Electronic Supplementary Material (ESI) for Dalton Transactions.
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Supporting information for:

Formation of metal-organic frameworks utilising a mechanically interlocked, hexadentate linker containing a tetra-carboxylate axle and a bis(pyridine) wheel

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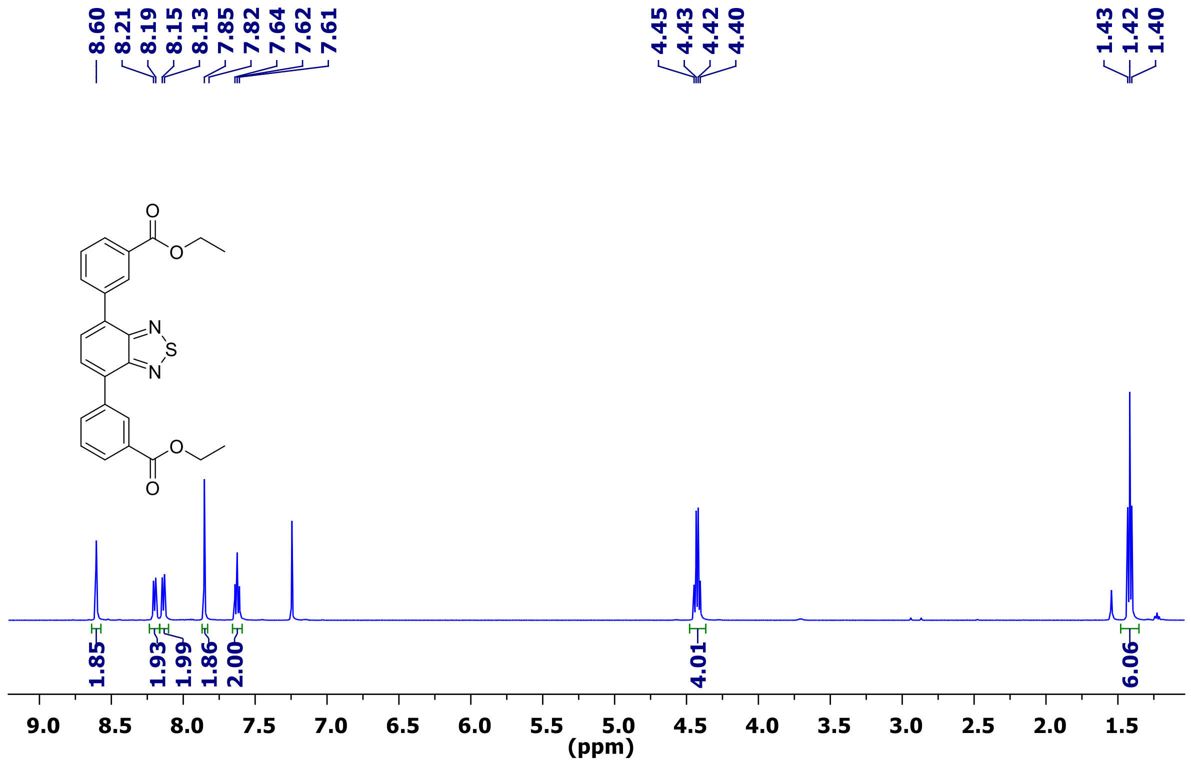
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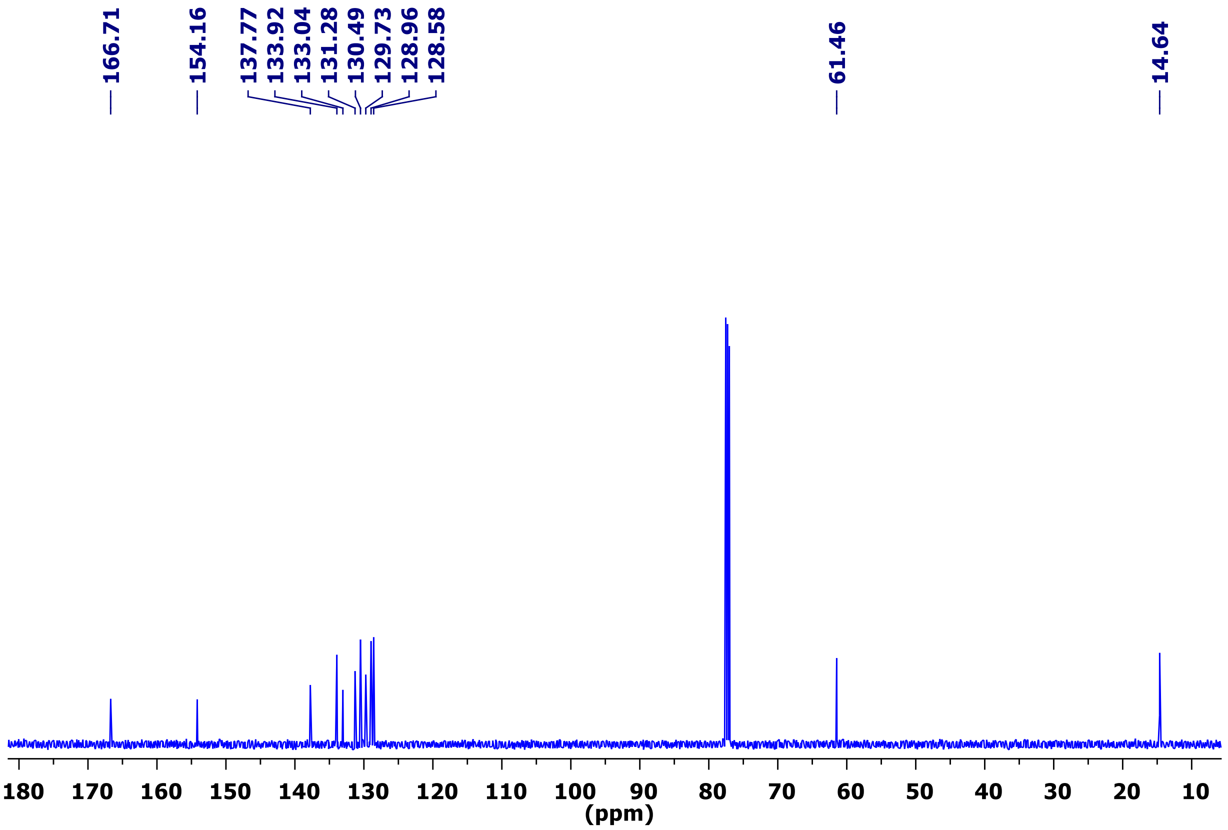
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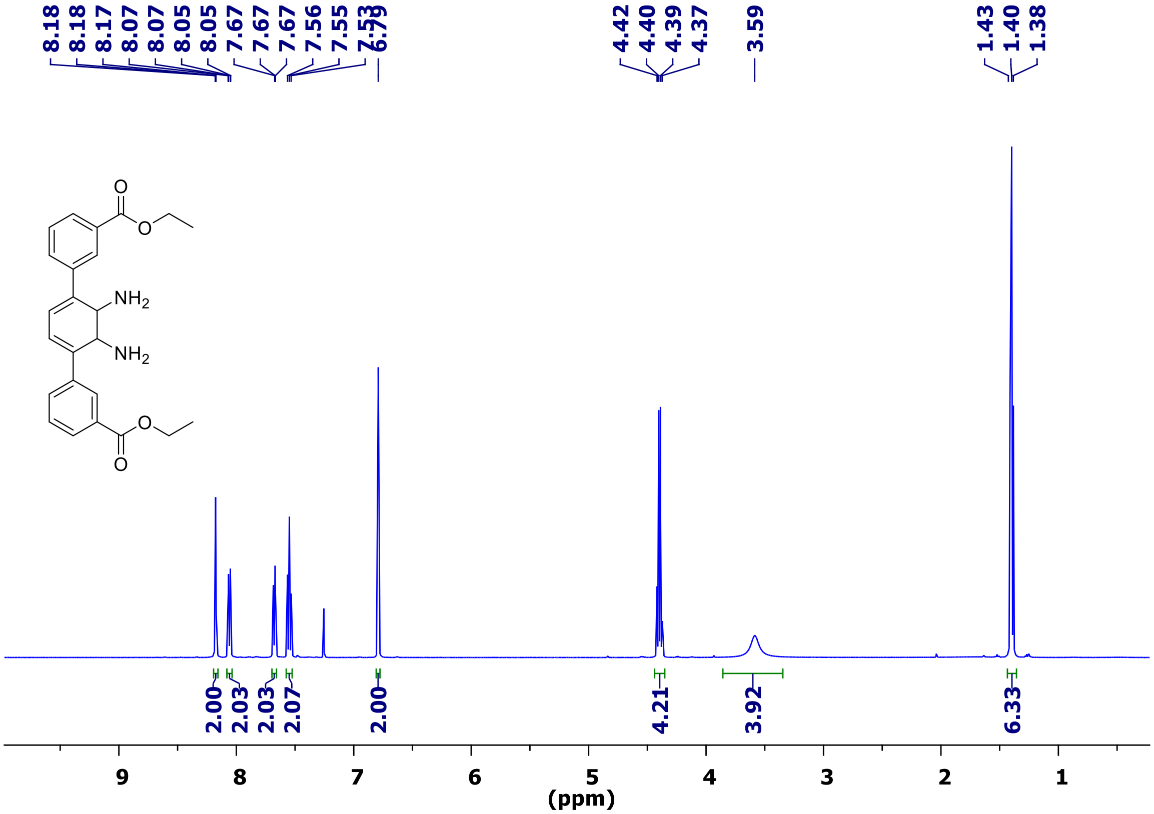
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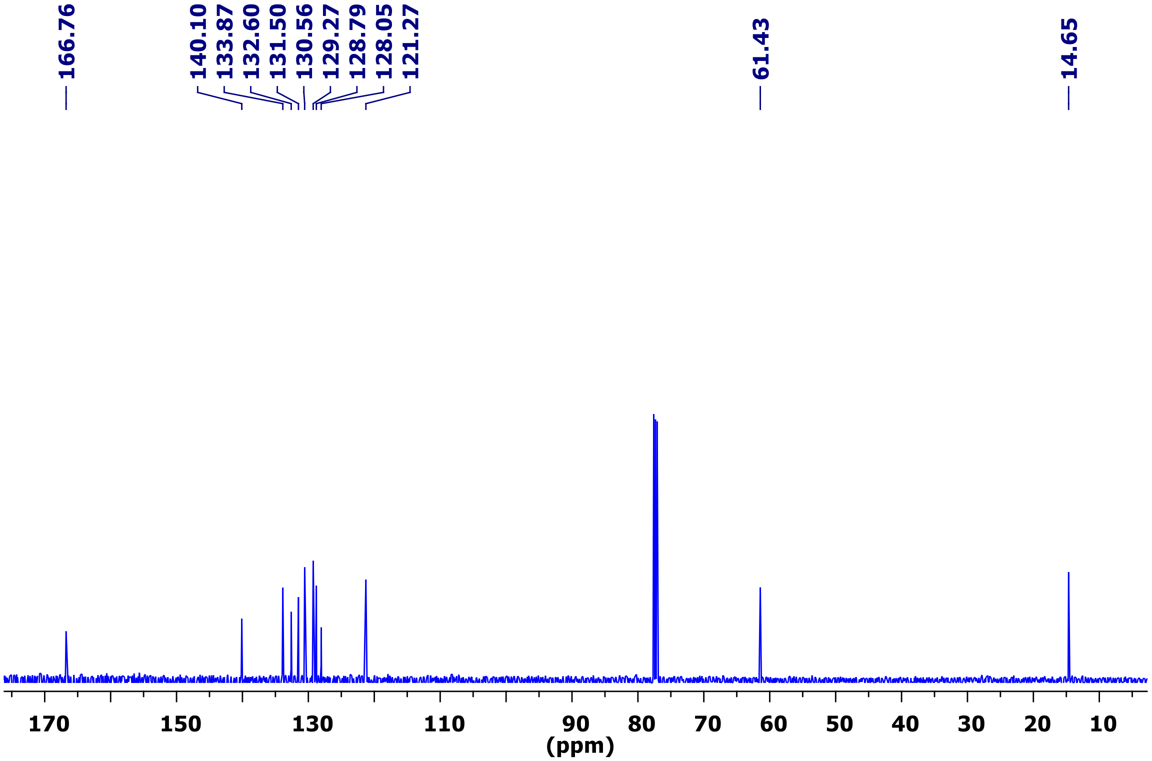
