Electronic supporting information

Topological control of 3,4-connected frameworks based on the Cu_2-paddle-wheel node: tbo or pto, and why?

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1. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction data were collected on a STOE STADI P diffractometer with Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å) at room temperature in transmission geometry. The samples were sealed in glass capillaries under argon atmosphere.

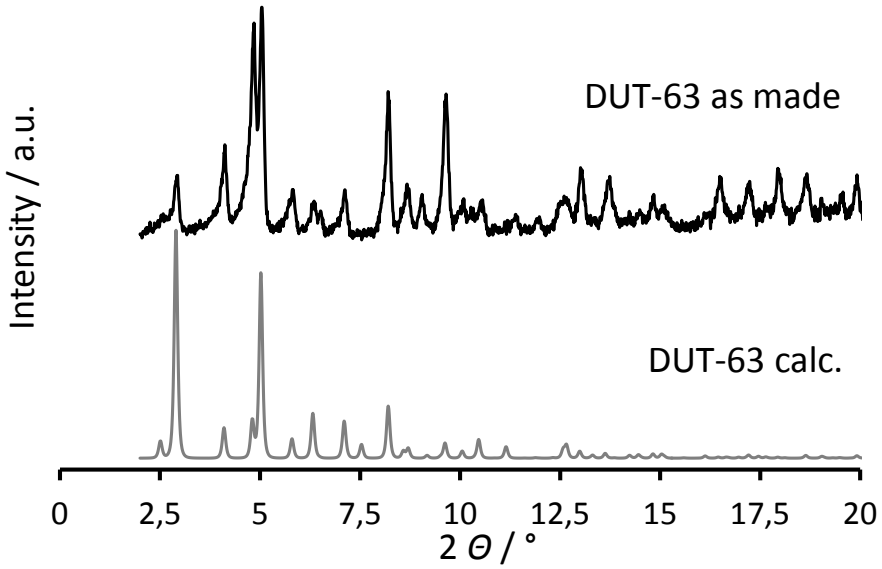

Figure S1. PXRD patterns of DUT-63.

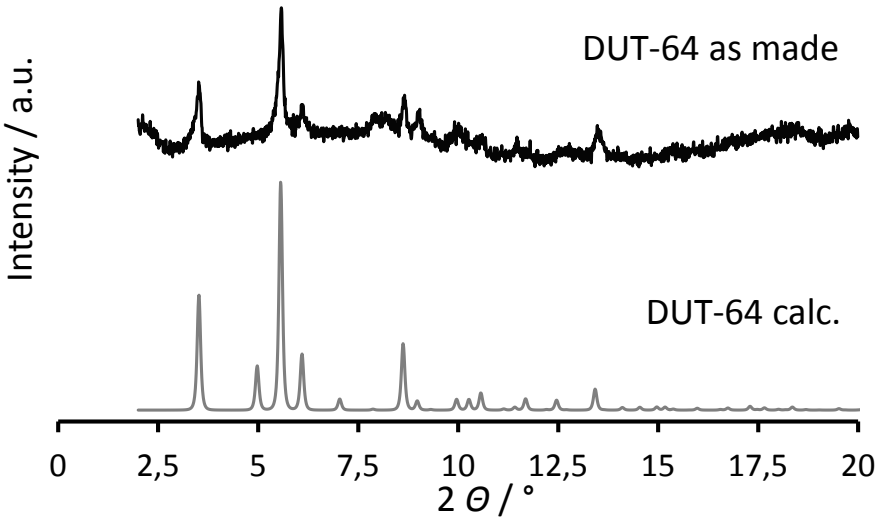

Figure S2. PXRD patterns of DUT-64.

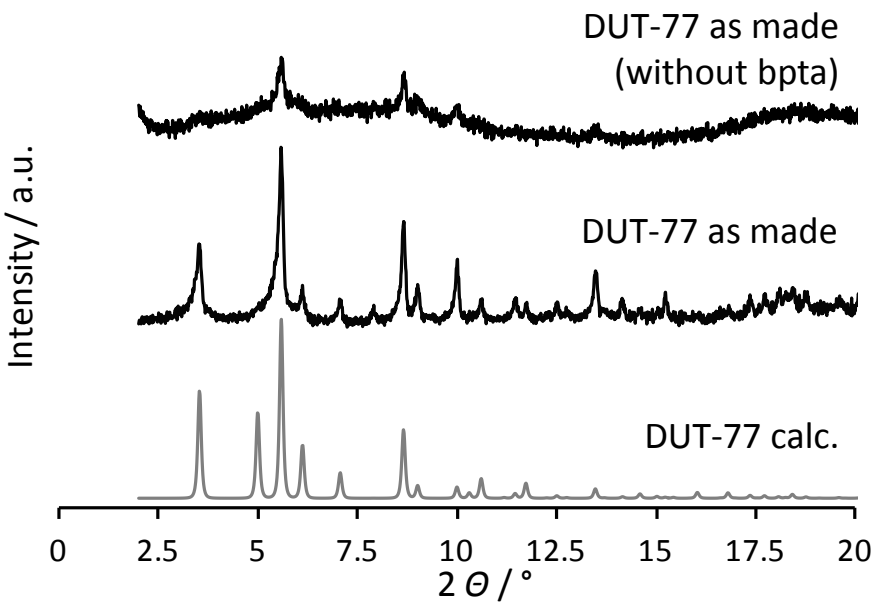

Figure S3. PXRD patterns of DUT-77.

