Electronic Supplementary Information

Dinuclear Clathrochelate Complexes with Pendent Cyano Groups as Metalloligands

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1 NMR Spectra

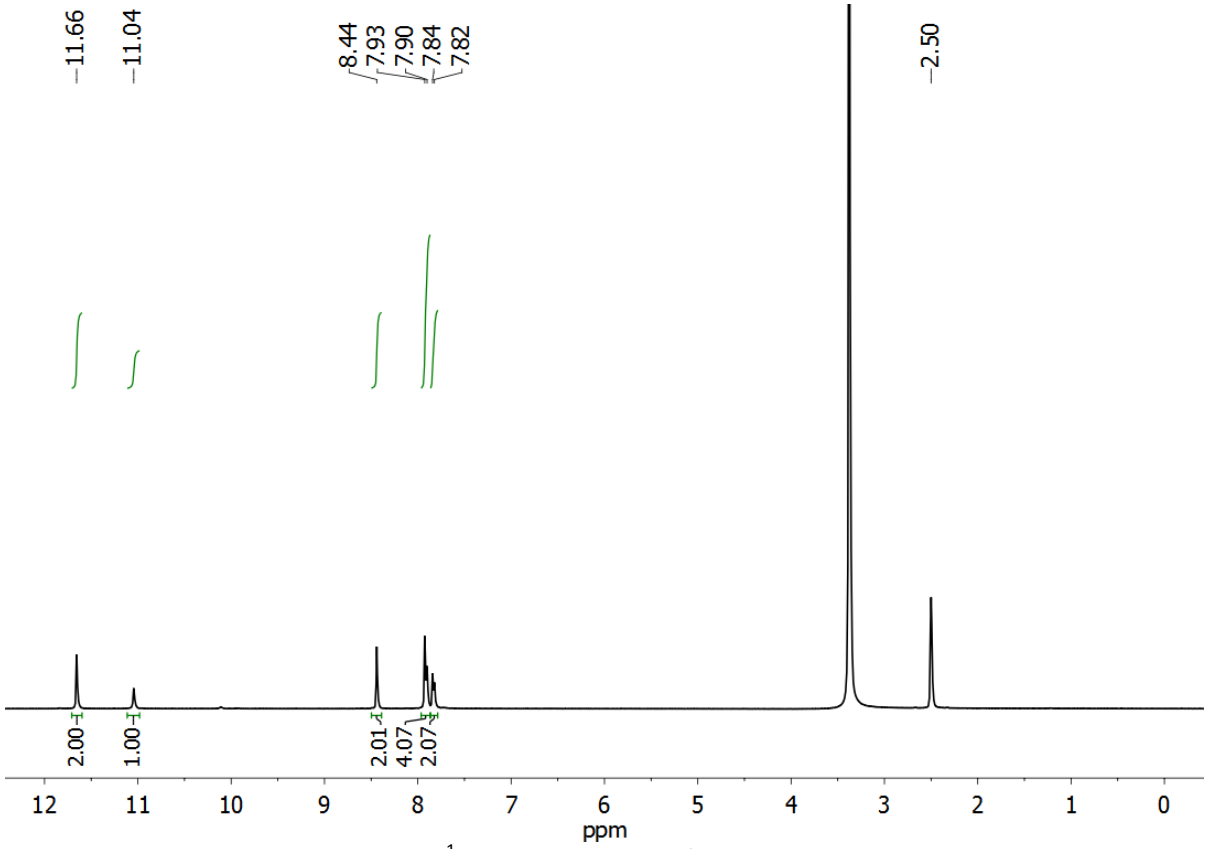

Figure S1 ^{1}H-NMR spectrum of **L2** in DMSO-d_6.

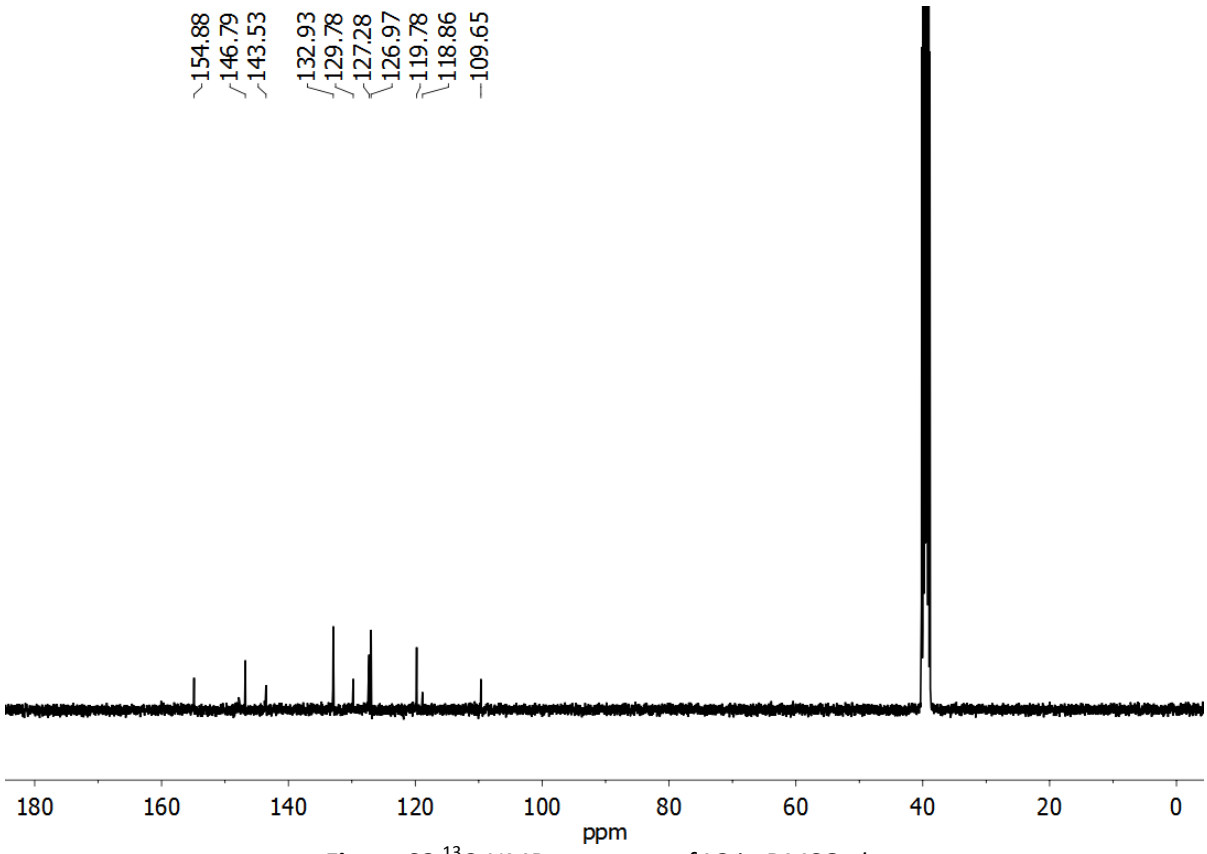

Figure S2 ^{13}C-NMR spectrum of **L2** in DMSO-d_6.