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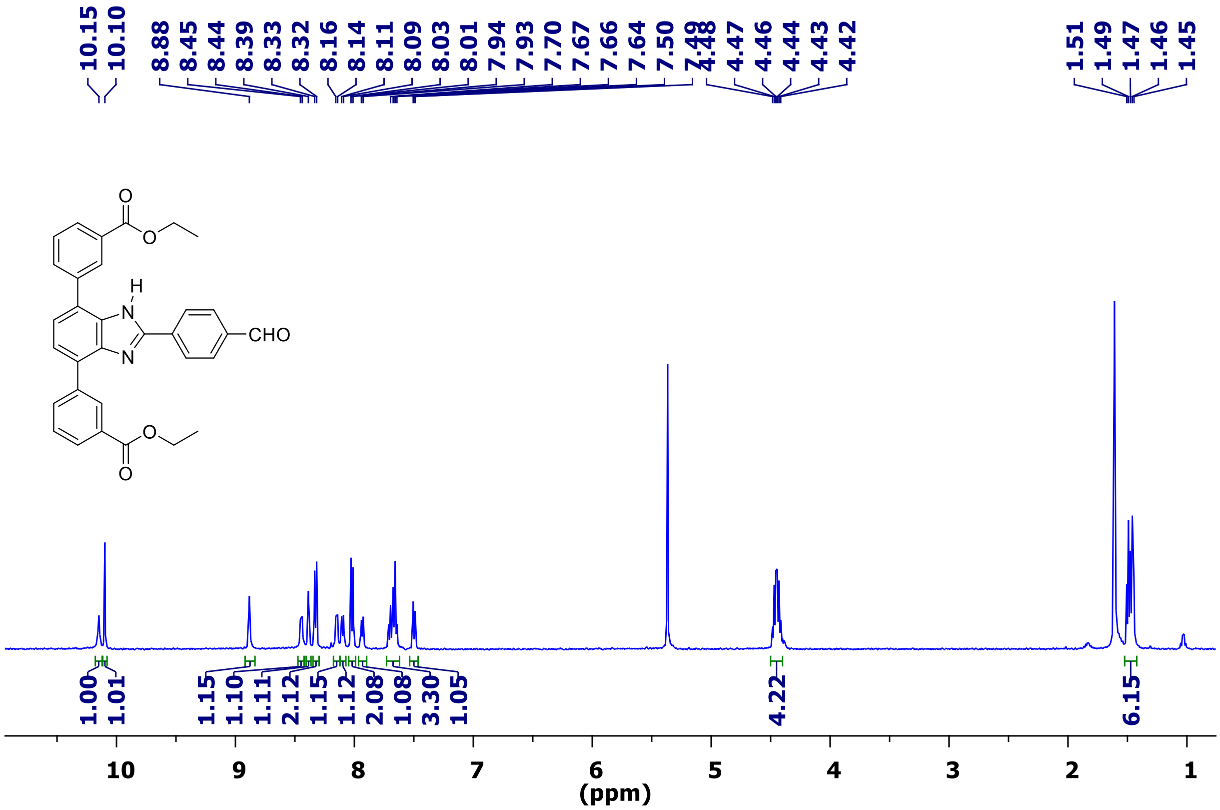
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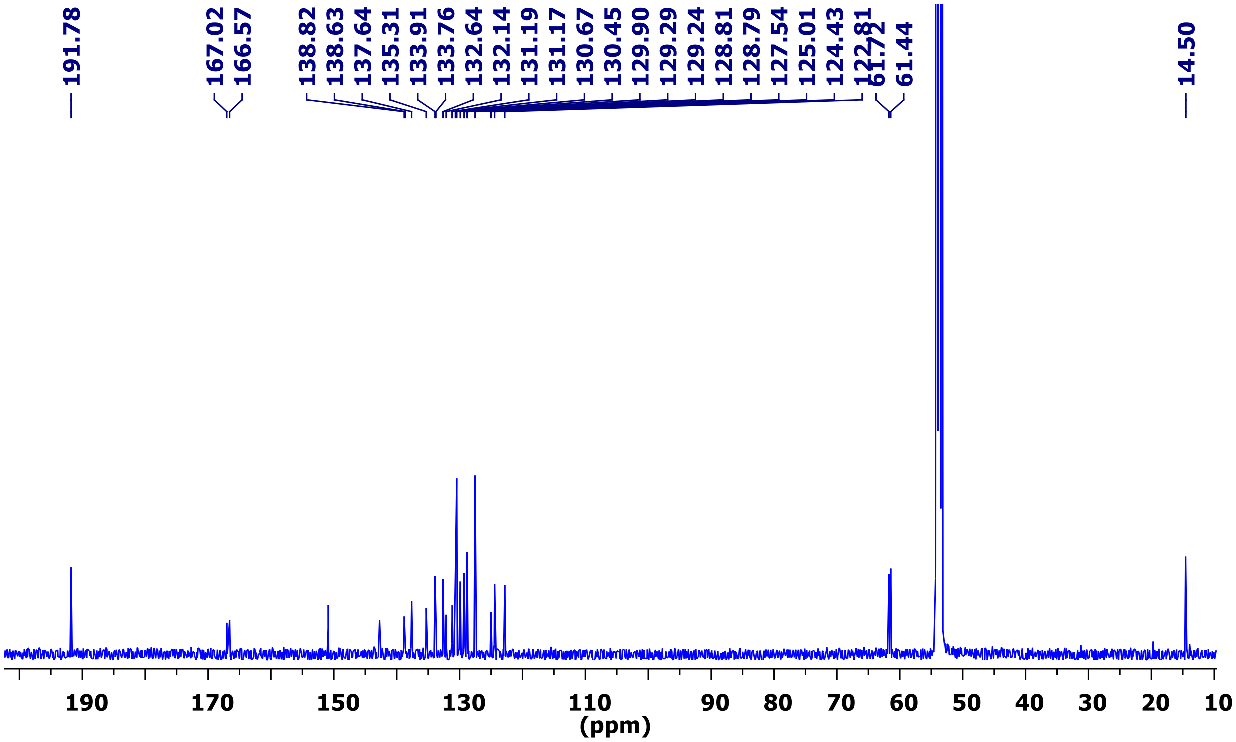
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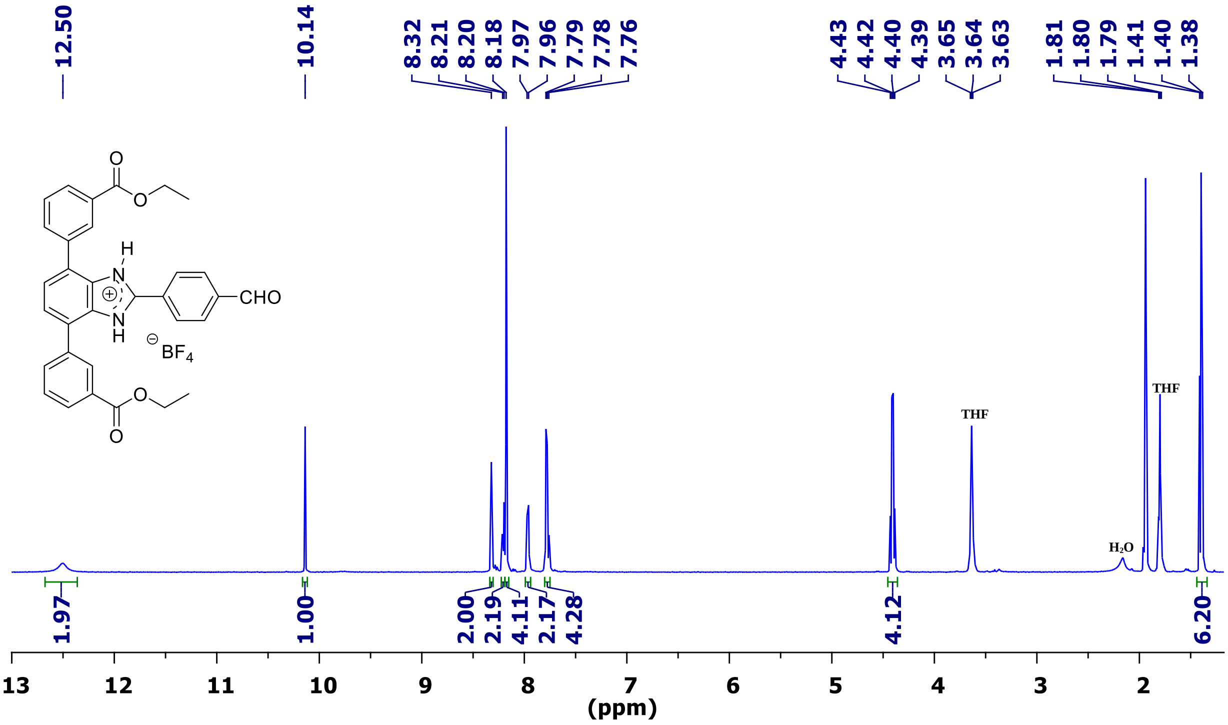