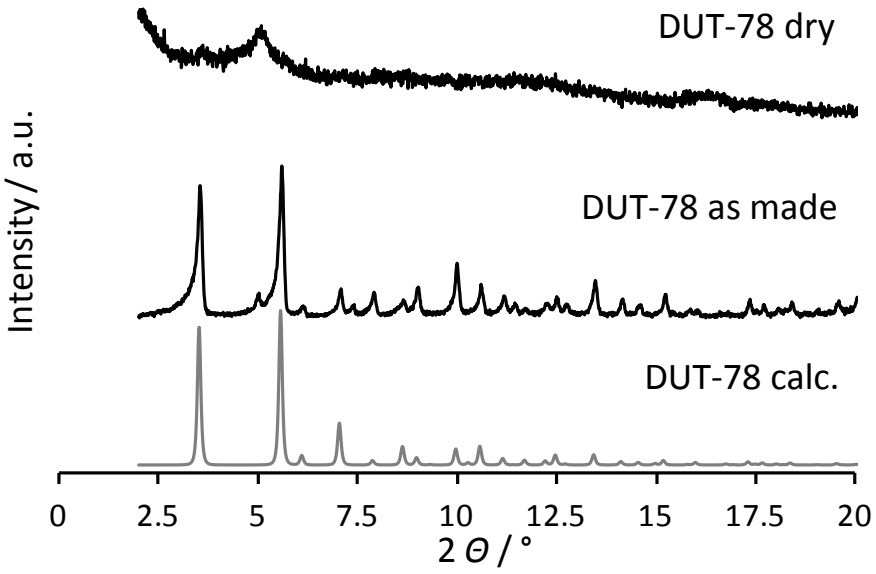

Figure S4. PXRD patterns of DUT-78.

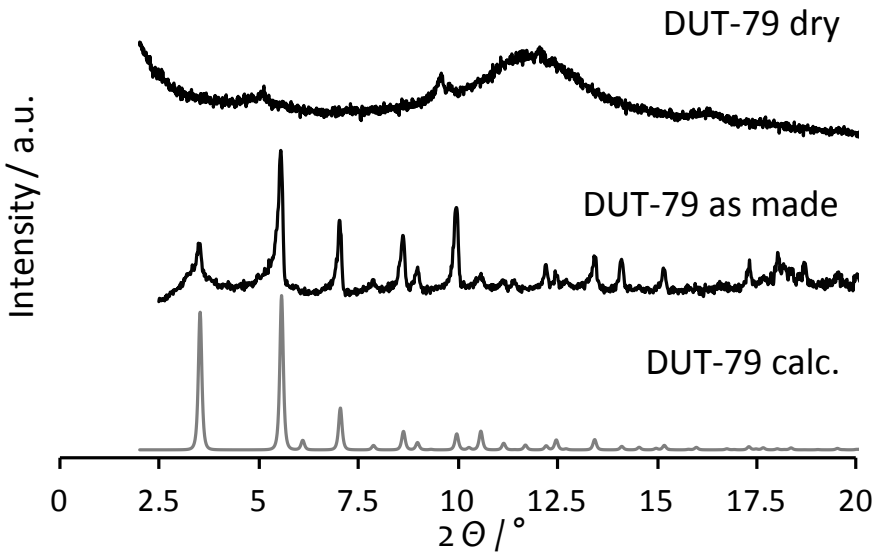

Figure S5. PXRD patterns of DUT-79.

2. Pore size distribution for DUT-63, DUT-64, DUT-77, DUT-78 and DUT-79

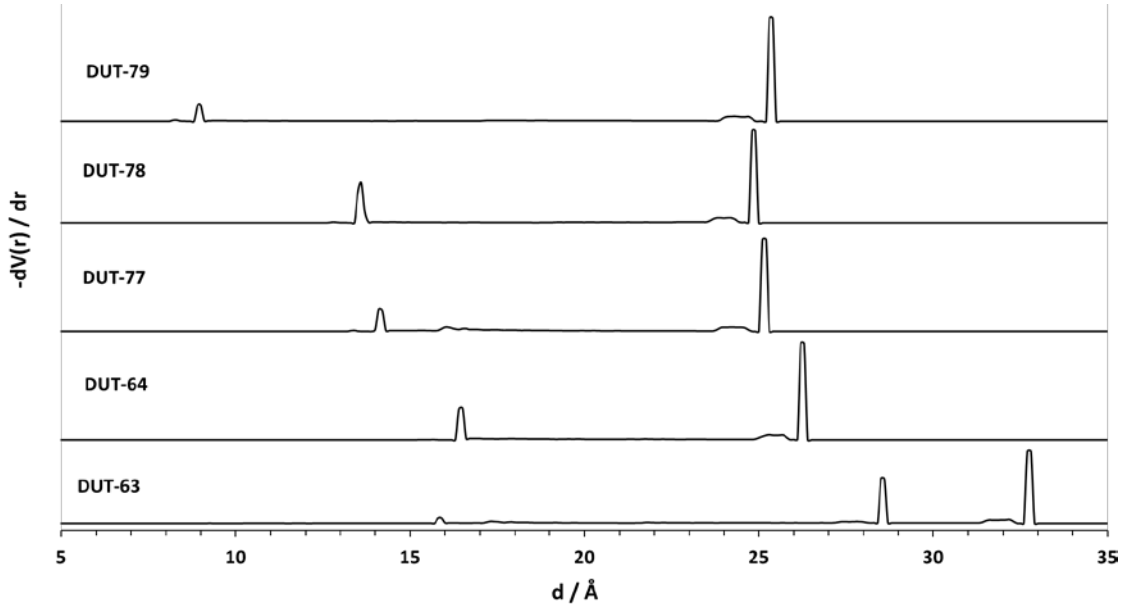

Figure S6. Pore size distribution for DUT-63, DUT-64, DUT-77, DUT-78 and DUT-79.