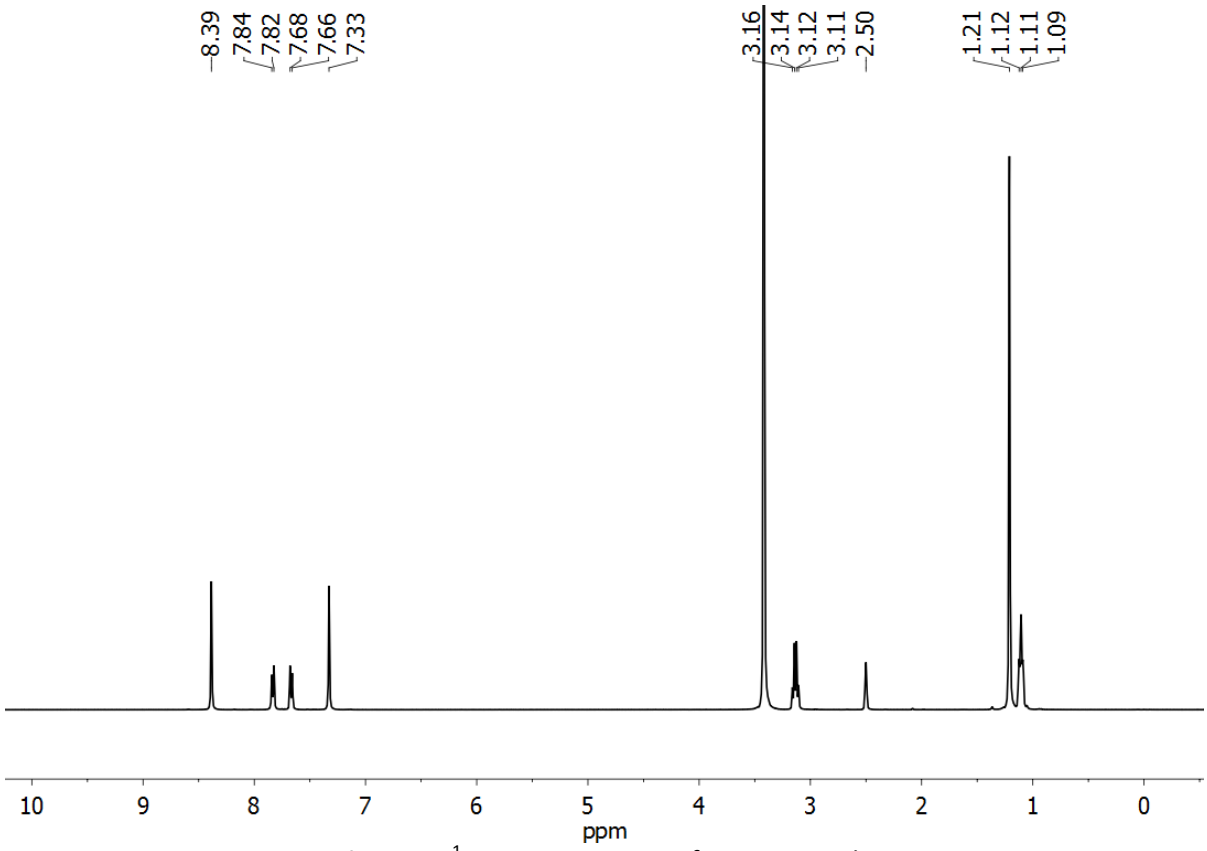

Figure S3 [1]H-NMR spectrum of **1** in DMSO-d_6.

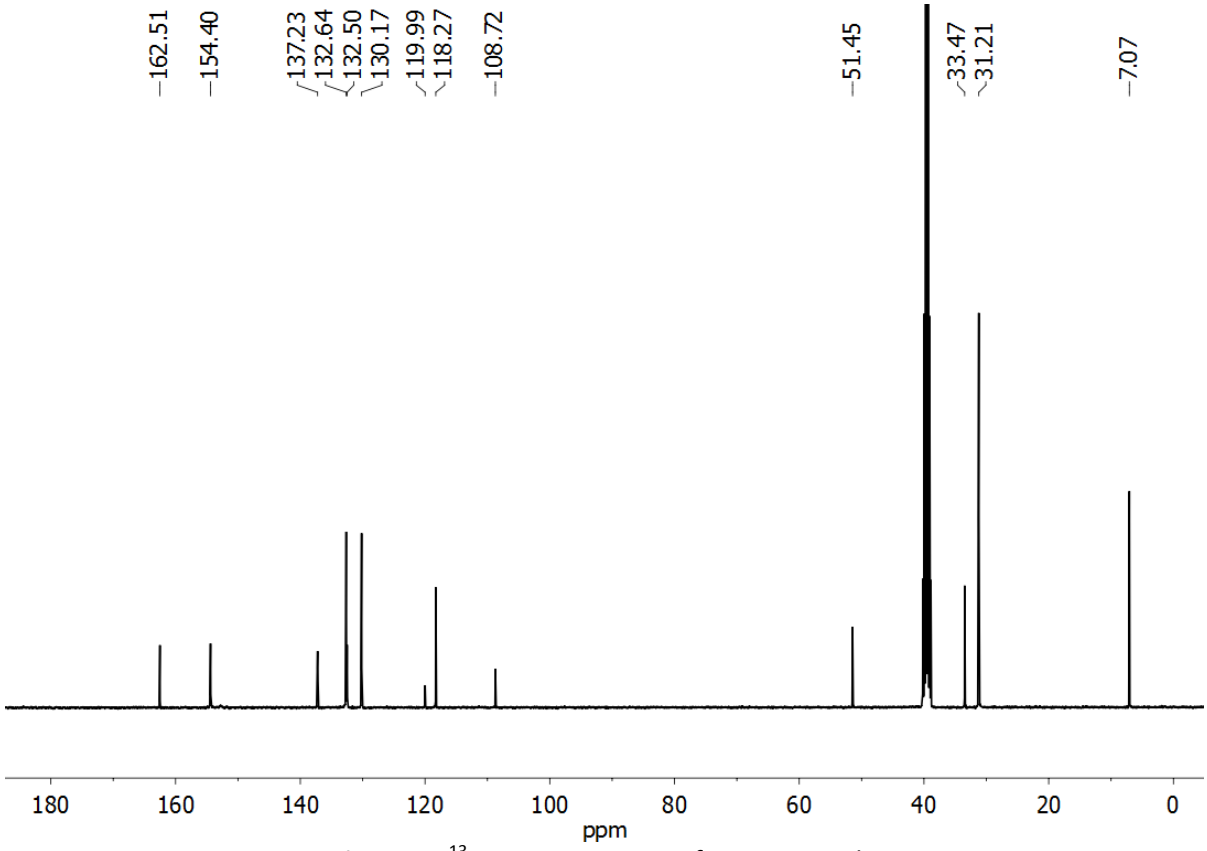

Figure S4 [13]C-NMR spectrum of **1** in DMSO-d_6.