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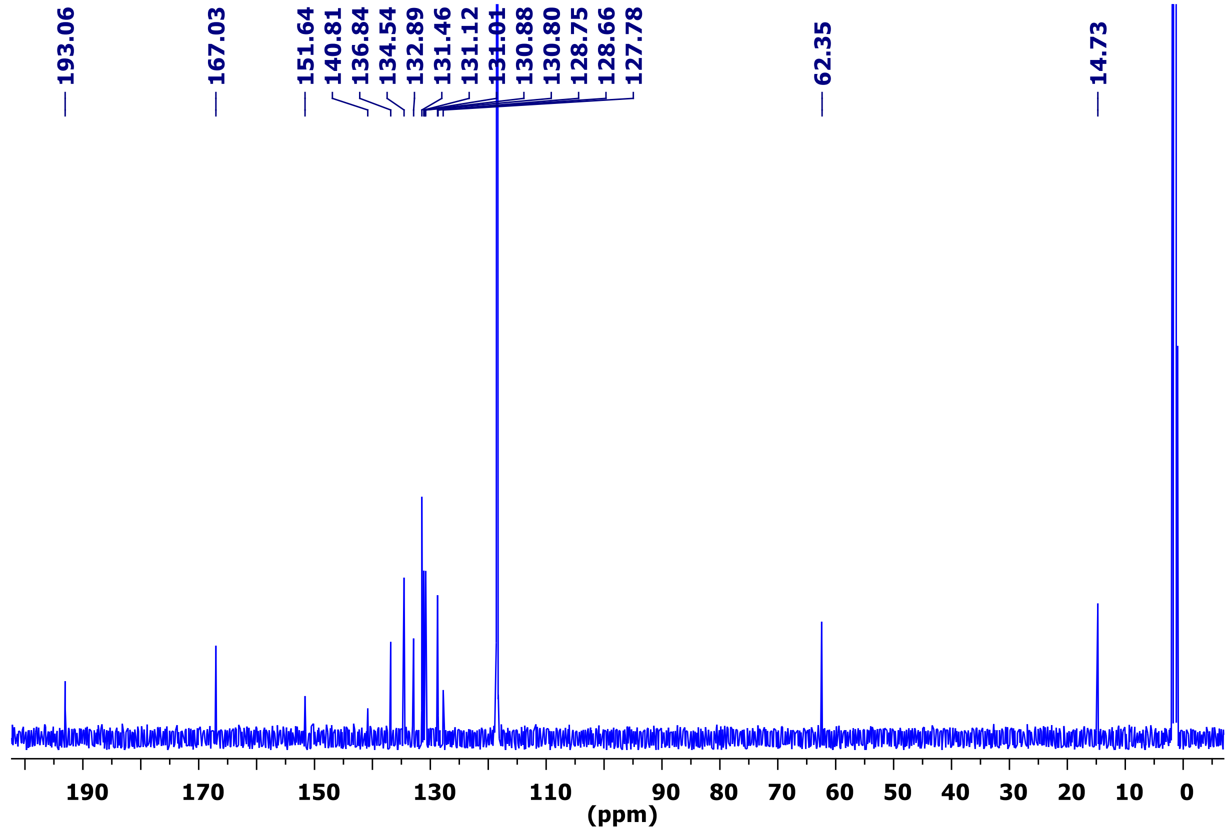
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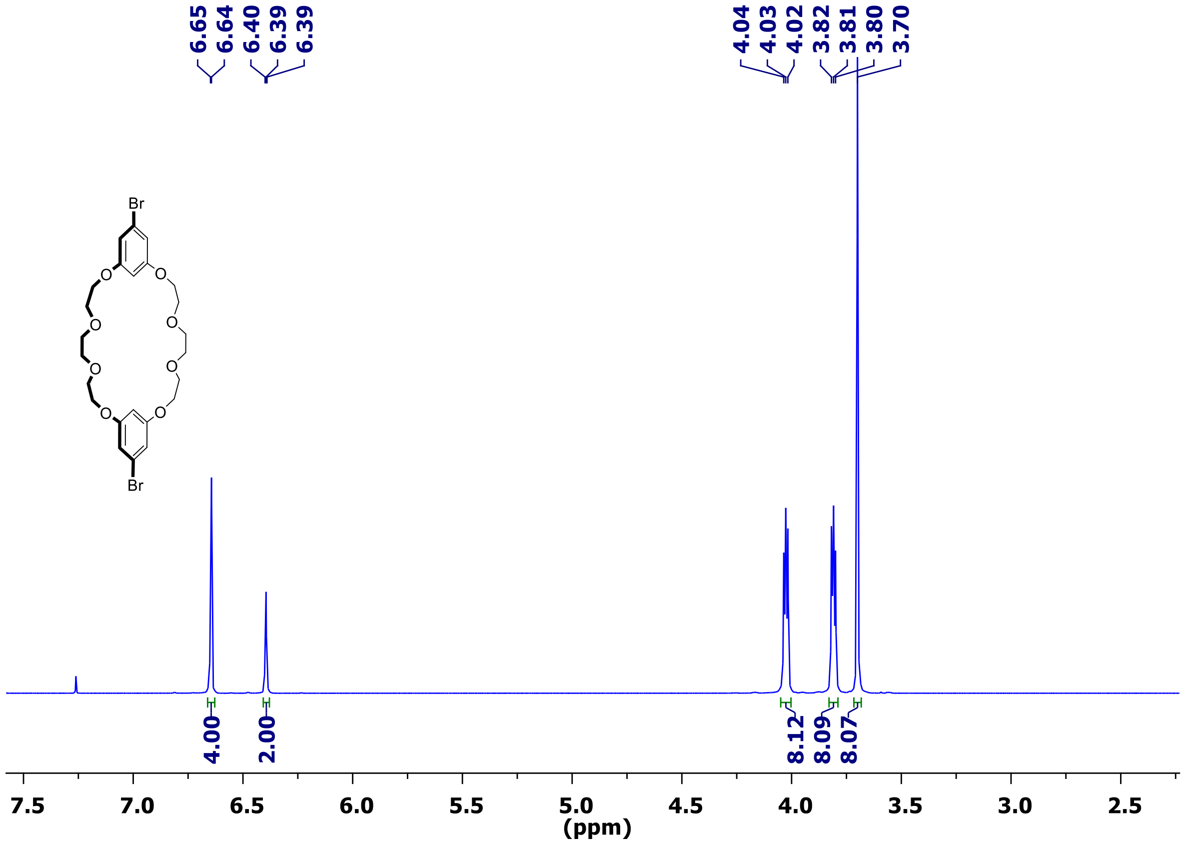
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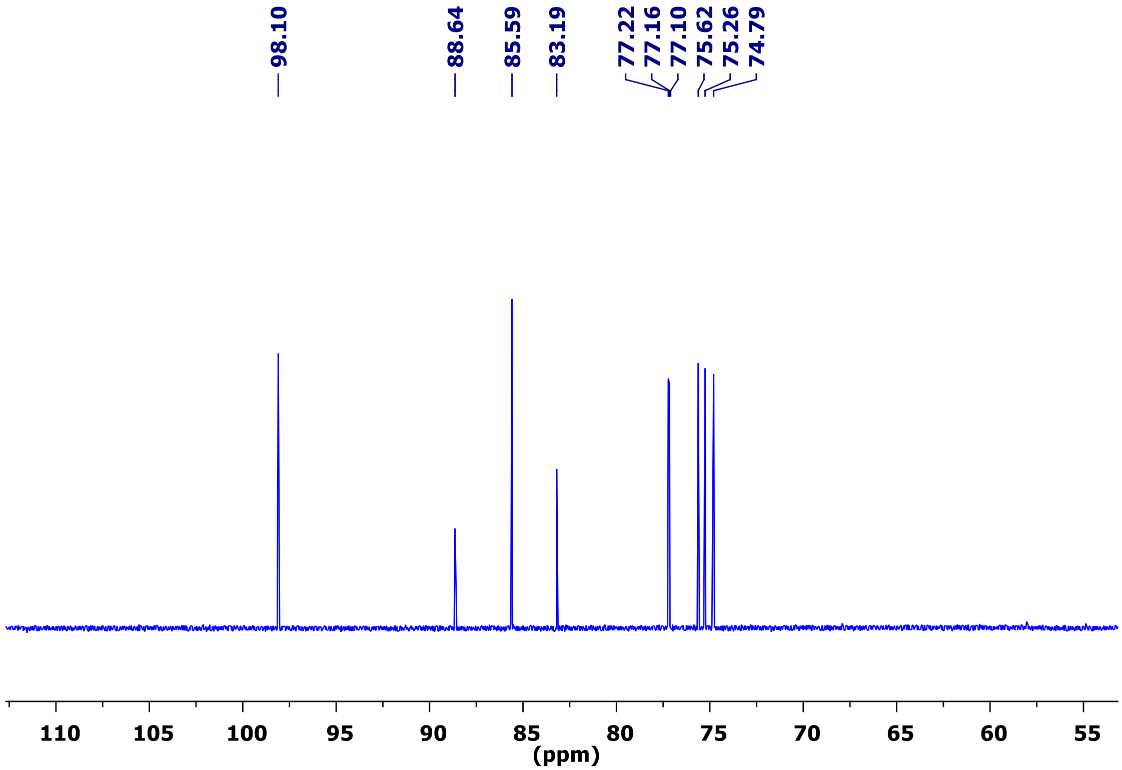
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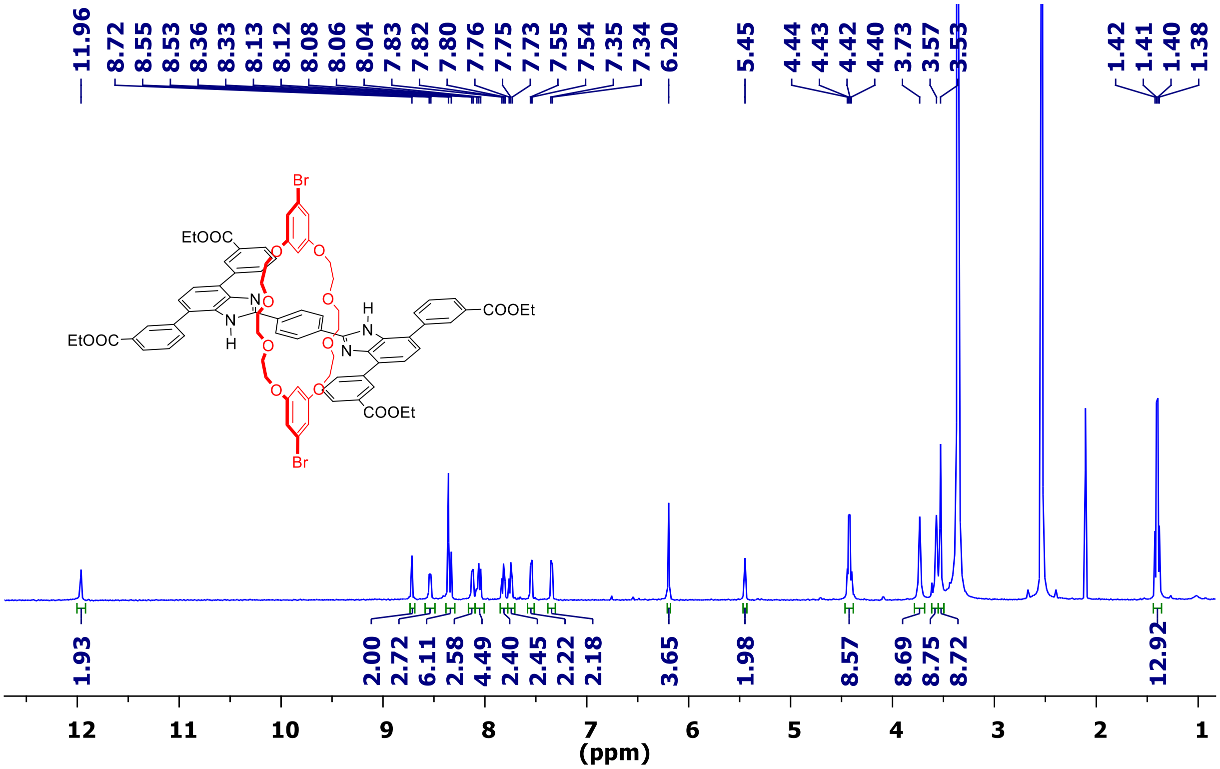