3. ^{1}H-NMR-spectra of dissolved MOFs

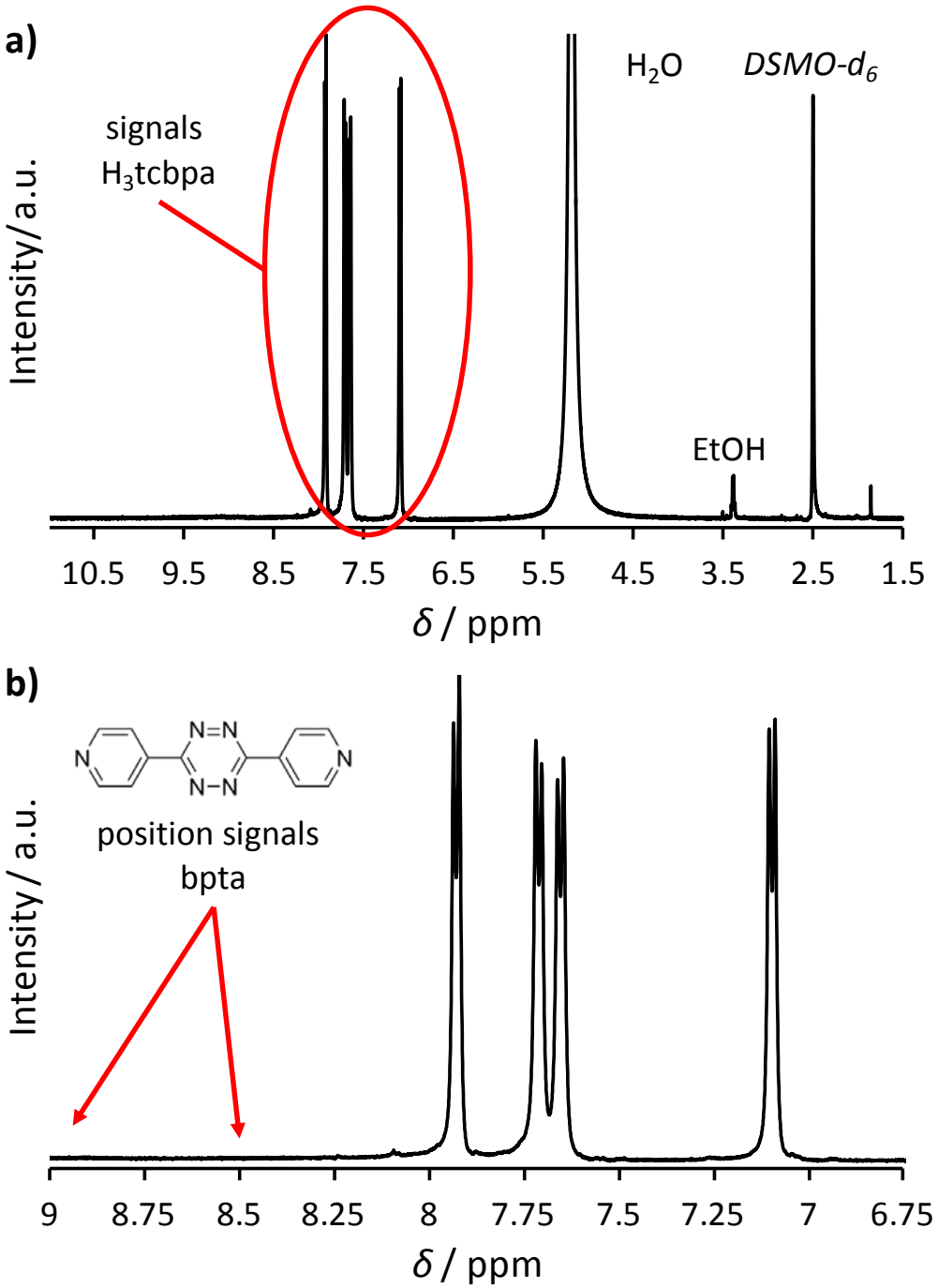

Figure S7. ^{1}H-NMR spectra of dissolved DUT-64 (*DMSO-d_6/DCl*).