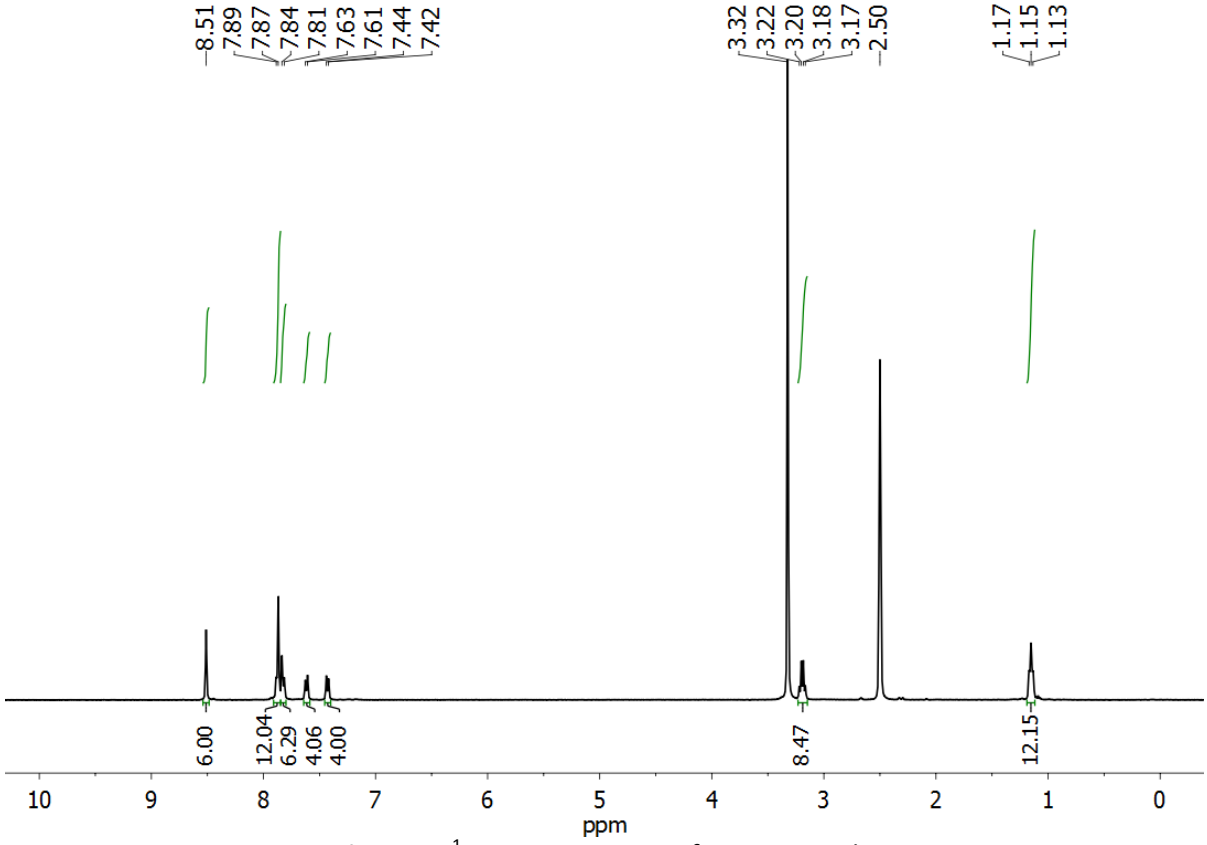

Figure S5 ^{1}H-NMR spectrum of **3** in DMSO-d_6.