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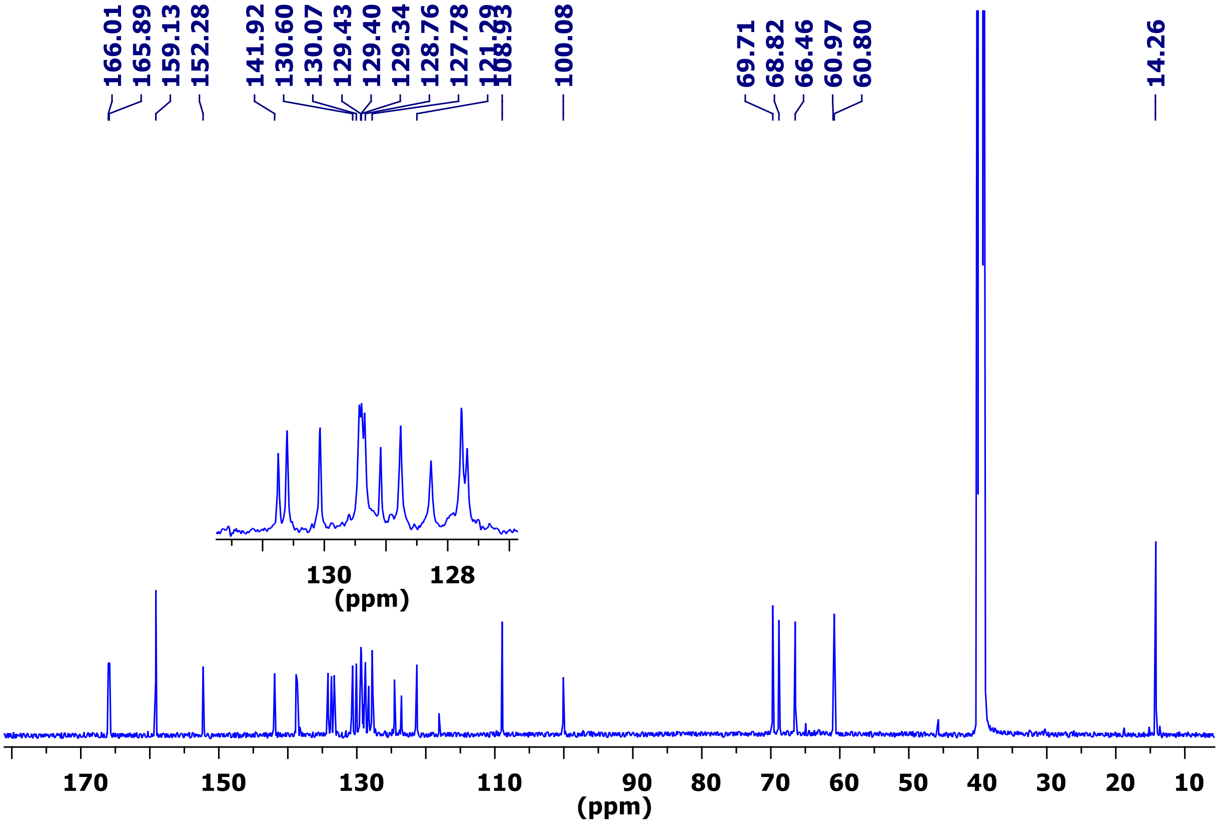
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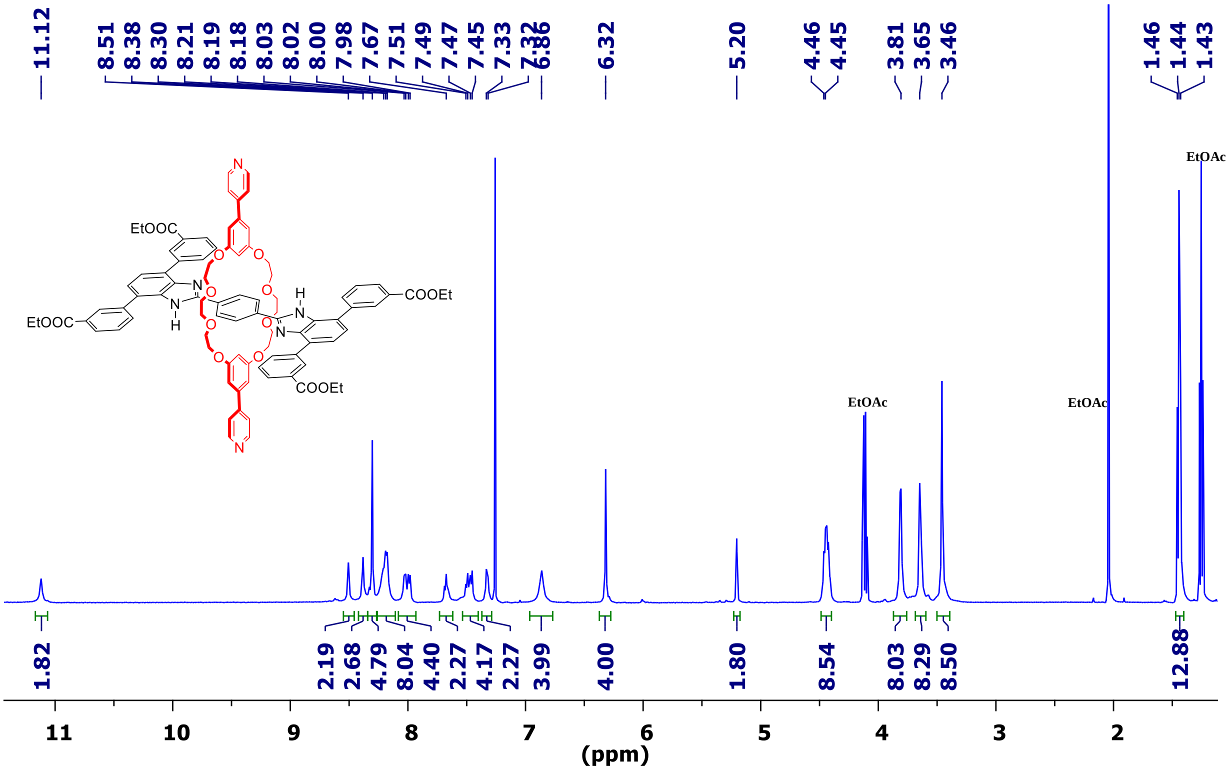
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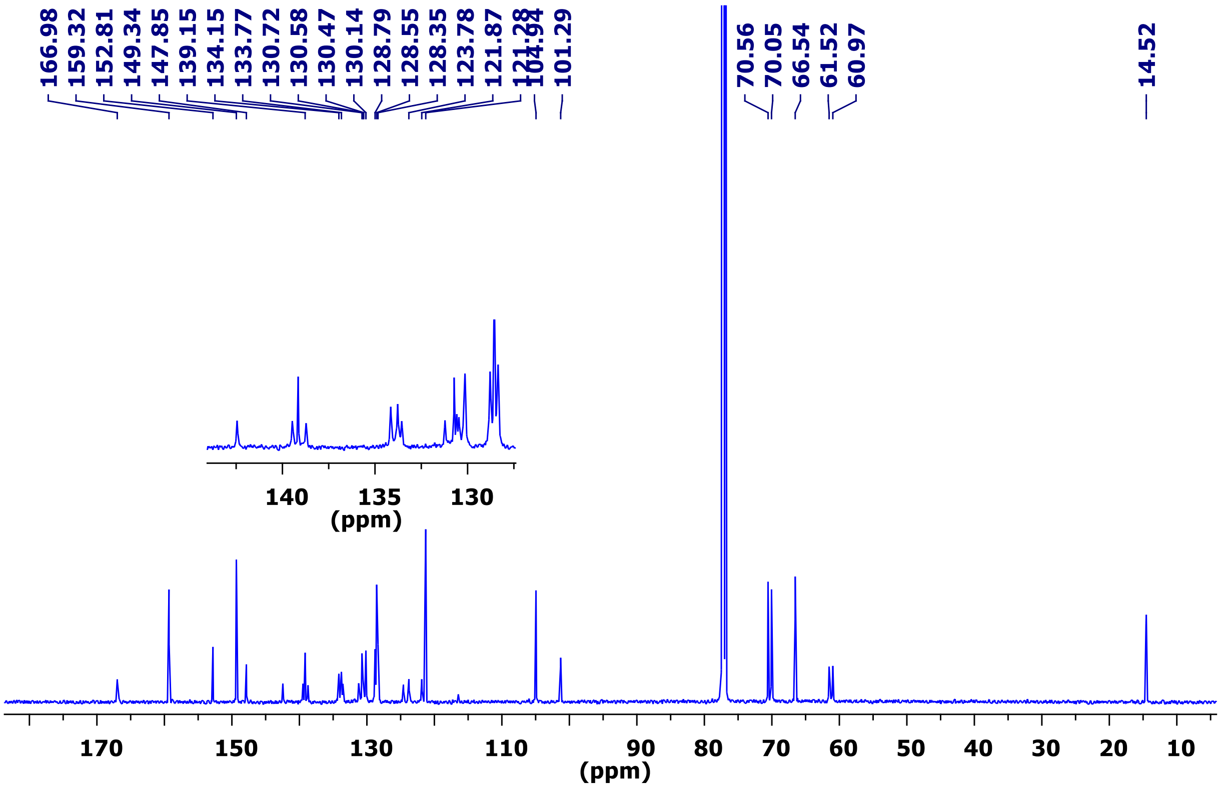