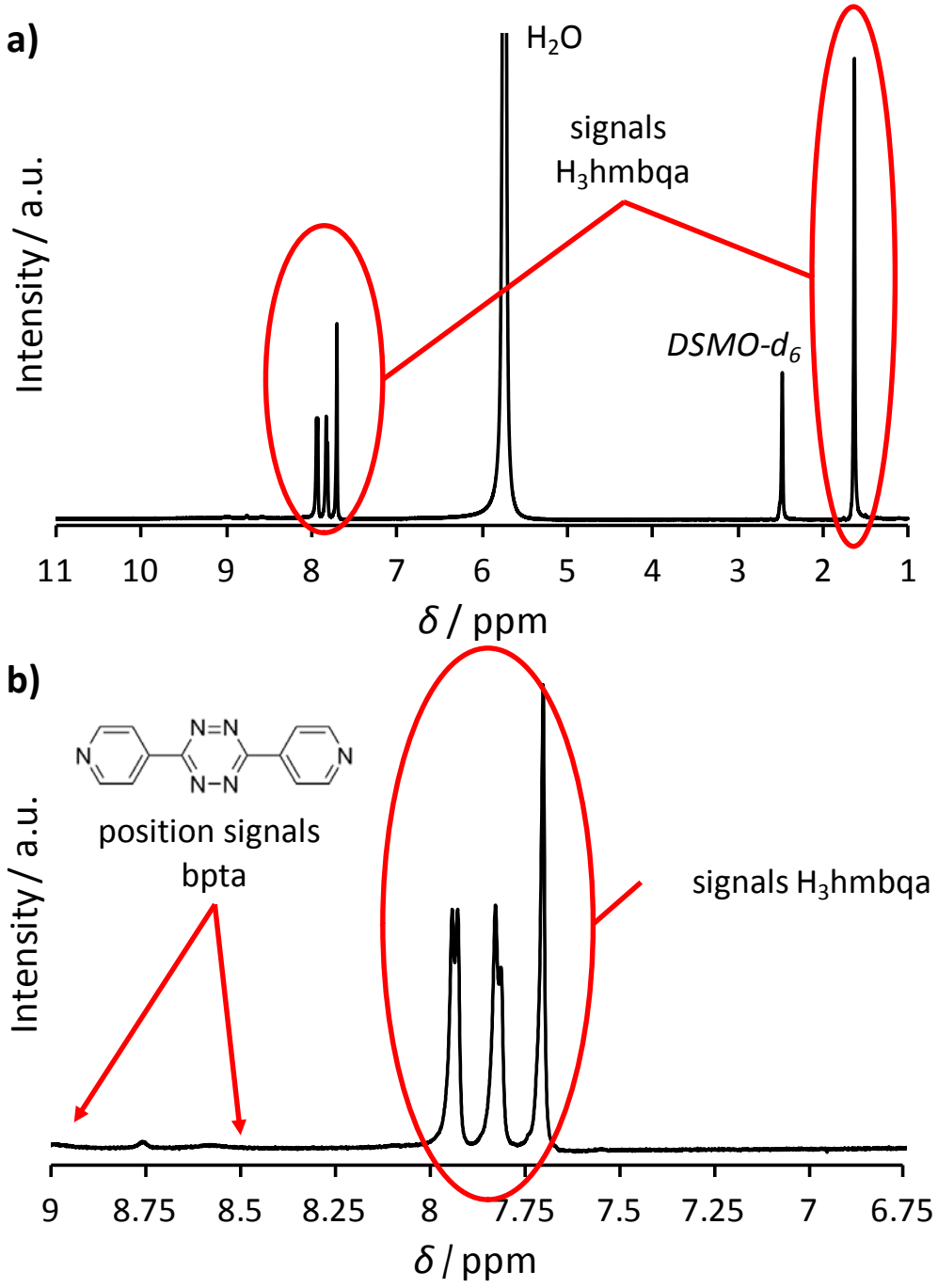

Figure S8. ^{1}H-NMR spectra of dissolved DUT-77 (*DMSO-d_6/DCl*).

