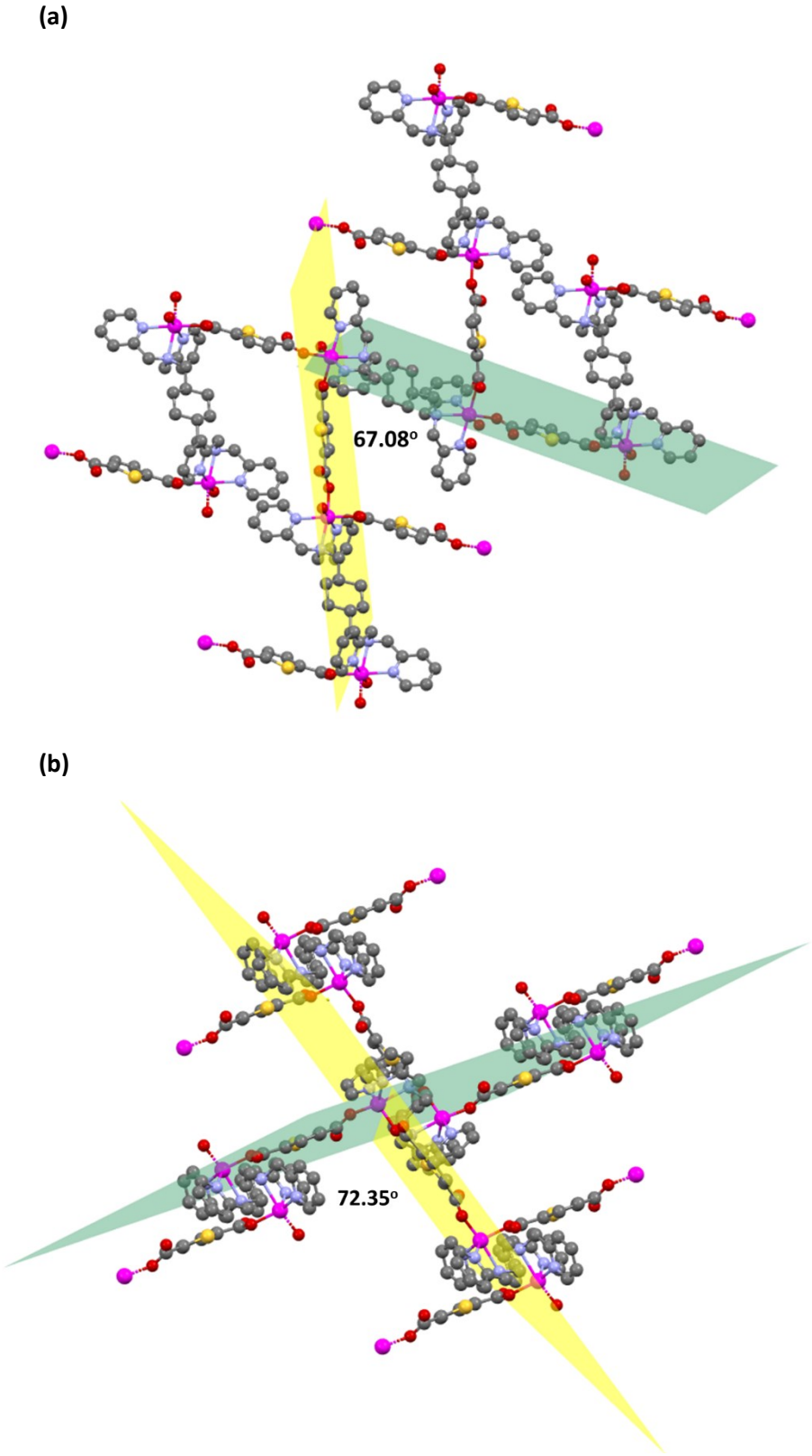


**Fig. S8** Schematic representation of the angle widening between the planes containing the thiophene dicarboxylate moieties in **3a** (a) and **4a** (b).

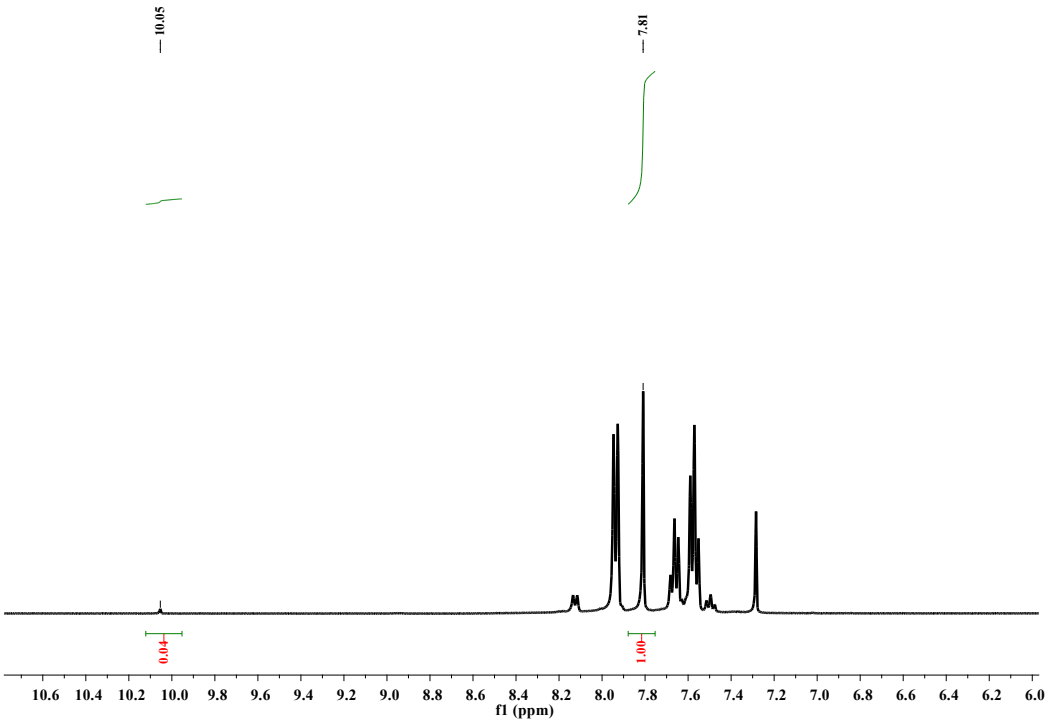


**Fig. S9** Example of integration in the $^{1}$H NMR spectrum for the determination of catalysis reaction product (Table 2, Entry 2).

**Calculation of the product yield in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by 4a**

Total amount of compounds at the end:
Unreacted bezaldehyde (10.05 ppm) + 2-(benzylidene)malononitrile (7.81 ppm) = 0.04 + 1.00 = 1.04
Yield of 2-(benzylidene)malononitrile = (1/1.04) * 100 = 96 %.