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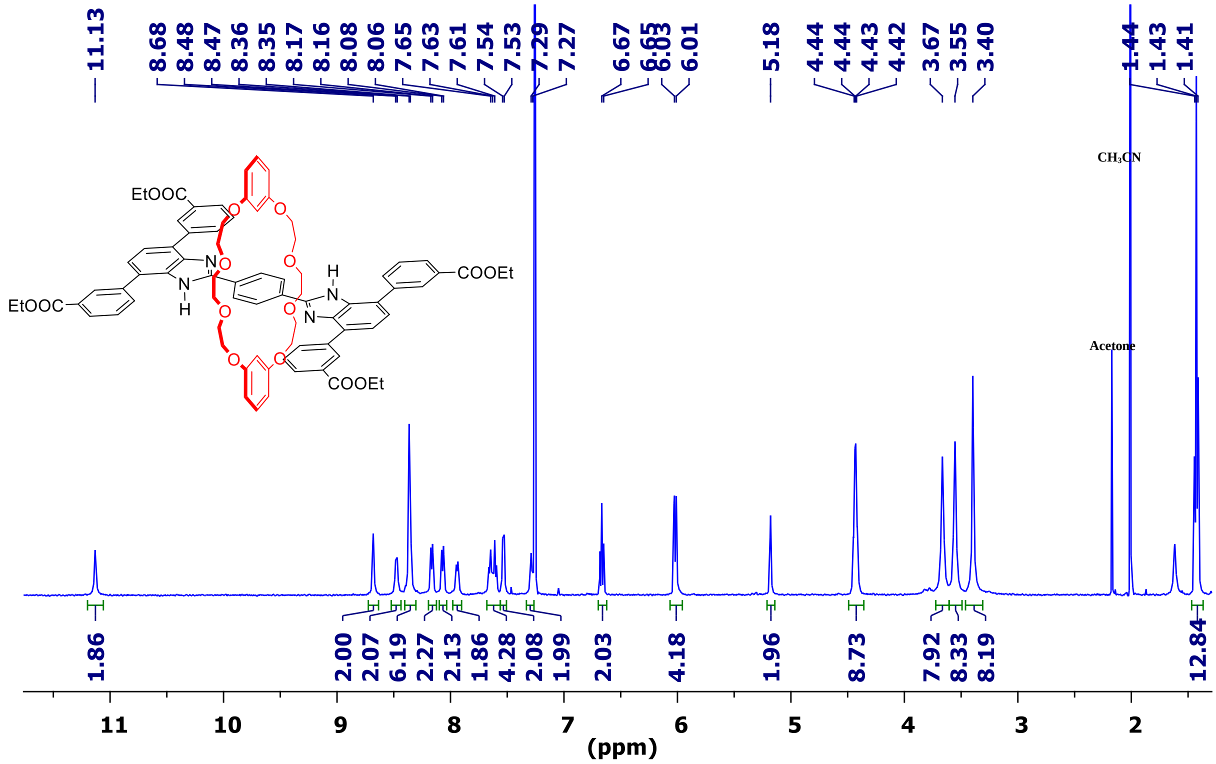
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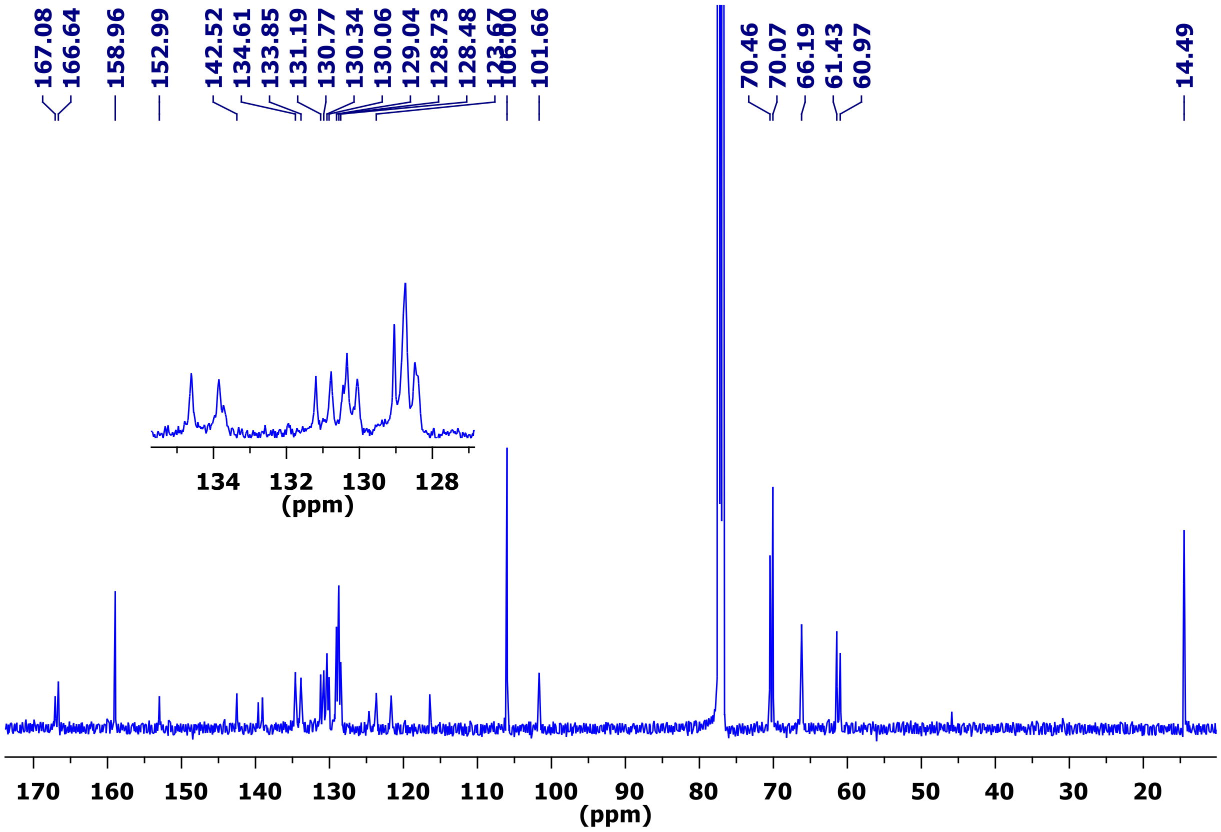
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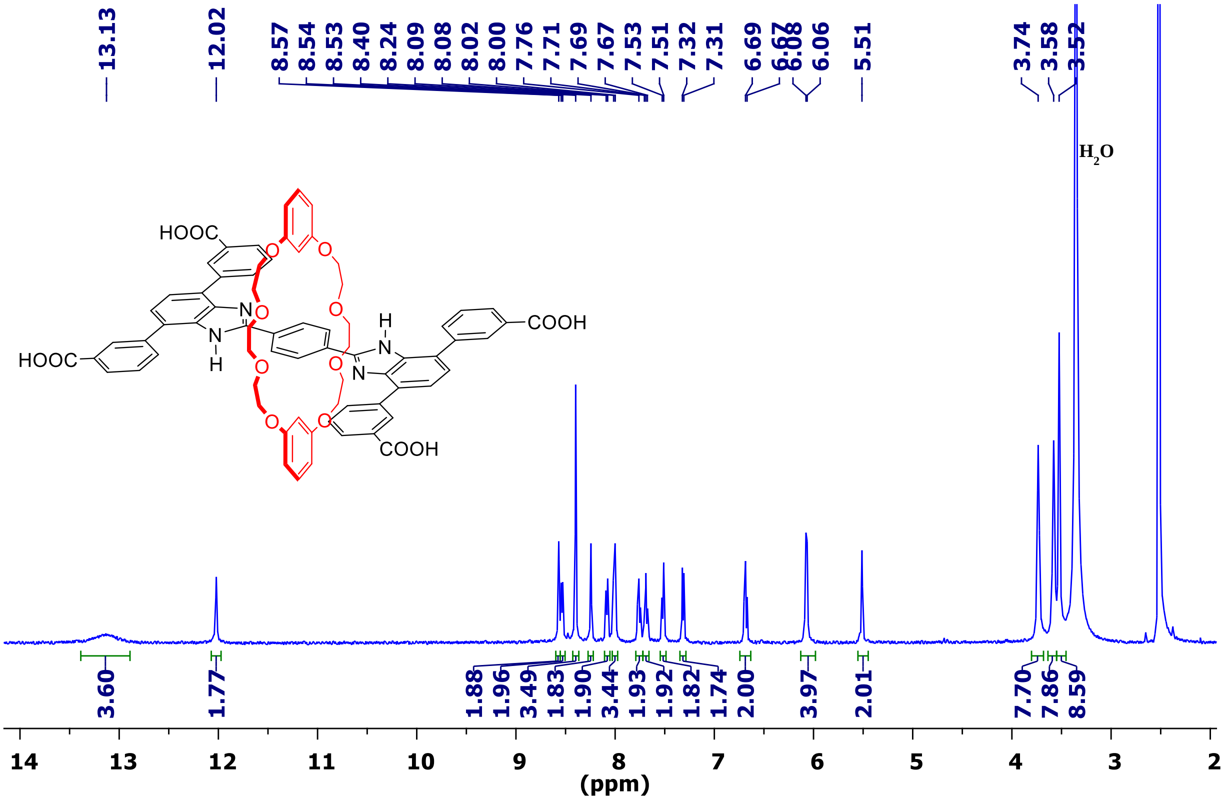
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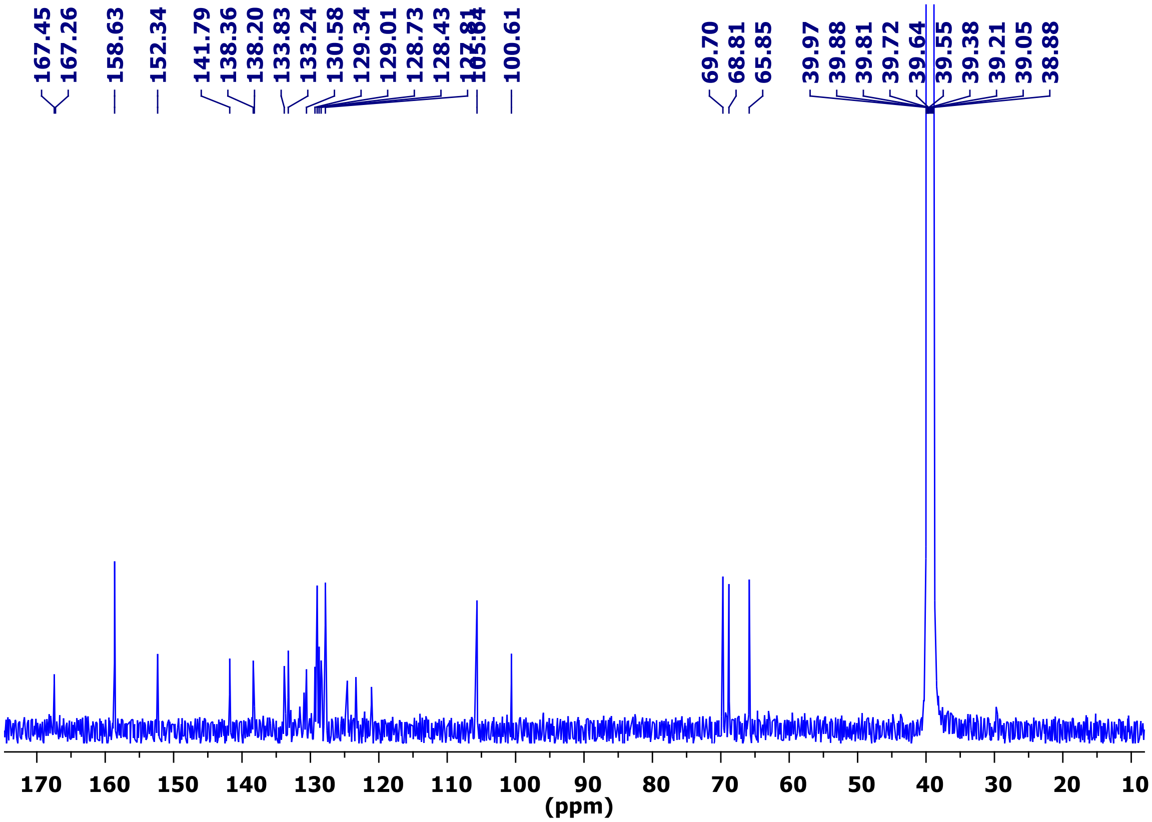