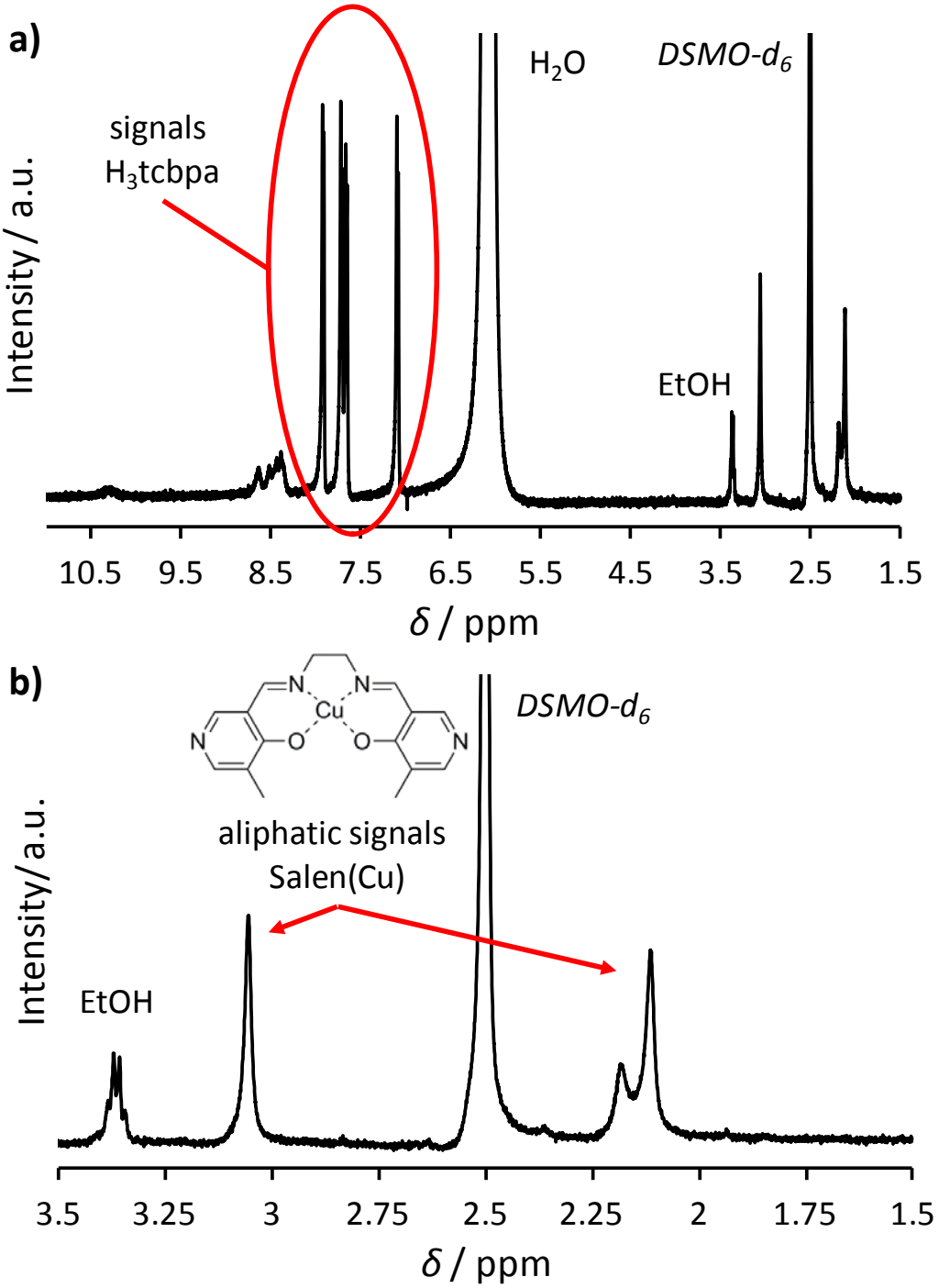

Figure S9. ^{1}H-NMR spectra of dissolved DUT-78 (*DMSO-d_6/DCl*).