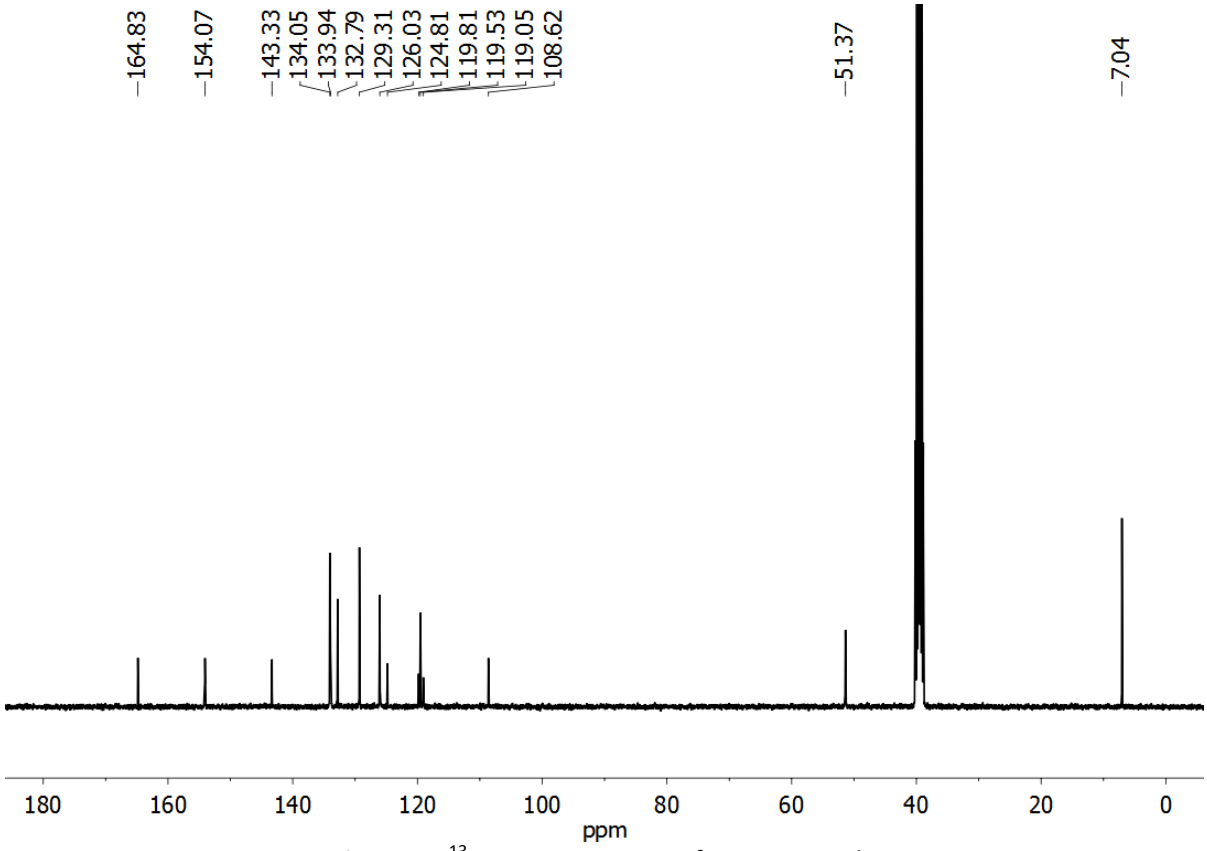

Figure S6 ^{13}C-NMR spectrum of **3** in DMSO-d_6.

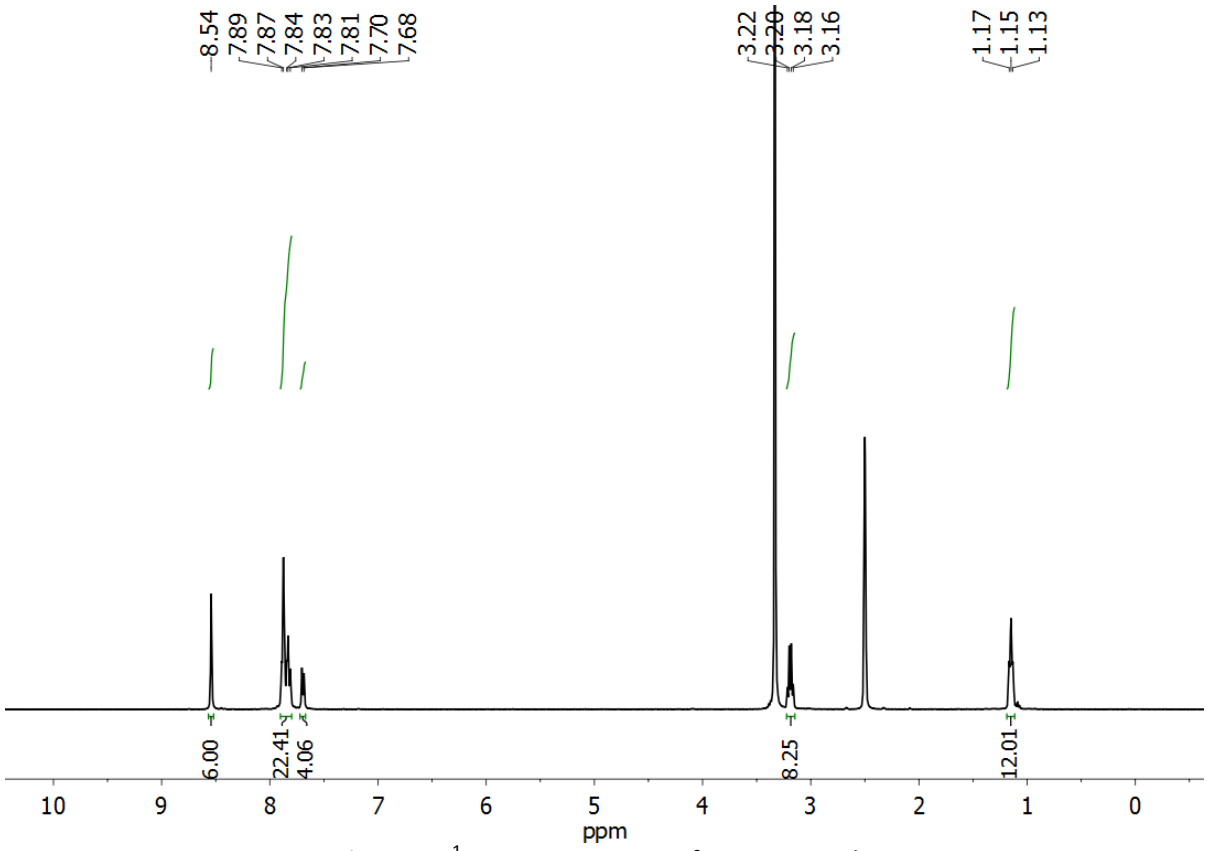

Figure S7 ^{1}H-NMR spectrum of **4** in DMSO-d_6.