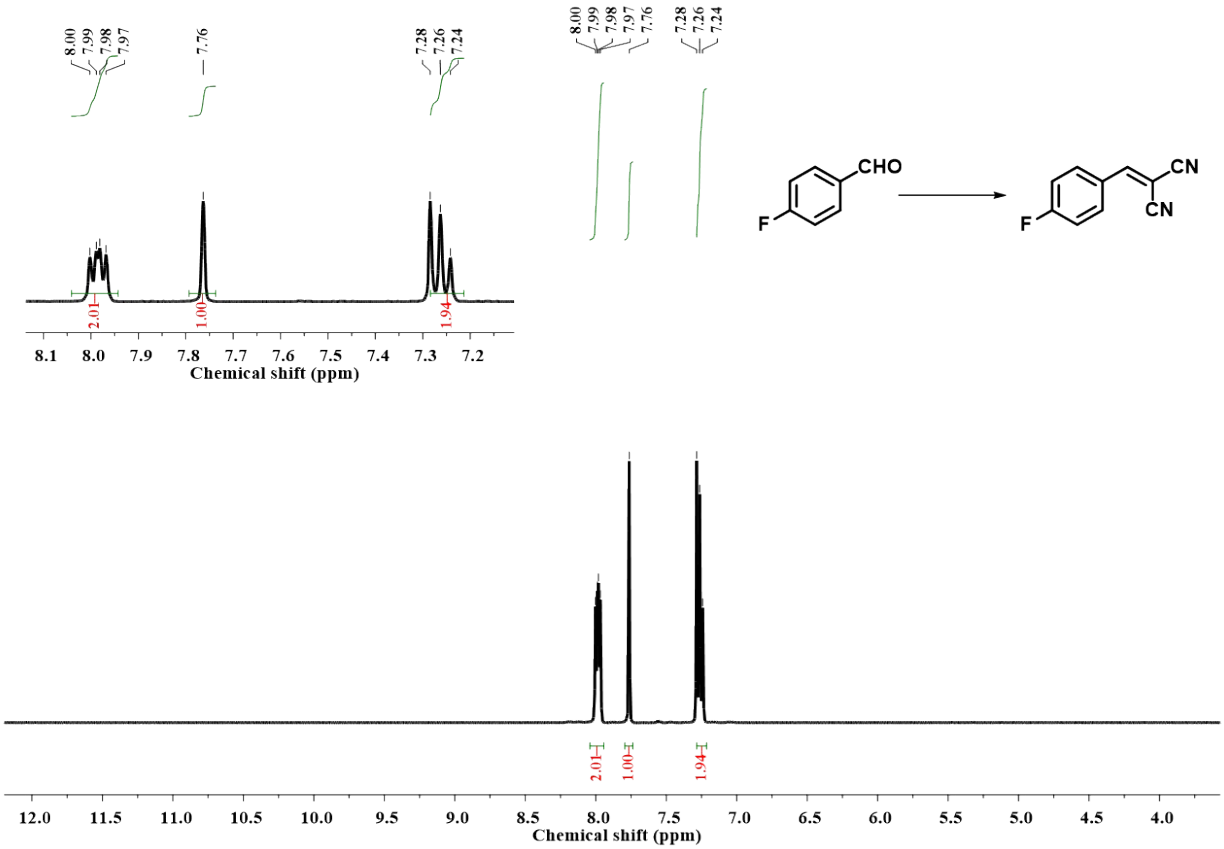


**Fig. S10** $^{1}$H NMR spectrum of 2-(4-fluorobenzylidene)malononitrile in $CDCl_3$.

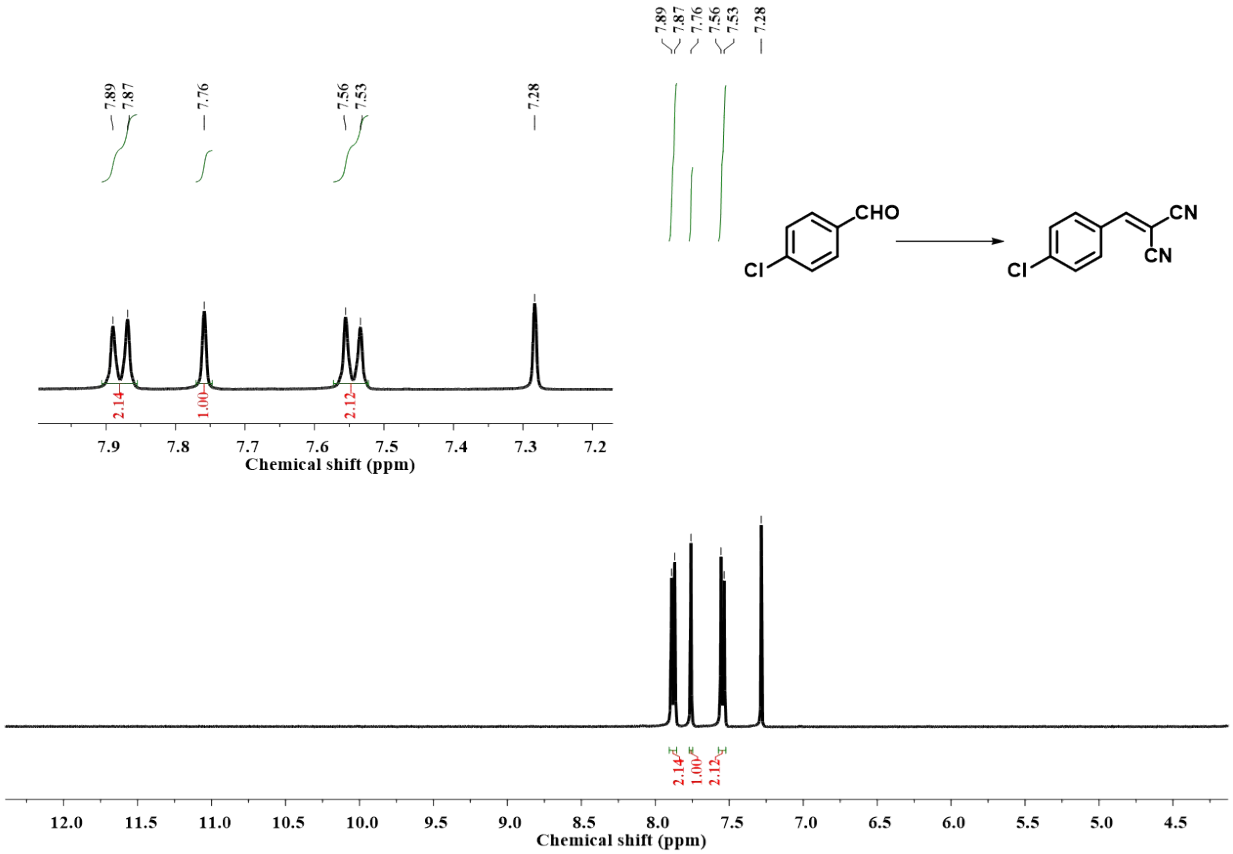


**Fig. 11** $^{1}$H NMR spectrum of 2-(4-chlorobenzylidene)malononitrile in $CDCl_3$.

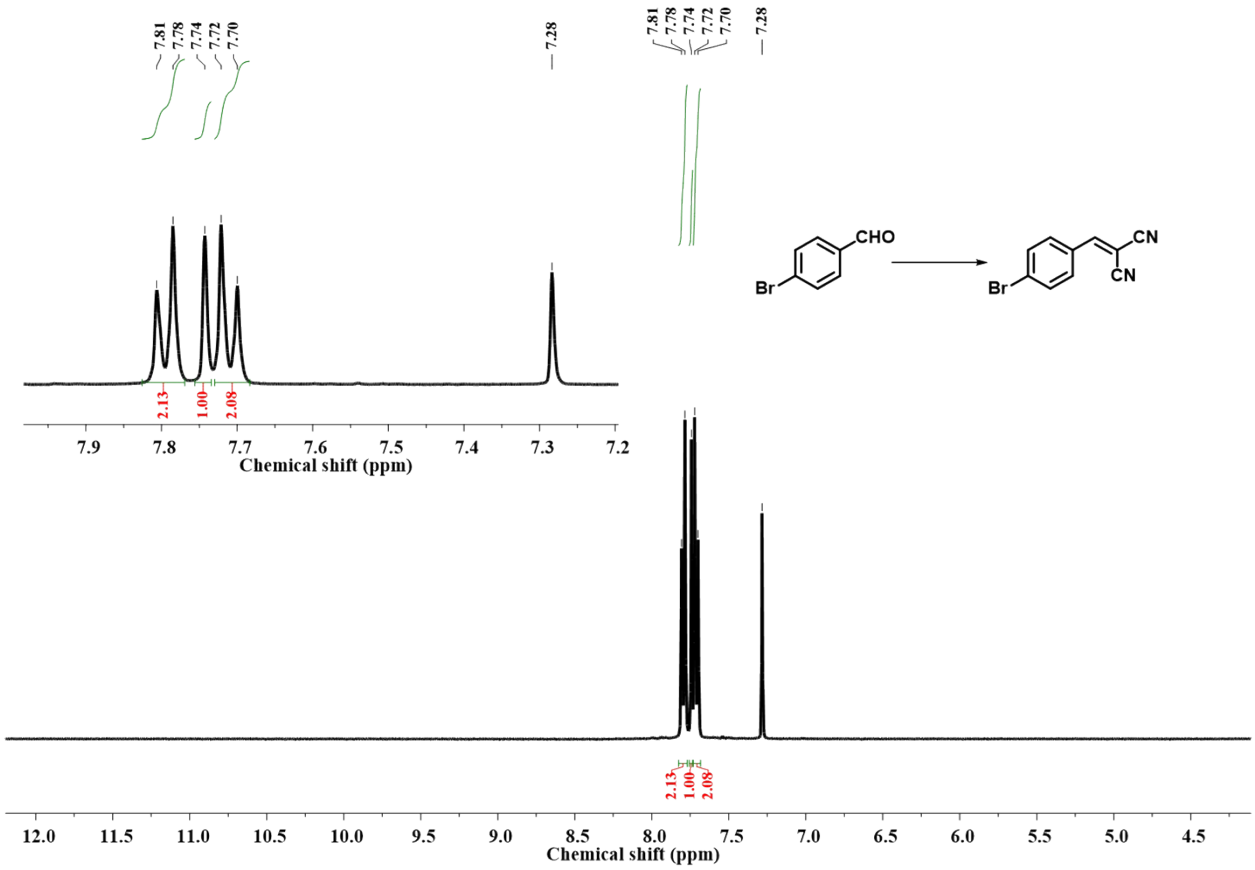


**Fig. S12** $^{1}$H NMR spectrum of 2-(4-bromobenzylidene)malononitrile in $CDCl_3$.

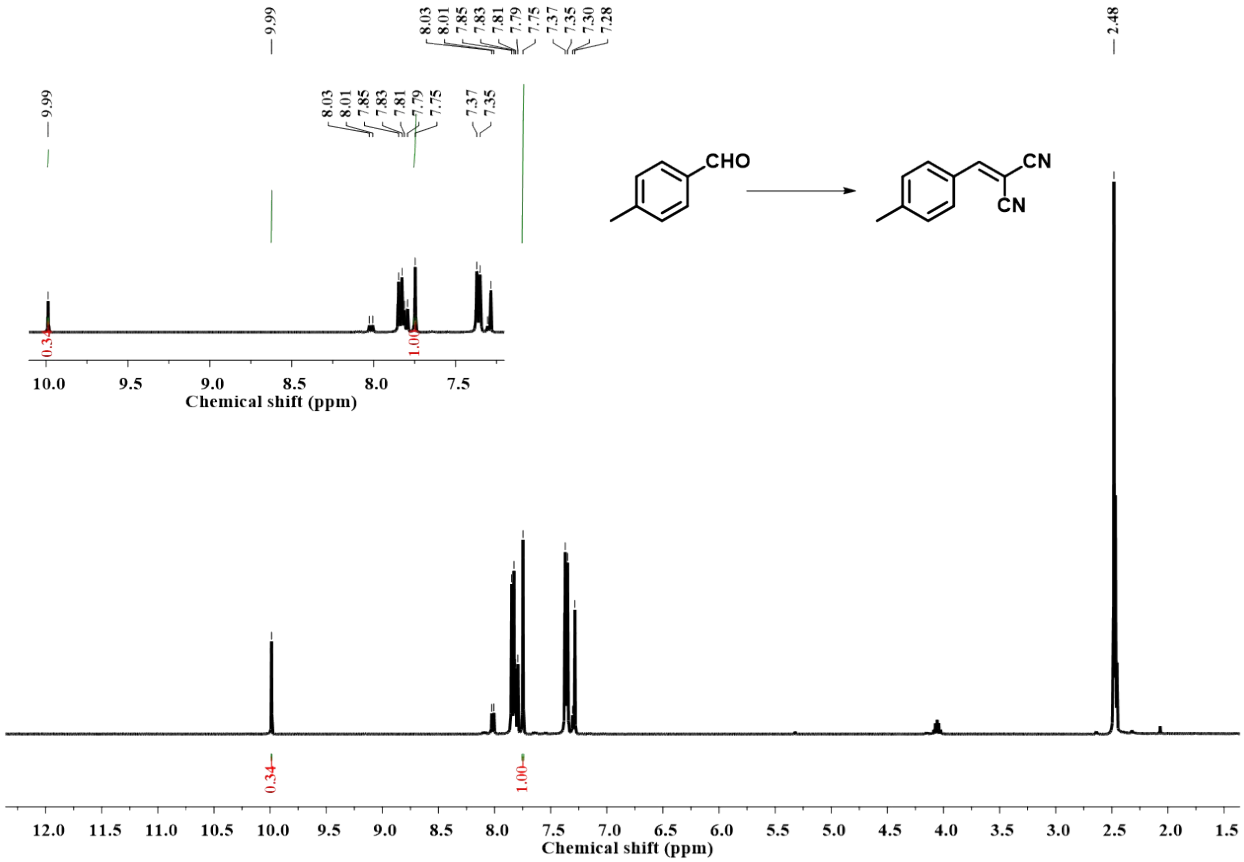


**Fig. S13** $^{1}$H NMR spectrum of 2-(4-methylbenzylidene)malononitrile in $CDCl_3$.

**Calculation of the product yield in the Knoevenagel condensation reaction of 4-methylbenzaldehyde with malononitrile catalyzed by 4a** (Table 3, entry 4)

Total amount of compounds at the end:
Unreacted bezaldehyde (9.99 ppm) + 2-(4-methylbenzylidene)malononitrile (7.79 ppm) = 0.34 + 1.00 = 1.07
Yield of 2-(4-methylbenzylidene)malononitrile = (1/1.34) * 100 = 74.62 %.