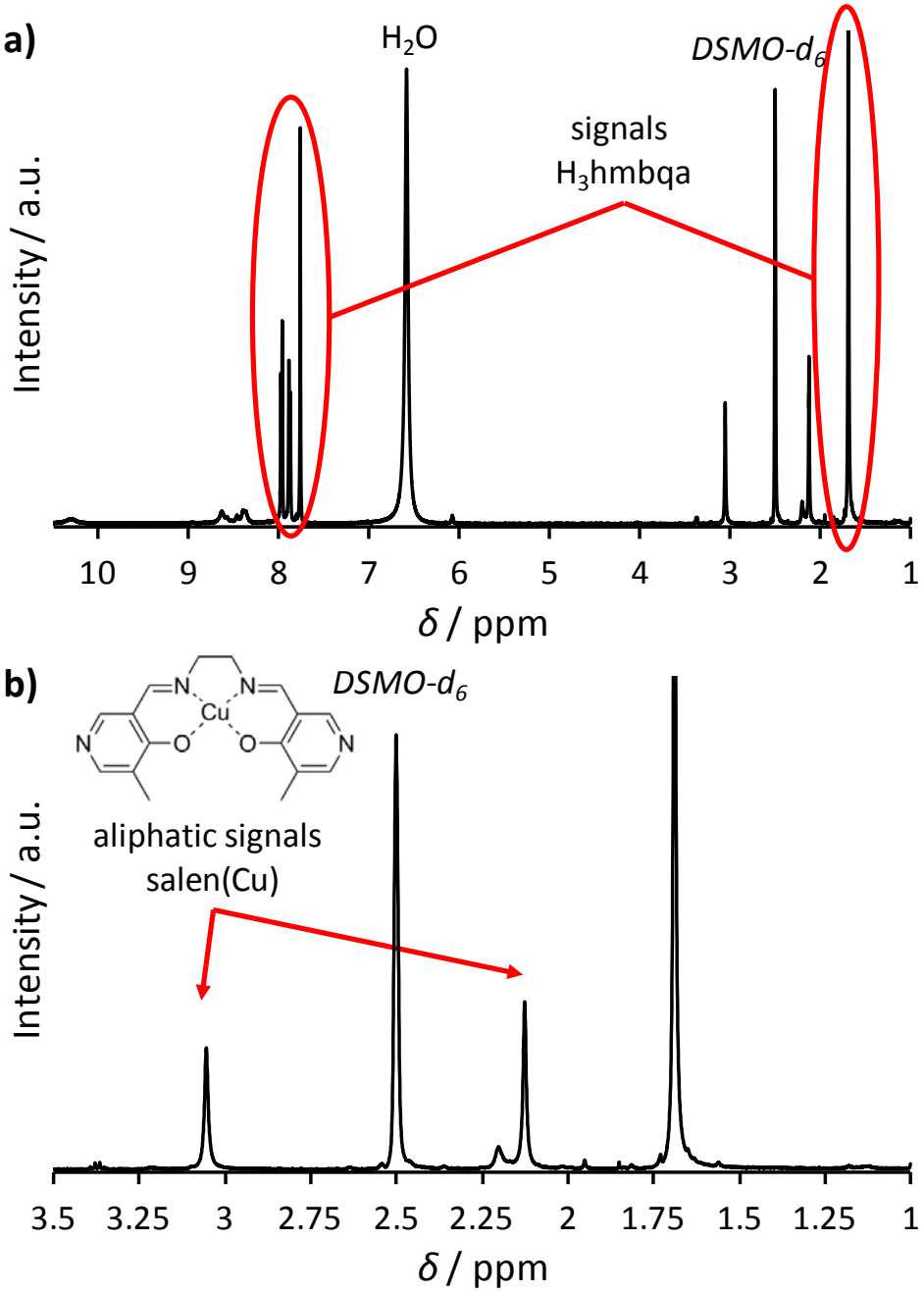

Figure S10. ^{1}H-NMR spectra of dissolved DUT-79 (*DMSO-d_6/DCl*).

4. Nitrogen physisorption at 77K

Nitrogen physisorption experiments were performed at 77 K up to 1 bar on Belsorb-max apparatus (Microtrac-BEL, Japan). In all isotherms, the solid symbols represent adsorption points and the empty symbols represent desorption points.

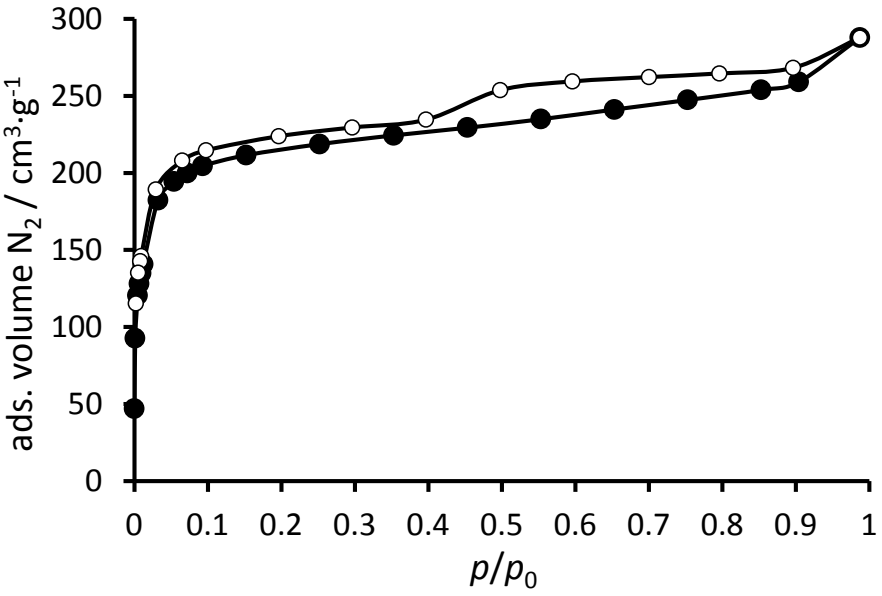

Figure S11. Nitrogen physisorption isotherm for DUT-64.

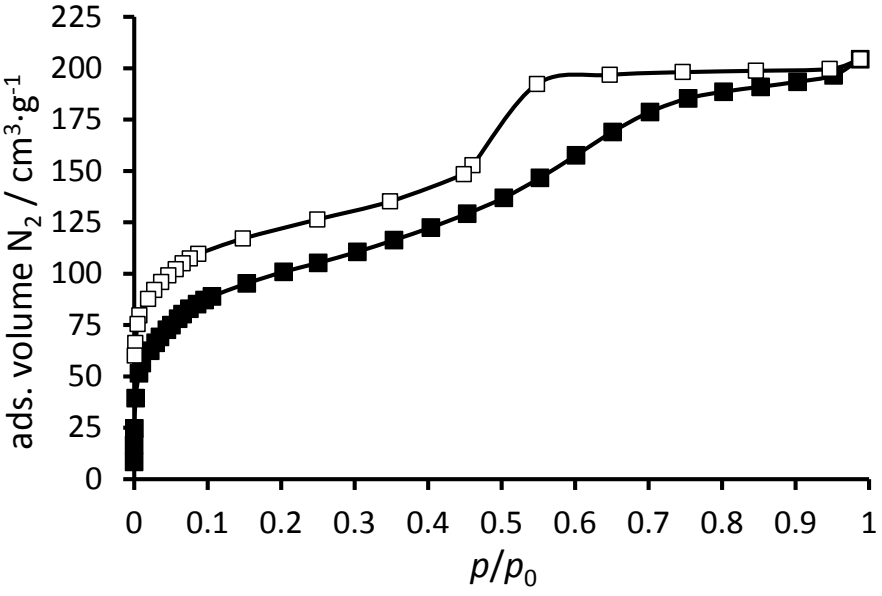

Figure S12. Nitrogen physisorption isotherm for DUT-77.