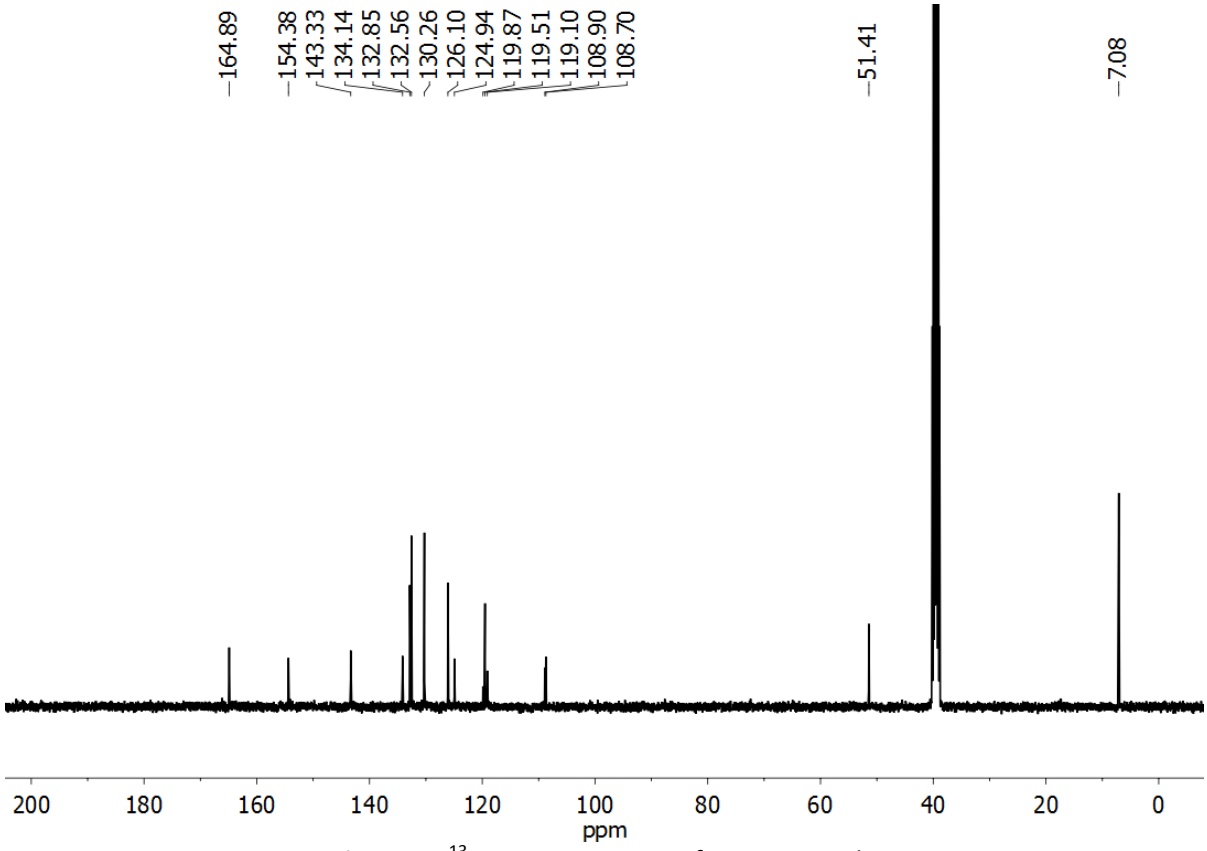

Figure S8 ^{13}C-NMR spectrum of **4** in DMSO-d_6.

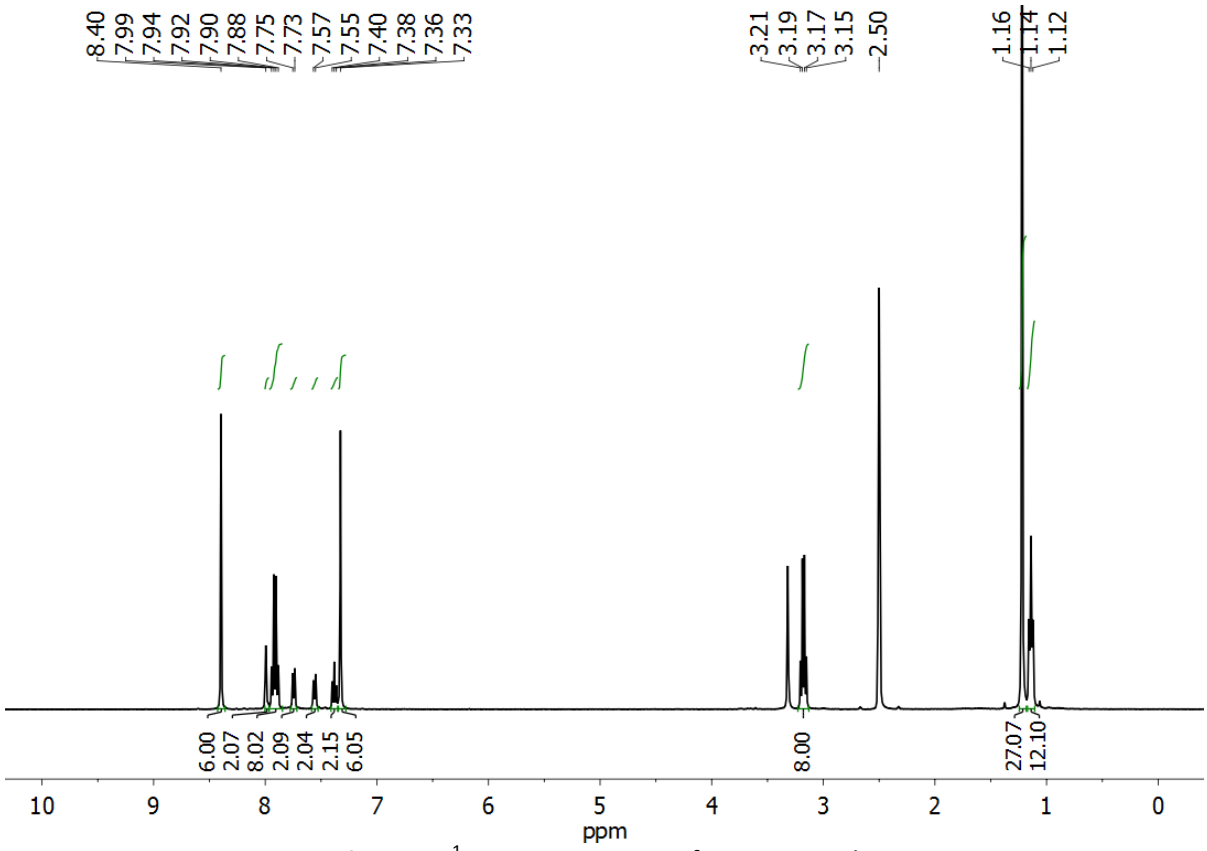

Figure S9 ^{1}H-NMR spectrum of **7** in DMSO-d_6.