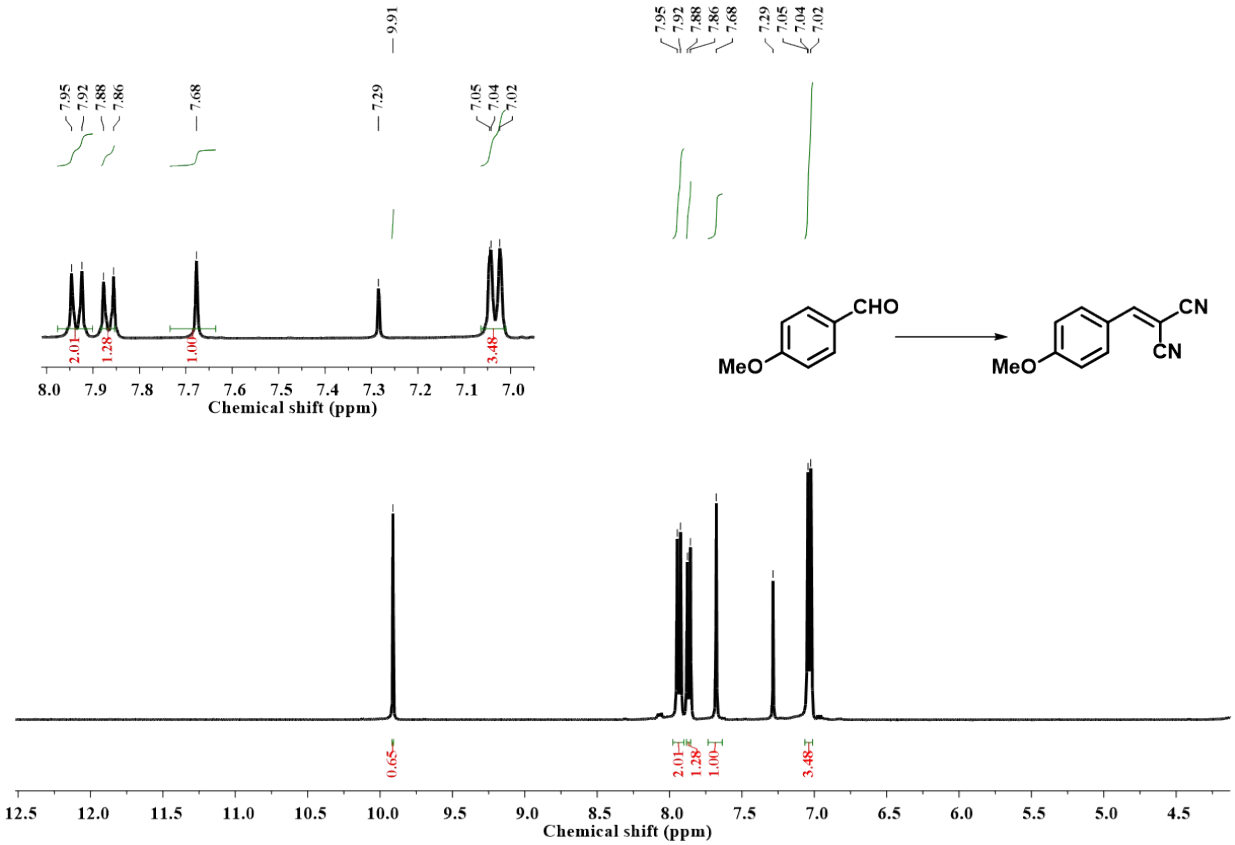


**Fig. S14** $^{1}$H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile in $CDCl_3$.

**Calculation of the product yield in the Knoevenagel condensation reaction of** 4-**methoxybenzaldehyde with malononitrile catalyzed by 4a** (Table 3, entry 5)

Total amount of compounds at the end (see Figure. S9):
Unreacted bezaldehyde (9.99 ppm) + 2-(4-methoxybenzylidene)malononitrile (7.68 ppm) = 0.65 + 1.00 = 1.65
Yield of 2-(4-methoxybenzylidene)malononitrile = (1/1.65) * 100 = 60.60 %.