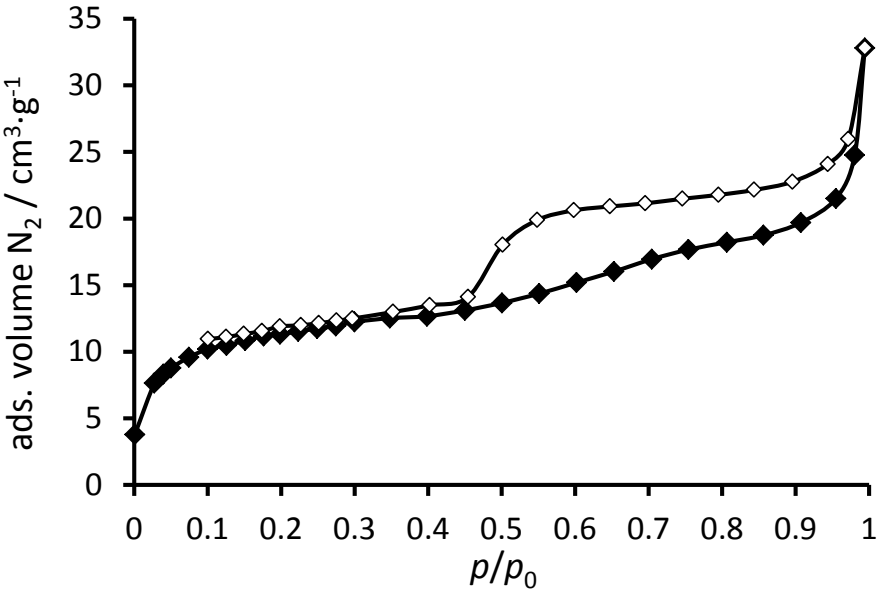

Figure S13**.** Nitrogen physisorption isotherm for DUT-78.

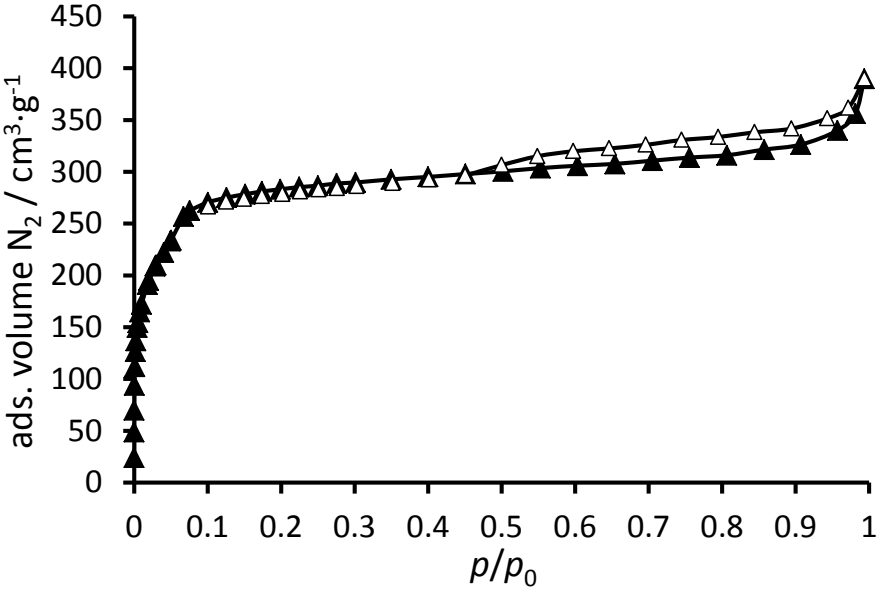

Figure S14. Nitrogen physisorption isotherm for DUT-79.