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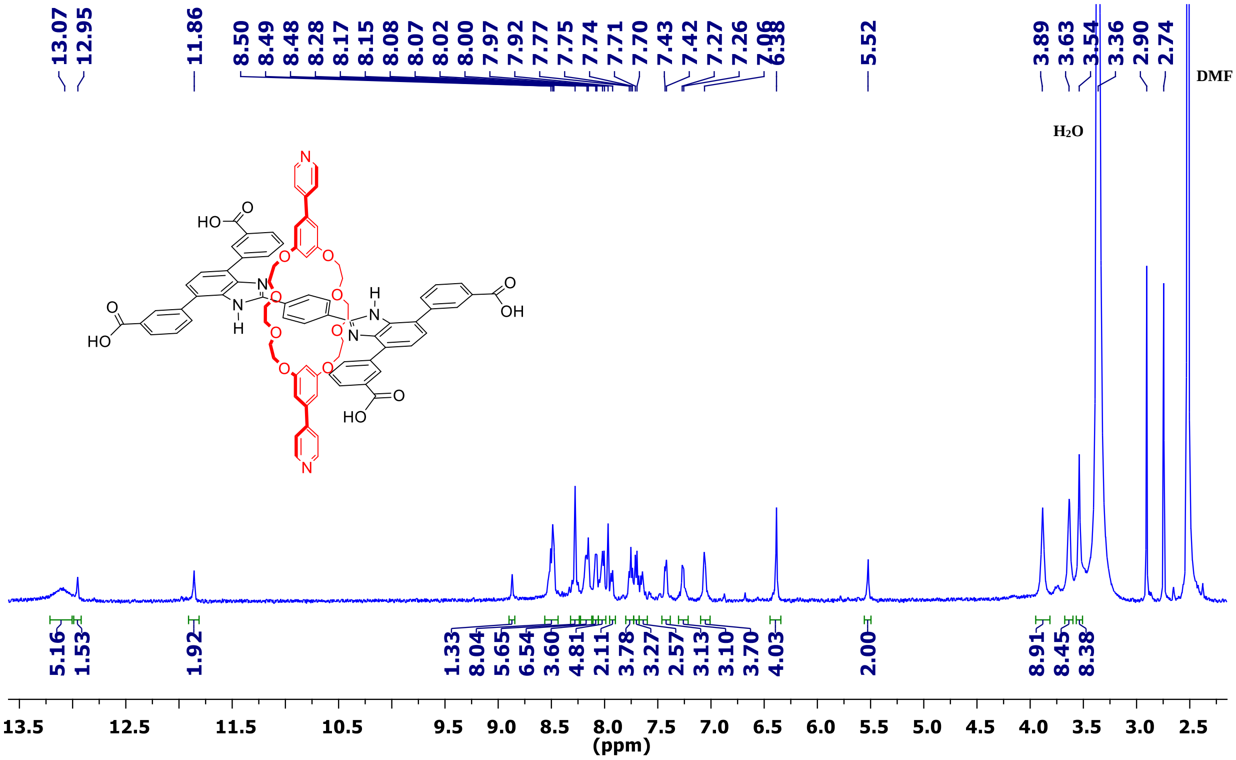
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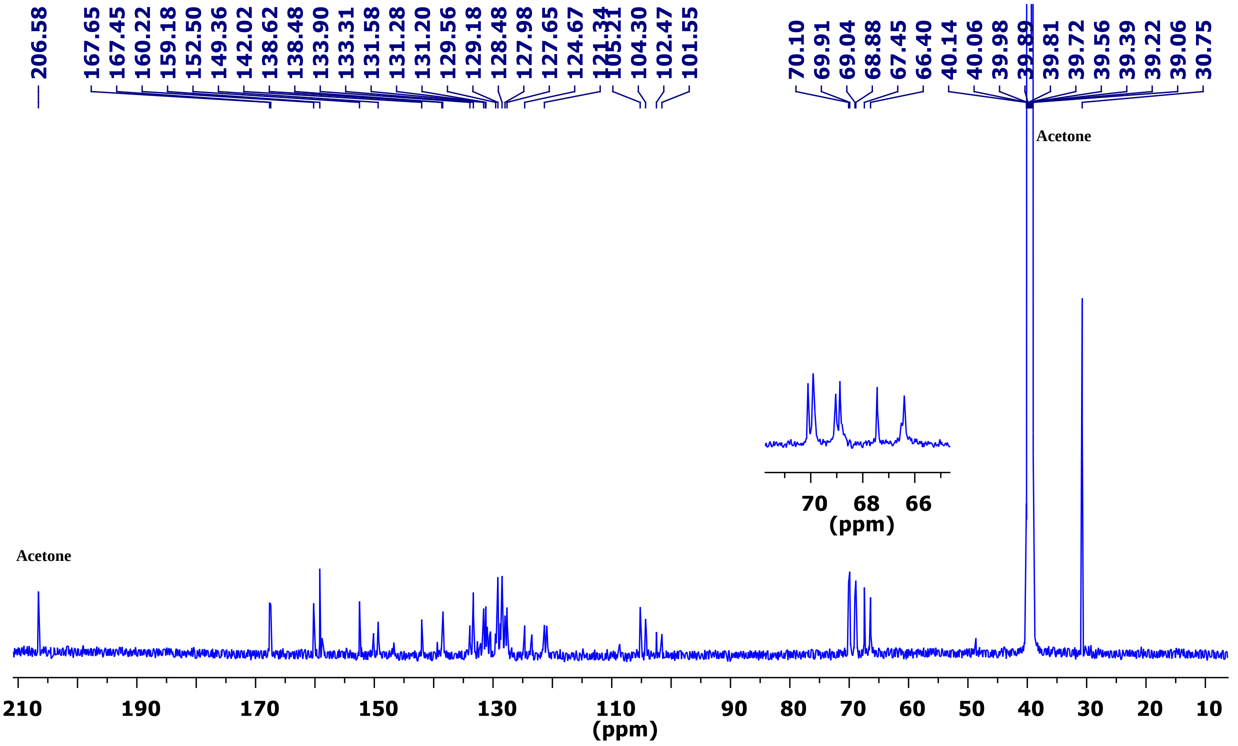
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Single-Crystal X-ray Diffraction Experiments