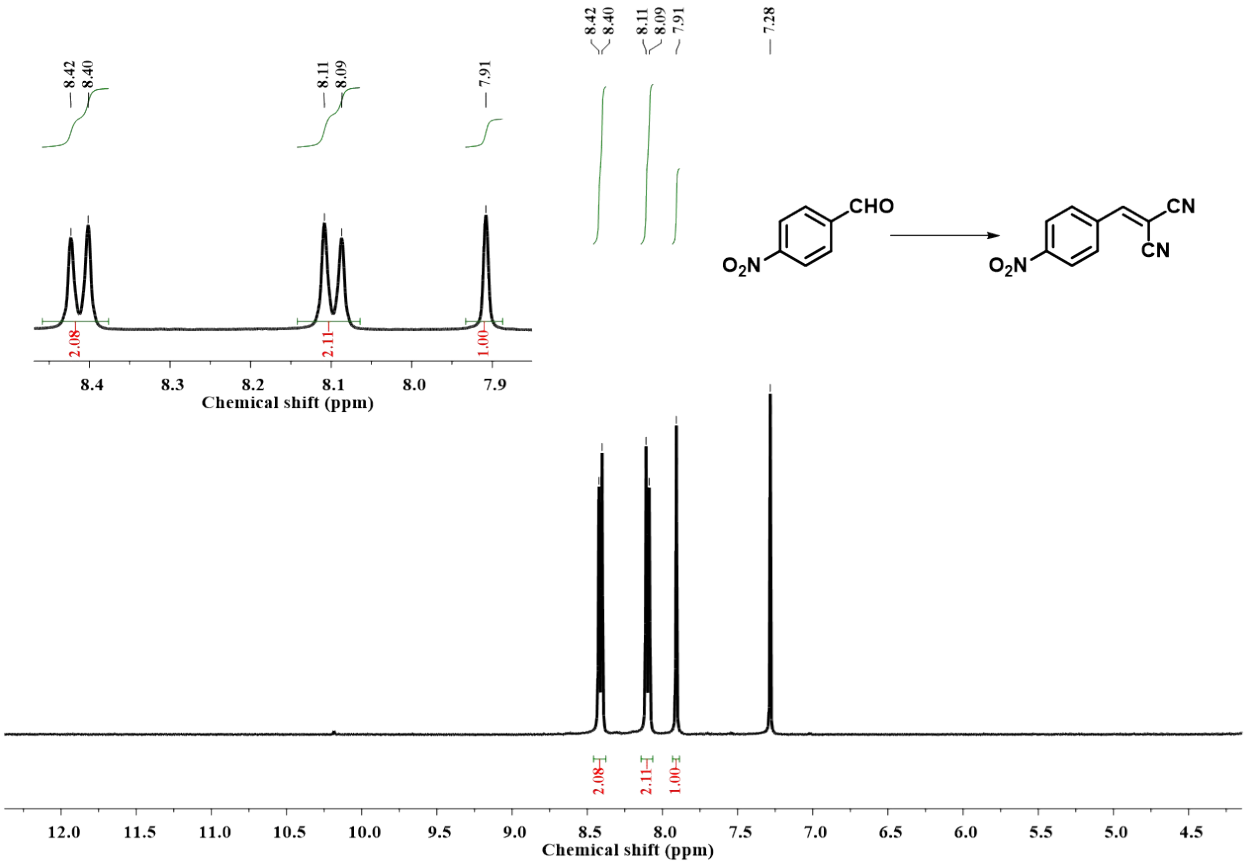


**Fig. S15** $^1$H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile in $CDCl_3$.

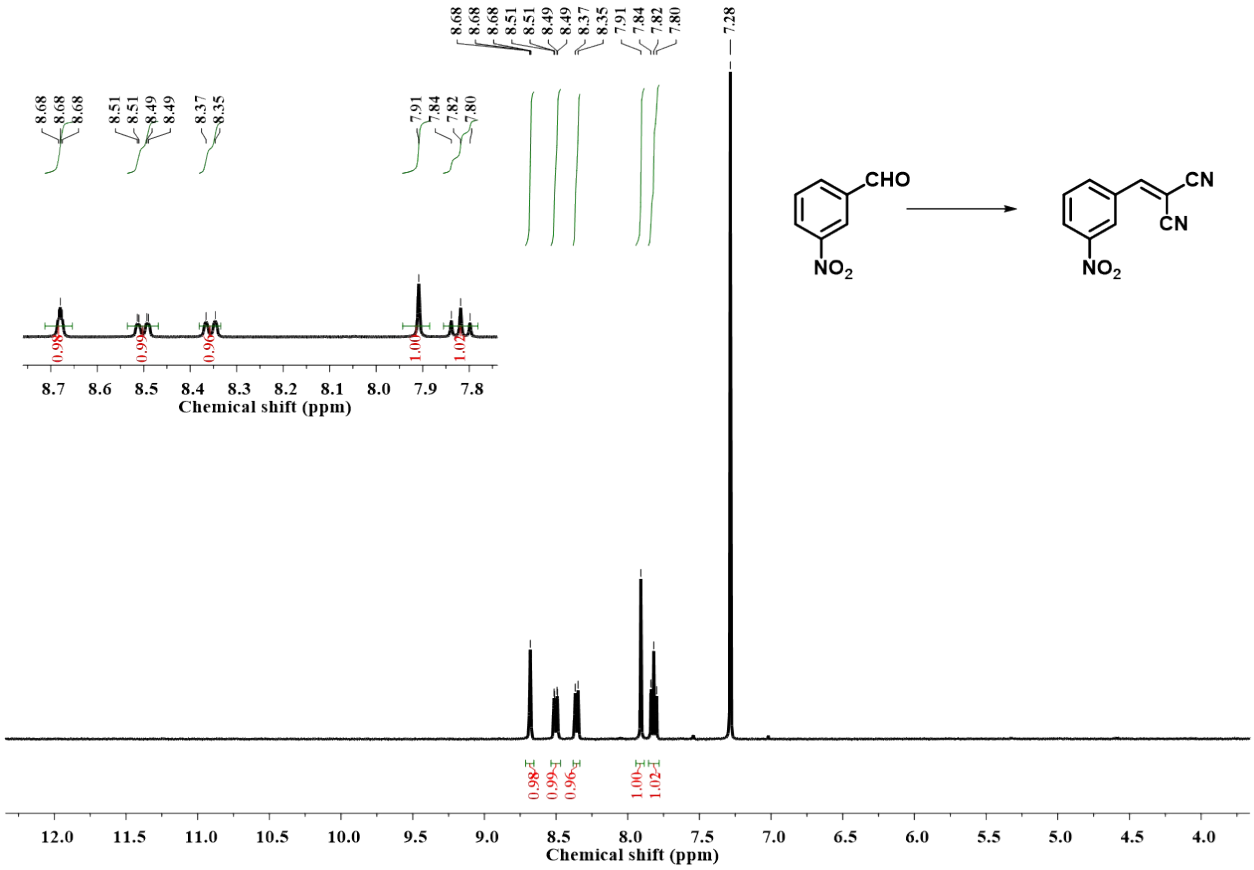


**Fig. S16** $^{1}$H NMR spectrum of 2-(pyridin-3-ylmethylene)malononitrile in $CDCl_3$.

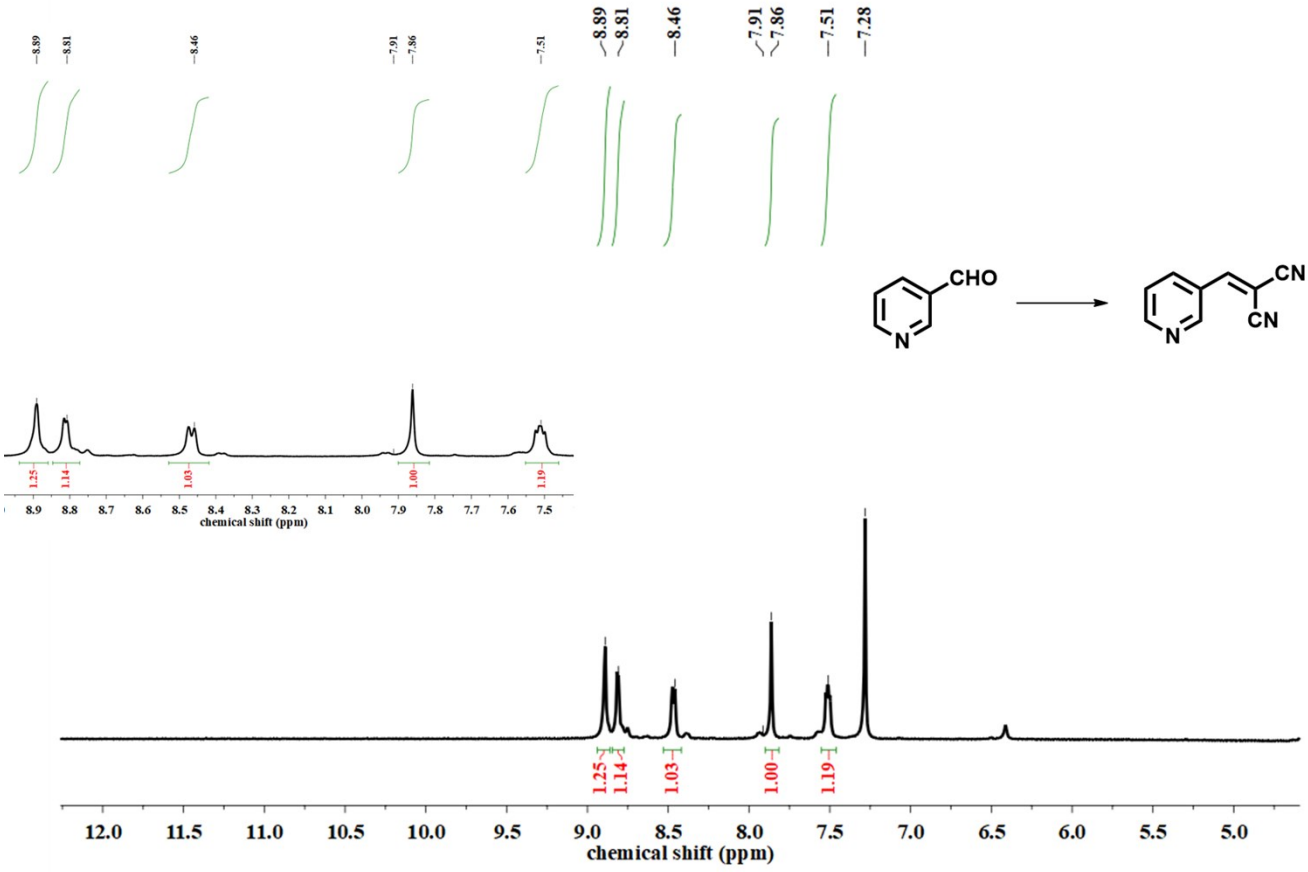