5. Experimental setup used for cyclisation of diethyl-2-((propylamino)methylene)malonate

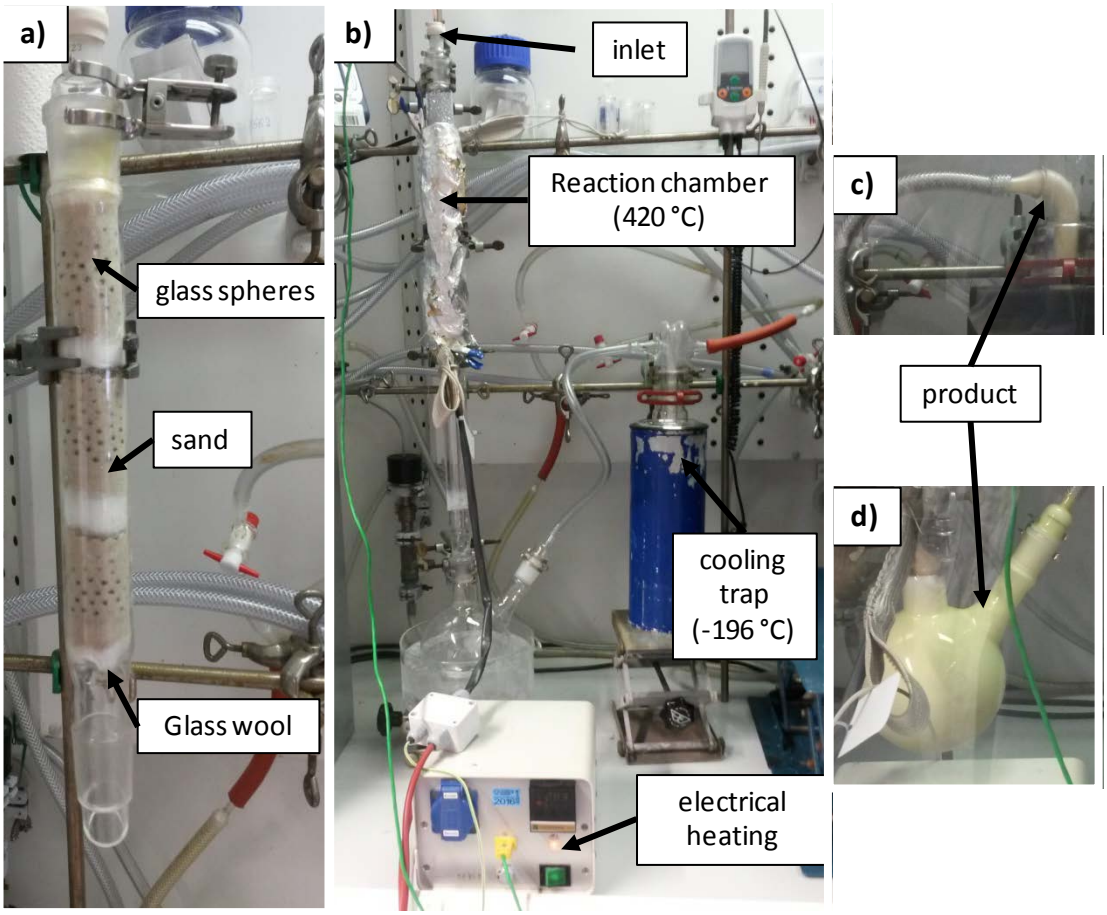

Figure S15. Reaction column (a), set up for cyclisation (b) and product (c and d).

6. Crystallographic data

Table S1. Experimental data for single crystal X-ray diffraction study of DUT-63, DUT-64, DUT-77, DUT-78, and DUT-79.

	DUT-63	DUT-64	DUT-77	DUT-78	DUT-79
Empirical formula	$C_{78}H_{48}Cu_3N_2O_{15}$	$C_{52}H_{32}Cu_2N_{1.33}O_{10}$	$C_{64}H_{48}Cu_2N_{1.33}O_{10}$	$C_{68}H_{48}Cu_3N_{5.33}O_{10}$	$C_{82}H_{64}Cu_3N_{7.33}O_{10}$
Formula weight	1443.80	962.53	1122.78	1290.40	1502.69
Temperature, K	296	296	296	296	296
Crystal size, mm	0.20x0.20x0.20	0.08x0.08x0.08	0.07x0.07x0.07	0.05x0.05x0.05	0.03x0.03x0.02
Crystal system, space group	Cubic, *F*432	Cubic, $Pm\bar{3}n$	Cubic, $Pm\bar{3}n$	Cubic, $Pm\bar{3}n$	Cubic, $Pm\bar{3}n$
Unit cell dimensions, Å	a = 60.910(7)	a = 35.490(4)	a = 35.400(4)	a = 35.510(4)	a = 35.490(4)
Volume, Å^3	225978(45)	44701(15)	44362(15)	44777(16)	44701(15)
Z	16	6	6	6	6
Calculated density, g/cm^3	0.170	0.215	0.252	0.287	0.335
μ, mm^{-1}	0.217	0.275	0.288	0.418	0.423
T_{min}, T_{max}	0.945, 0.945	0.978, 0.978	0.980, 0.980	0.979, 0.979	0.987, 0.992
ϑ range, deg	2.6 – 25.0	1.4 – 23.5	1.4 – 23.1	1.0 – 28.1	1.0 – 22.5
Radiation wavelength, *Å*	0.88561	0.88561	0.89499	0.89499	0.89499
Limiting indices	$0 \le h \le 33$ $2 \le k \le 58$ $0 \le l \le 57$	$0 \le h \le 18$ $1 \le k \le 32$ $0 \le l \le 31$	$-30 \le h \le 28$ $-31 \le k \le 28$ $-31 \le l \le 31$	$-37 \le h \le 20$ $-37 \le k \le 37$ $-37 \le l \le 29$	$-30 \le h \le 27$ $-30 \le k \le 28$ $-25 \le l \le 7$
Reflections collected / unique	8853 / 8549	5818 / 3055	102331 / 2666	94817 / 4827	23231 / 2632
R(*int*)	0.1282	0.0203	0.1150	0.1076	0.2472
Data / parameters	8549 / 125	3055 / 83	2666 / 95	4827 / 127	2362 / 141
Flack parameter	0.278(13)	-	-	-	-
SU (max) last refinement cycle	0.000	0.000	0.000	0.000	0.000
SQUEEZEd electrons / unit cell	29745	6923	9958	10859	6972
GooF on F^2 [$I>2\sigma(I)$]	0.650	0.827	1.131	1.06	1.135
GooF on F^2 (all data)	0.658	0.843	1.217	1.14	1.205
R^1 [$I>2\sigma(I)$]	0.0540	0.0771	0.1101	0.0673	0.0998
wR^2 [$I>2\sigma(I)$]	0.1205	0.2502	0.3135	0.1999	0.2748
R^1 (all data)	0.1126	0.1268	0.1351	0.1009	0.1558
wR^2 (all data)	0.1324	0.2861	0.3458	0.2455	0.3243
Largest diff. peak / hole, *e*Å^{-3}	0.208 / -0.191	0.110 / -0.249	0.262 / -0.250	0.37 / -0.41	0.53 / -0.63