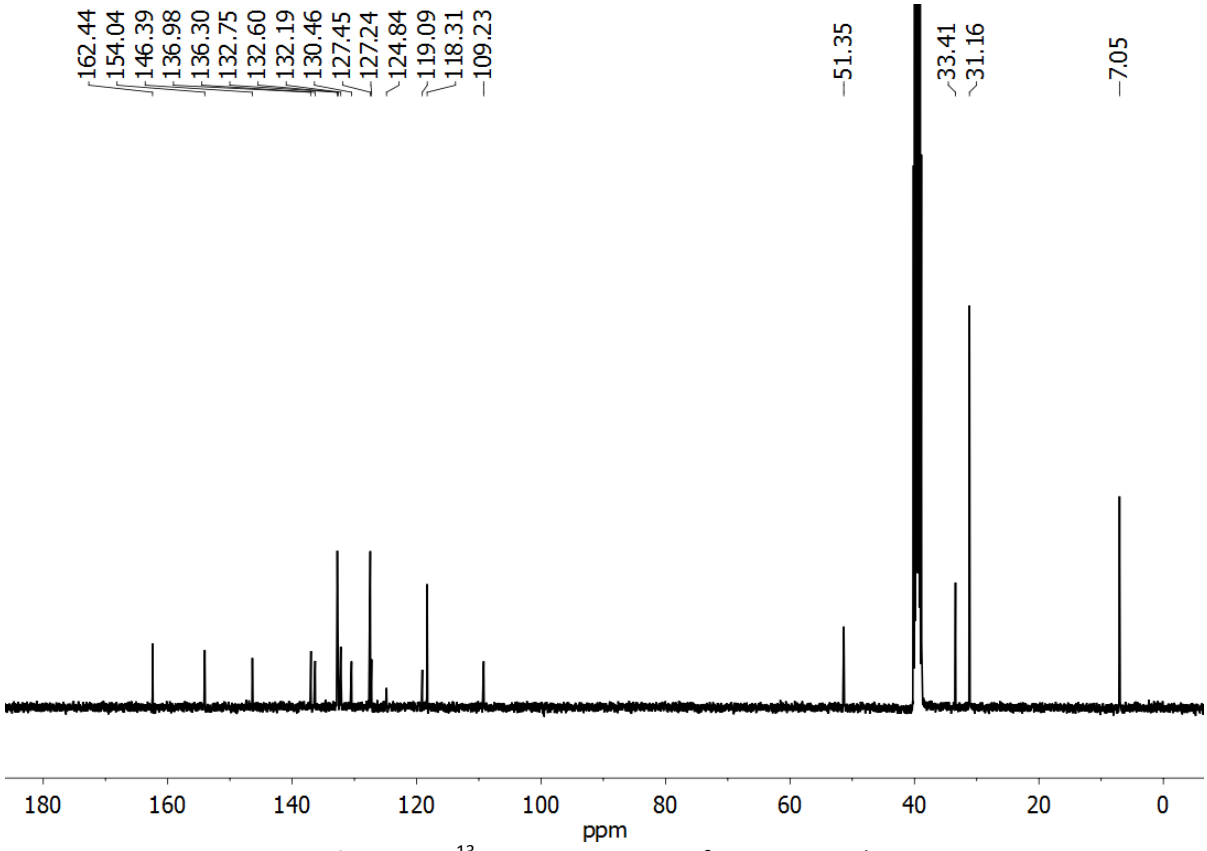

Figure S10 ^{13}C-NMR spectrum of **7** in DMSO-d_6.

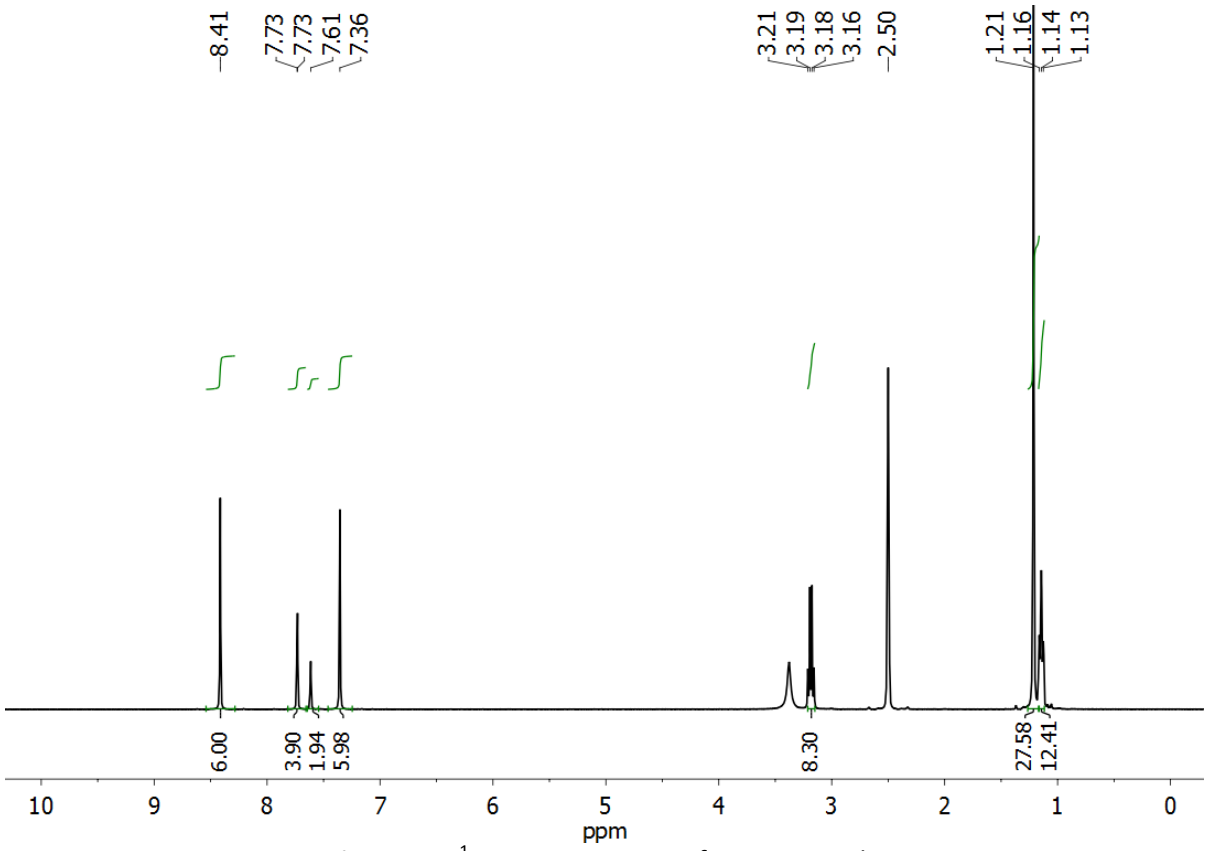

Figure S11 ^{1}H-NMR spectrum of **8** in DMSO-d_6.