**Fig. S17** $^{1}$H NMR spectrum of 2-(3-nitrobenzylidene)malononitrile in $CDCl_3$.

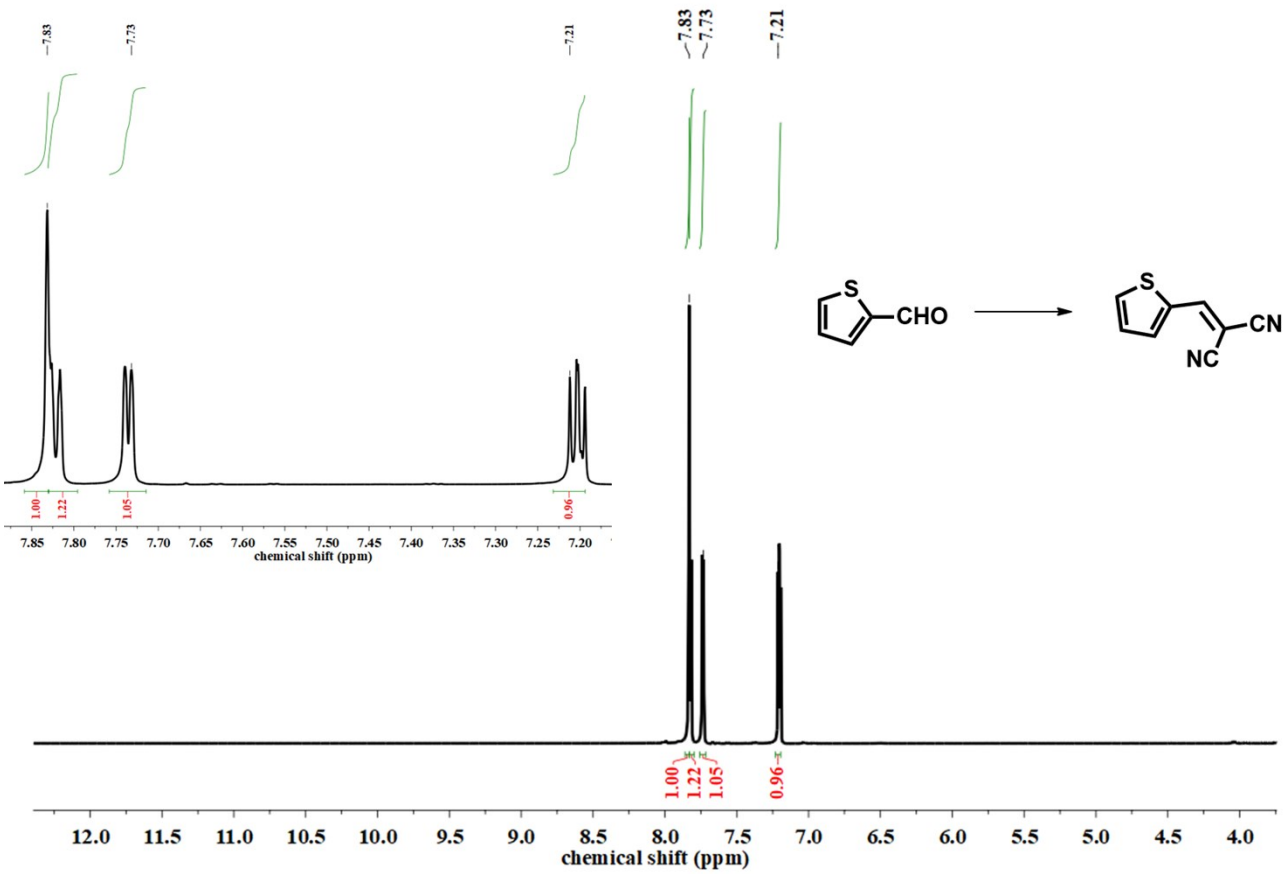


**Fig. S18** $^{1}$H NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile in $CDCl_3$.

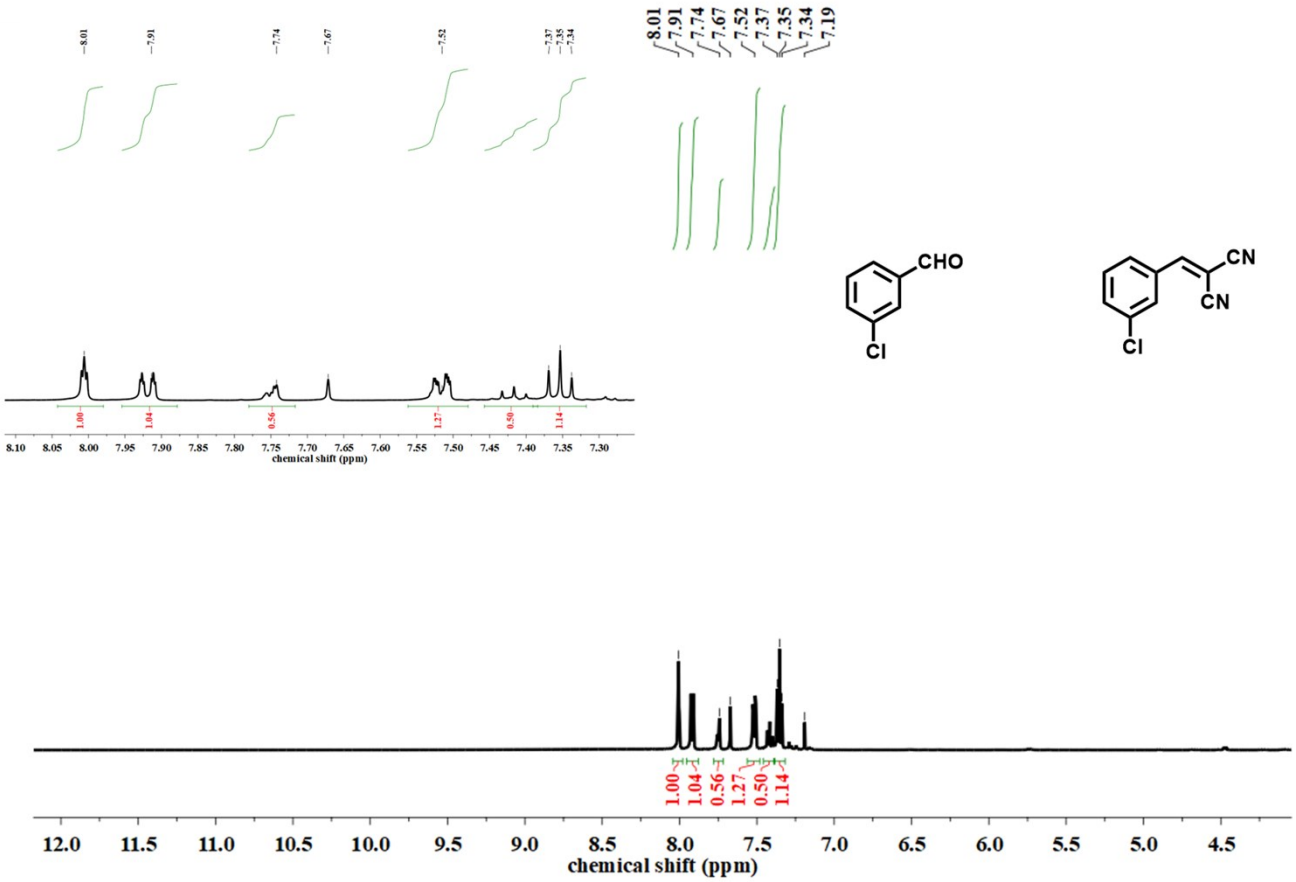