General: Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2. X-ray intensity data were collected at 173(2) K using a Bruker D8 Venture diffractometer equipped with a PHOTON 100 CMOS area detector. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[S1] Final unit cell parameters were determined by least-squares refinement taken from the data set. Diffraction data and unit-cell parameters were consistent with the assigned space groups. The structures were solved by direct methods with SHELXT.[S2] Subsequent difference Fourier calculations and full-matrix least-squares refinement against $|F^2|$ were performed with SHELXL-2014[S2] using OLEX2.[S3] All non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model. See Table S1 for a summary of data collection, solution and refinement details. Complete details of the structures can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers 1519348-1519352.

X-ray structure of Linker 6a

Crystals of formula **6a**$(DMF)_2$ were of good quality. Data was collected using $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The asymmetric unit contained half a molecule of the tetra-acid ligand ($C_{74}H_{62}N_4O_{20}$) and one molecule of DMF. The structure was solved in the triclinic space group P-1. No restraints were required. See Table S1 for details.

X-ray structure of MOF Zn-6a

Crystals of formula $\{[Zn_2(H_2O)_2($**6a**$)](DEF)_2(H_2O)_2\}$ were of good quality. Data was collected using $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The asymmetric unit contained half a tetra-carboxylate linker, one zinc(II) ion with a coordinated water molecule, two molecules of DEF and two molecules of water. The structure was solved in the triclinic space group P-1. No restraints were required. See Table S1 for details.

X-ray structure of MOF Zn-6c

Crystals of formula $\{[Zn_2($**6c**$)](DEF)_2\}$ were of good quality. Data was collected using $Cu_{K\alpha}$ radiation (λ = 1.54178 Å). The asymmetric unit contained half a molecule of the linker **6c** coordinated to one zinc(II) ion and one molecule of DEF in the lattice. The structure was solved in the monoclinic space group $P2_1/c$. One of the ethyl groups of the DEF molecule was disordered with approximately 50:50 site occupancy; the C-C bonds were restrained to 1.40 Å and SIMU used to even out the electron density on these atoms. See Table S1 for details.

X-ray structure of MOF Cu-6c

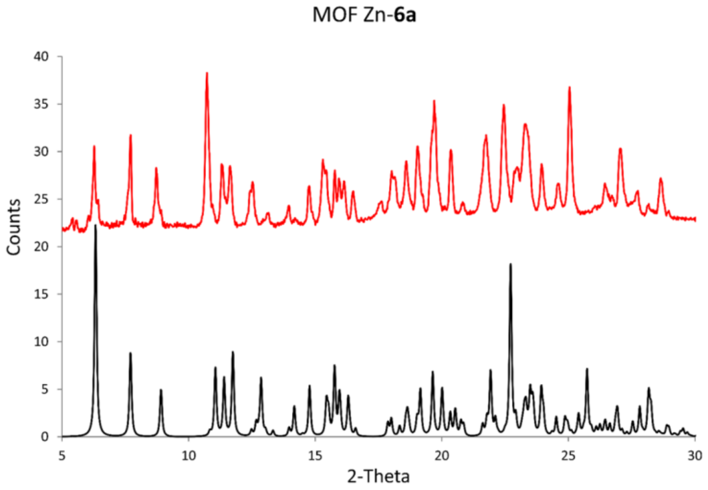
Crystals of formula $\{[Cu($**6c**$)](DEF)_x(H_2O)_x\}$ were of moderate quality. Data was collected using $Cu_{K\alpha}$ radiation (λ = 1.54178 Å). The asymmetric unit contained half a molecule of linker **6c** coordinated to one copper(II) ion with one partially occupied molecule of DEF and one fully occupied molecule of water in the lattice. The structure was solved in the monoclinic space group $P2_1/n$. The full extent of the disorder was discovered and modelled with the necessary restraints (numerous AFIX, SAME, FLAT commands were required); three PARTS for the axle component and disordered DEF and water molecules. Although this provided a chemically sensible result and a reasonable final residuals, the data to parameters/restraints ratio was clearly unacceptable. The solid-state structure and atom connectivity is sensible. See Table S1 and archived CIF files for more details.

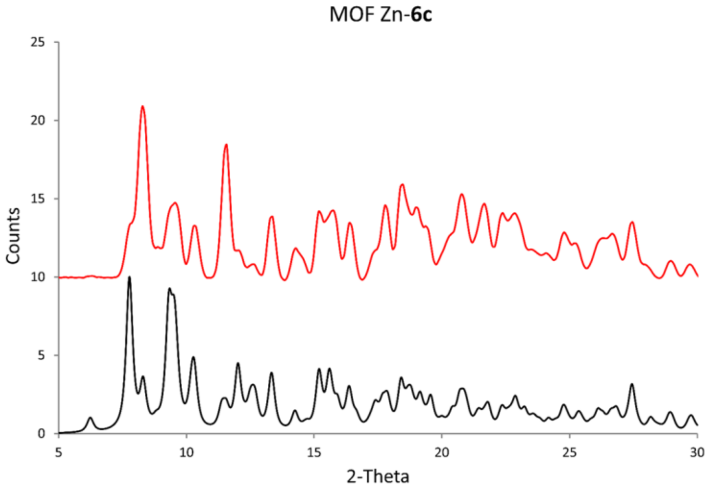
Table S1. Single-crystal X-ray data collection, solution and refinement details for **6a** and MOFs Zn-**6a**, Zn-**6c**, Cu-**6c**.

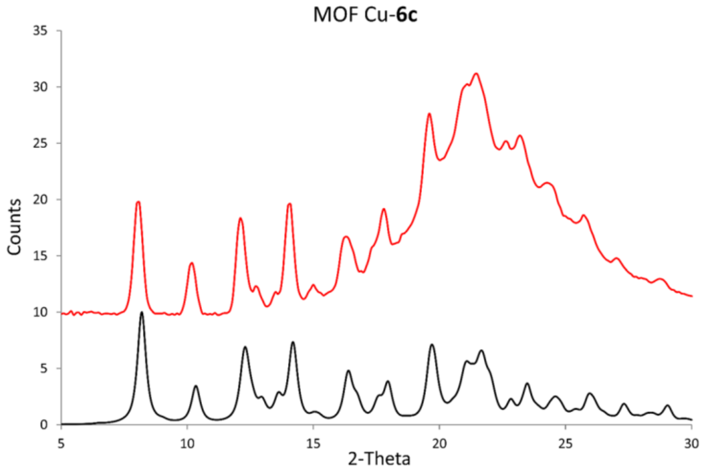
CCDC No.	1519348	1519349	1519350	1519351
Compound	**6a**(DMF)$_2$	{[Zn$_2$(H$_2$O)$_2$(**6a**)](DEF)$_2$(H$_2$O)$_2$}	{[Zn$_2$(**6c**)](DEF)$_4$}	{[Cu(**6c**)](DEF)$_{1.5}$(H$_2$O)$_2$}
Formula	$C_{76.8}H_{73.2}N_{5.6}O_{17.6}$	$C_{82}H_{88}N_6O_{22}Zn_2$	$C_{102}H_{108}N_{10}O_{20}Zn_2$	$C_{89.5}H_{86.5}CuN_{7.5}O_{19.5}$
M [gmol^{-1}]	1356.21	1640.32	1924.72	1641.03
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1 (No. 2)	P-1 (No. 2)	P2$_1$/c (No. 14)	P2$_1$/n (No. 14)
a [Å]	8.0014(3)	8.2465(4)	11.4221(4)	17.2427(6)
b [Å]	14.3032(6)	14.4619(6)	21.2742(8)	14.0544(5)
c [Å]	15.5636(8)	15.5490(8)	19.0647(7)	17.5540(8)
α [°]	76.9517(16)	97.0926(17)	90	90
β [°]	79.6241(15)	94.778(2)	95.4192(19)	103.263(2)
γ [°]	81.520(2)	102.6227(18)	90	90
V [Å^3]	1696.19(13)	1898.76(15)	4611.9(3)	4140.5(3)
Z	1	1	2	2
$D_{calcd.}$ [gcm^{-3}]	1.328	1.435	1.386	1.006
μ[mm^{-1}]	0.095	0.714	1.285	1.320
Reflections	6336	7692	6673	6343
R_{int}	0.0222	0.0407	0.0558	0.0495
Parameters	474	568	562	1066
Restraints	0	156	74	2324
$R1$ [$I > 2\sigma(I)$]^a	0.0449	0.0403	0.0683	0.1241
$R1$ (all data)	0.0665	0.0541	0.0889	0.1674
$wR2$ [$I > 2\sigma(I)$]^b	0.1059	0.0954	0.1795	0.3419
$wR2$ (all data)	0.1179	0.1027	0.1957	0.3843
GoF (F^2)	1.019	1.026	1.074	1.488
$\Delta\rho$ [e Å^{-3}]	+0.48 (-0.24)	+0.62 (-0.60)	+1.06 (-0.37)	+0.55 (-0.41)

$^a R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $R2w = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, $^b w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

Powder X-ray Diffraction Experiments







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