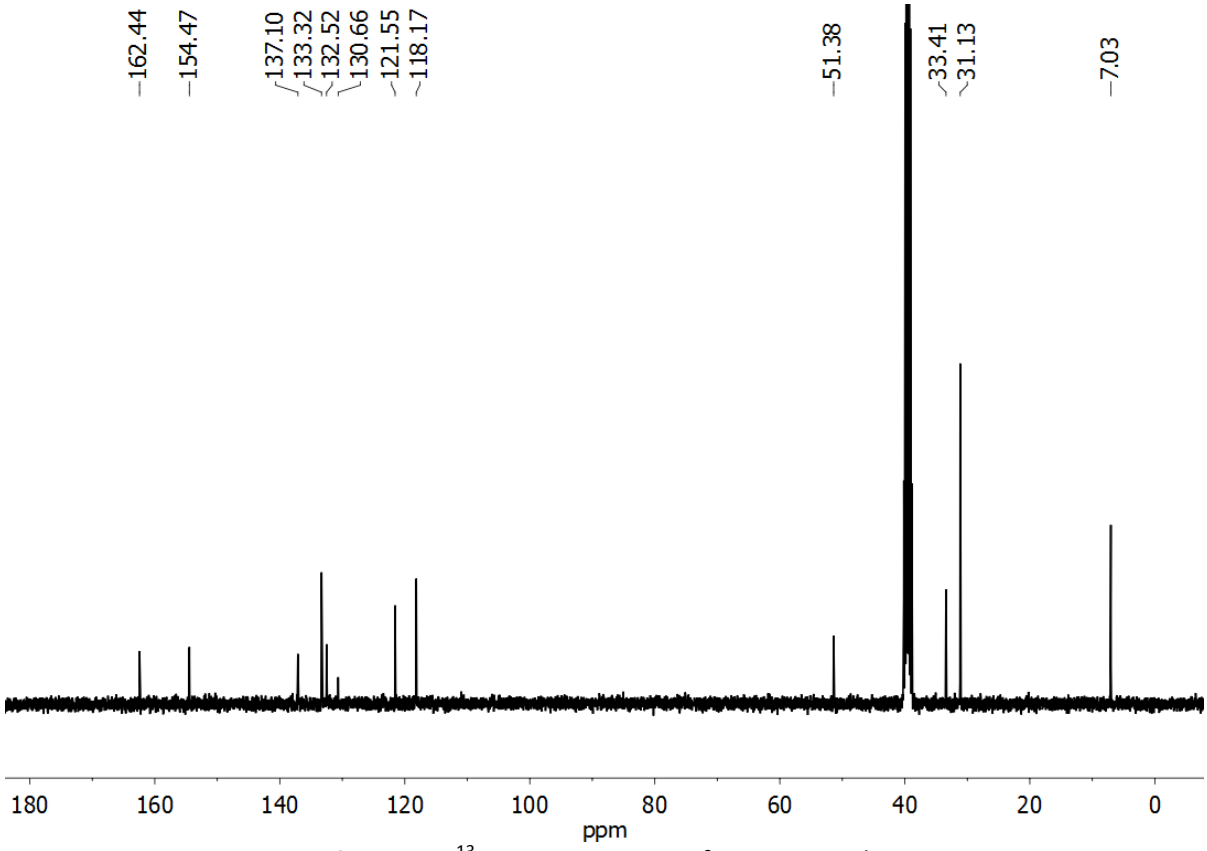

Figure S12 ^{13}C-NMR spectrum of **8** in DMSO-d_6.

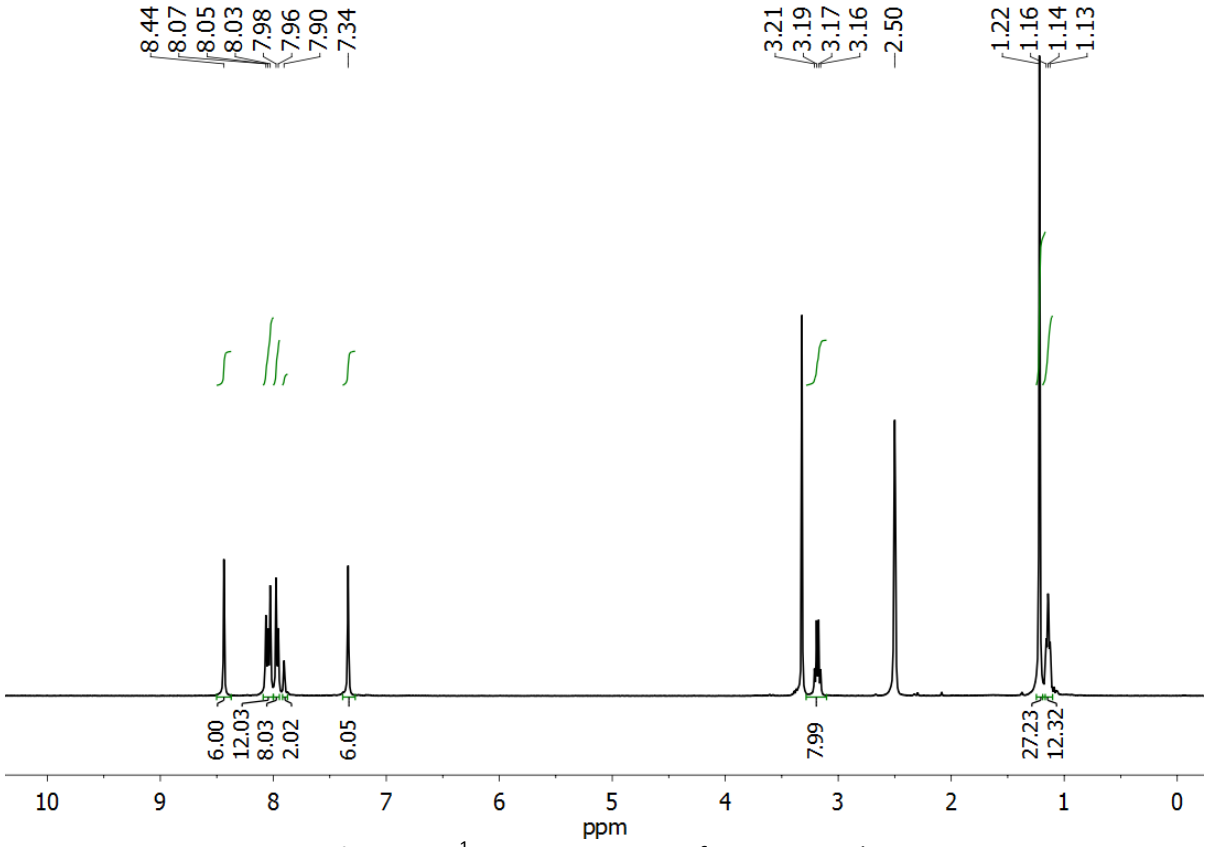

Figure S13 ^{1}H-NMR spectrum of **9** in DMSO-d_6.