**Fig. S19** $^{1}$H NMR spectrum of 2-(3-chlorobenzylidene)malononitrile in $CDCl_3$.

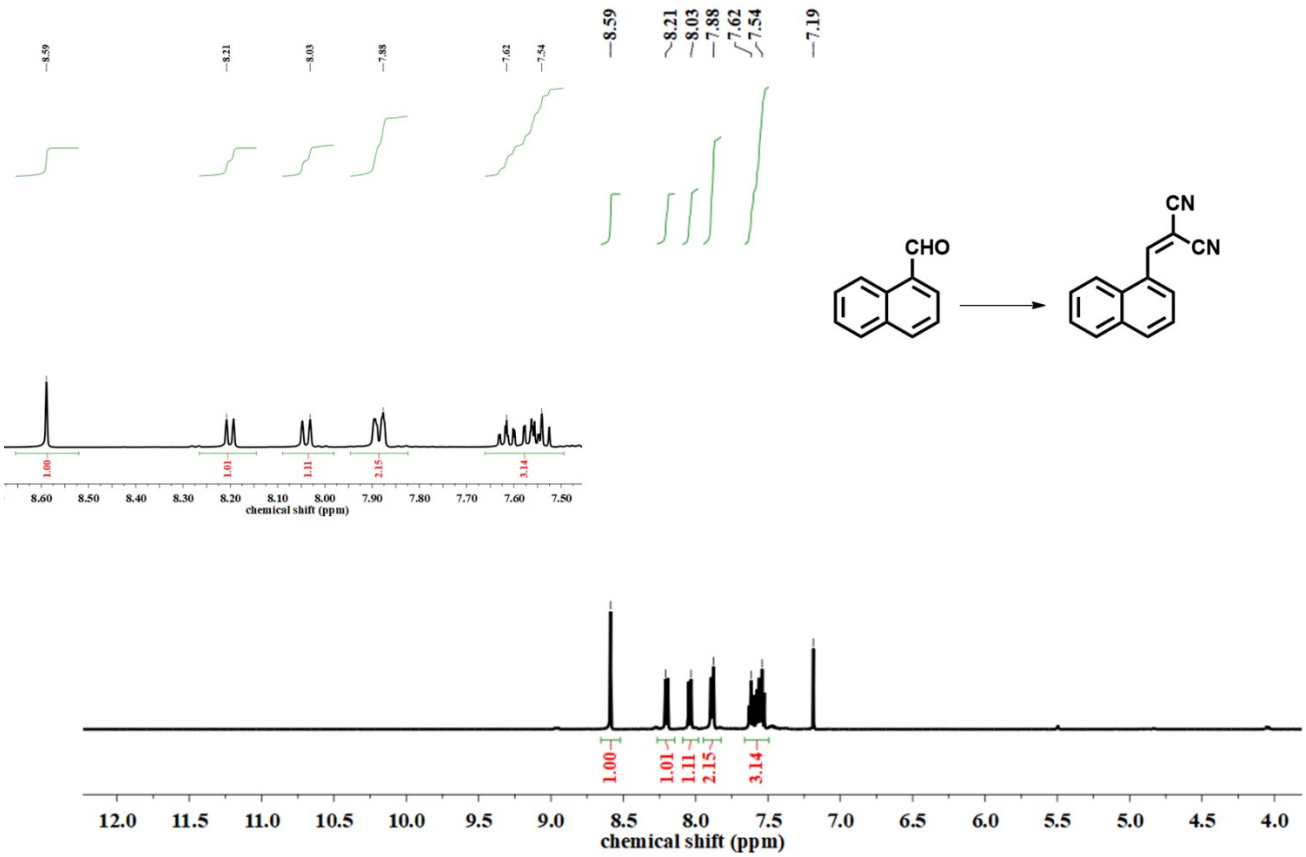


**Fig. S20** $^{1}$H NMR spectrum of 2-(naphthalen-1-ylmethylene)malononitrile in $CDCl_3$.

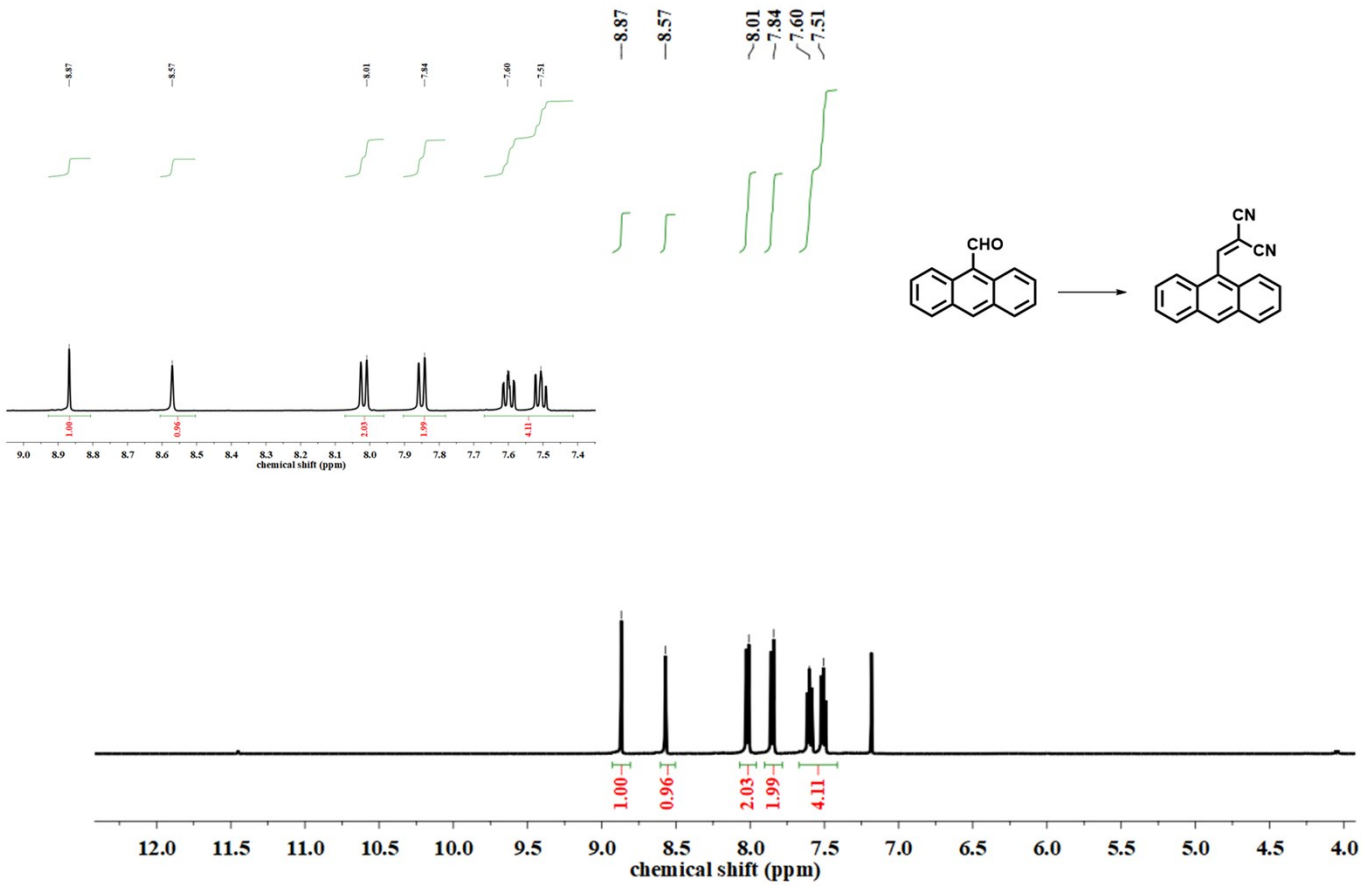


**Fig. S21** $^{1}$H NMR spectrum of 2-(anthracen-9-ylmethylene)malononitrile in $CDCl_3$.

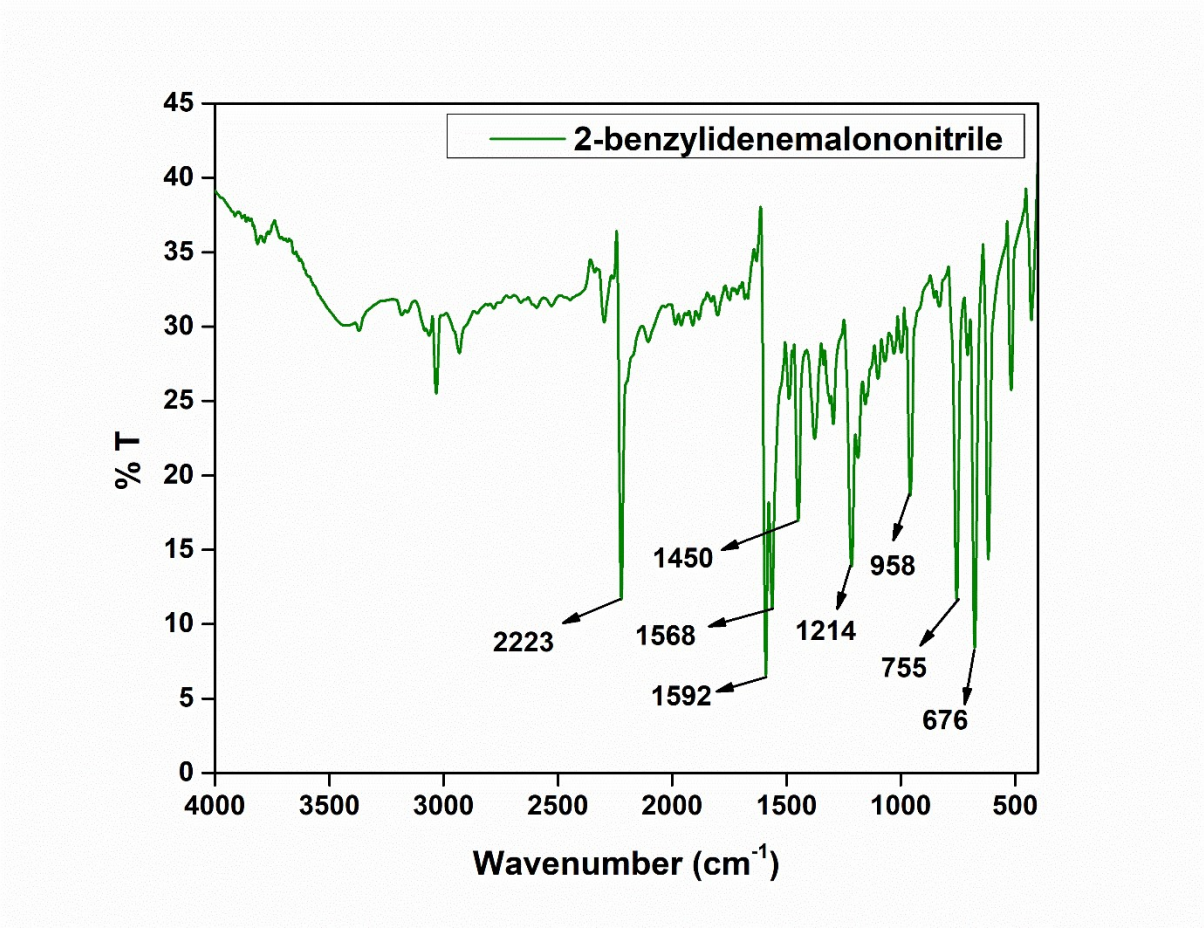


**Fig. S22** FTIR spectrum of 2-benzylidenemalonitrile.

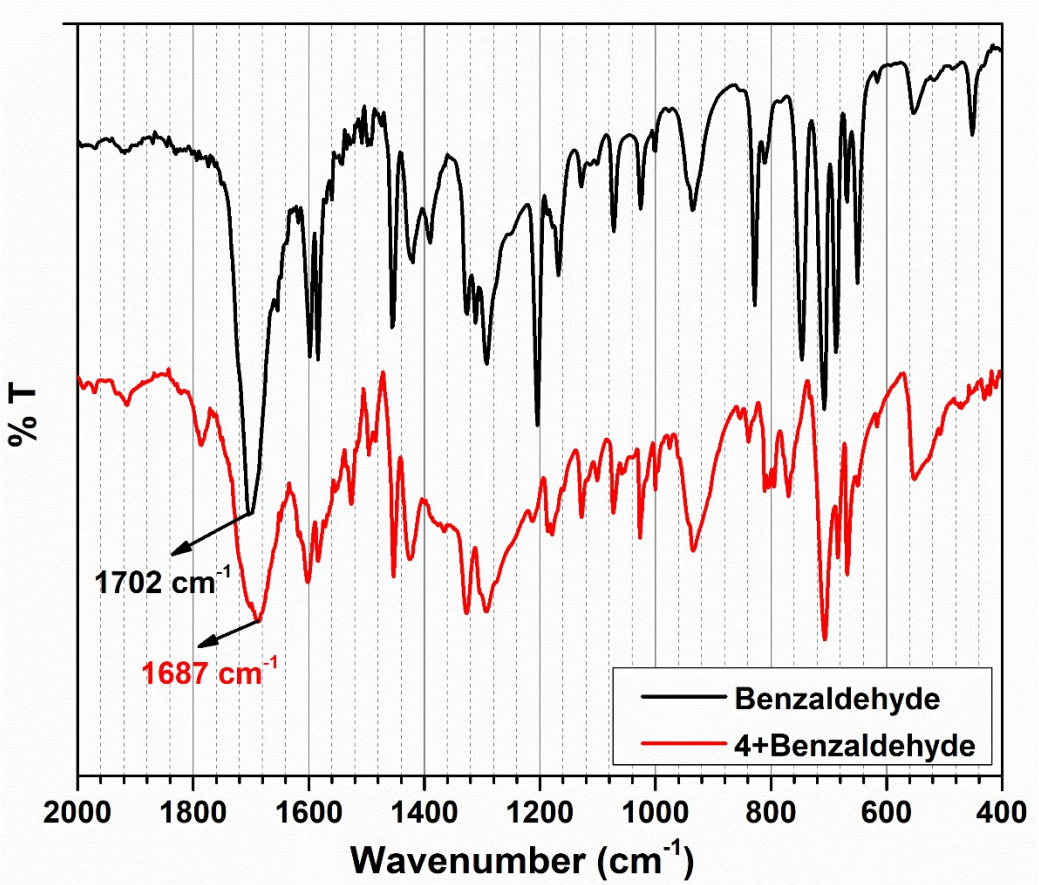


**Fig. S23** FTIR spectra of benzaldehyde (black), and benzaldehyde complexed with **4** (red).