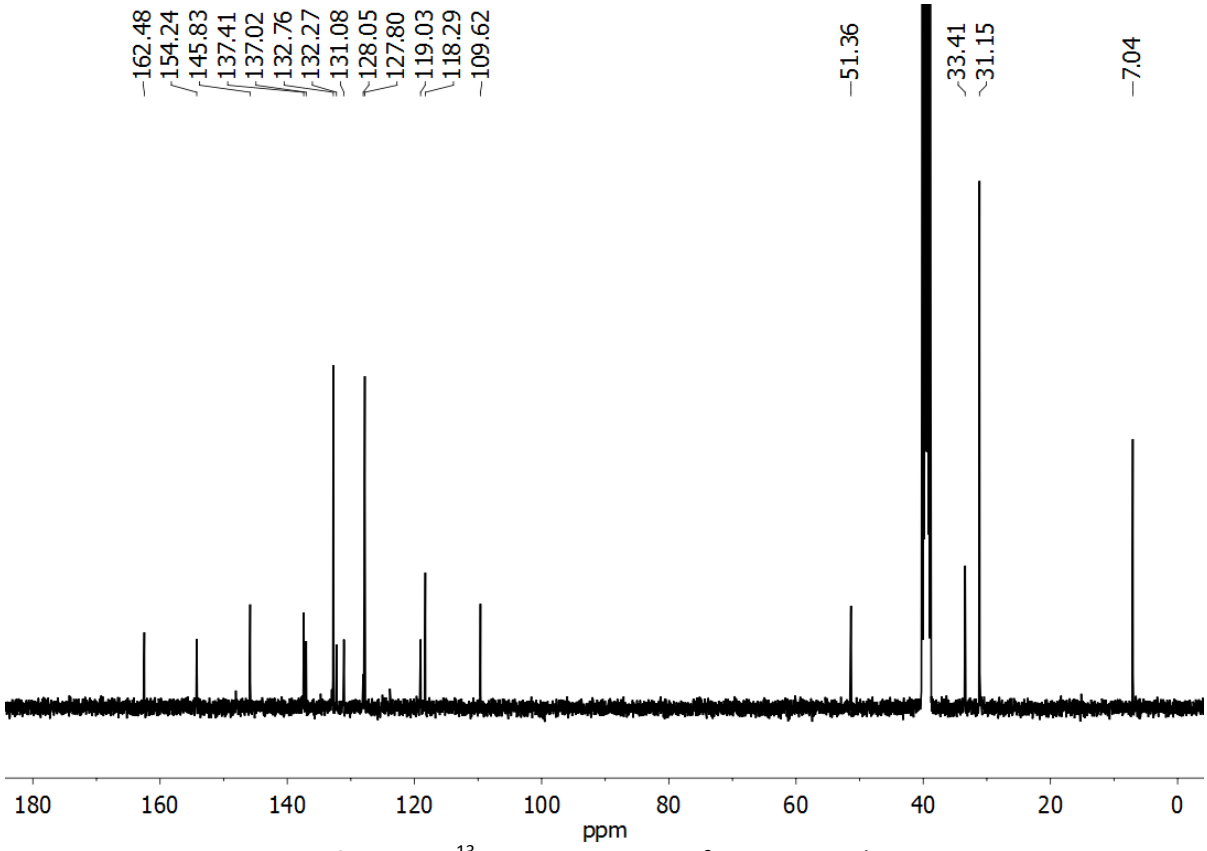

Figure S14 ^{13}C-NMR spectrum of **9** in DMSO-d_6.

2 Emission and Excitation Spectra

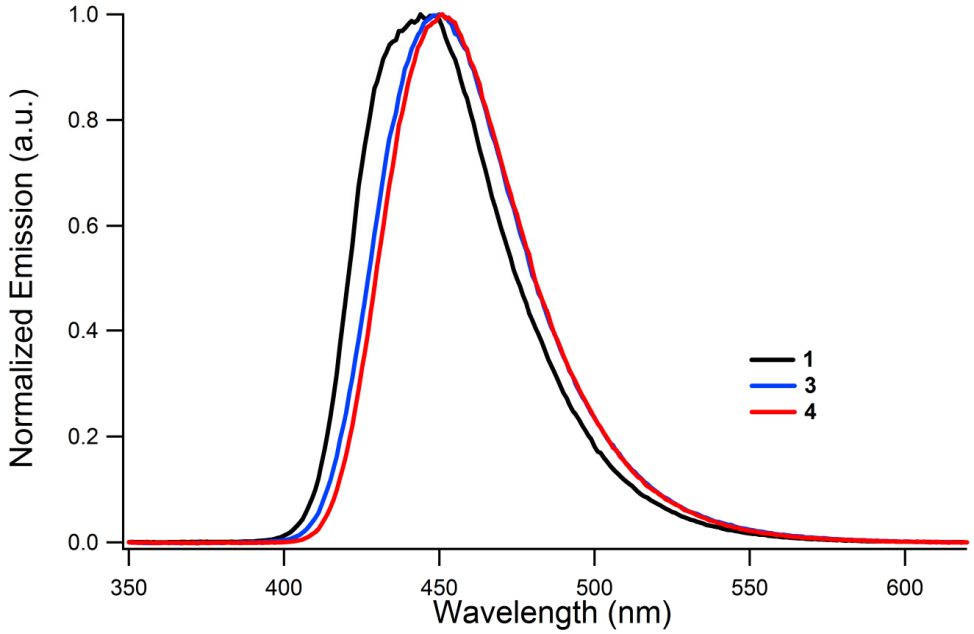

Figure S15 Emission spectra of DMF solutions containing complex **1**, **3** or **4** (λ_{ex} = 335 nm).

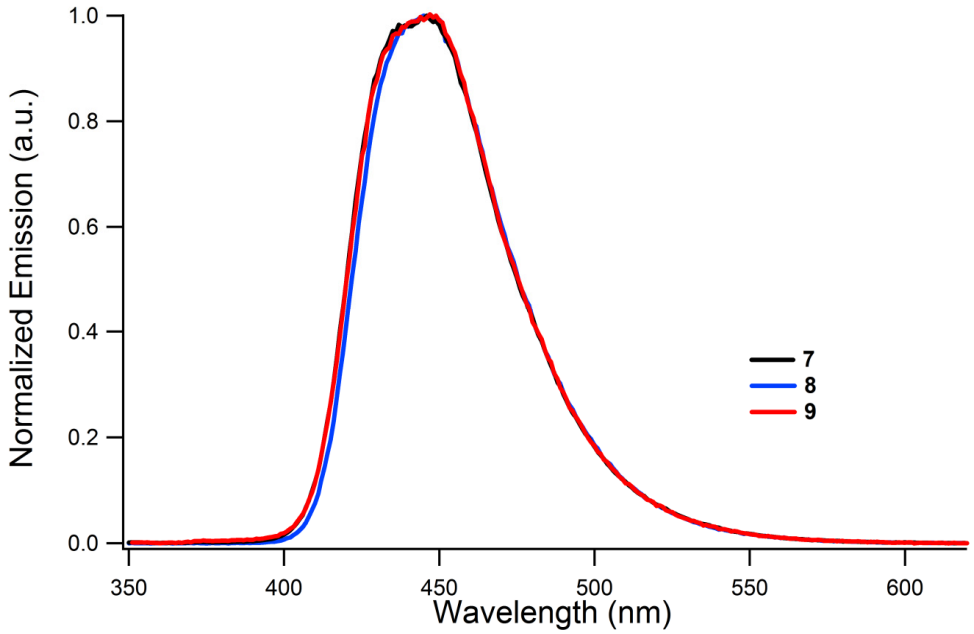

Figure S16 Emission spectra of DMF solutions containing complex **7**, **8** or **9** (λ_{ex} = 335 nm).

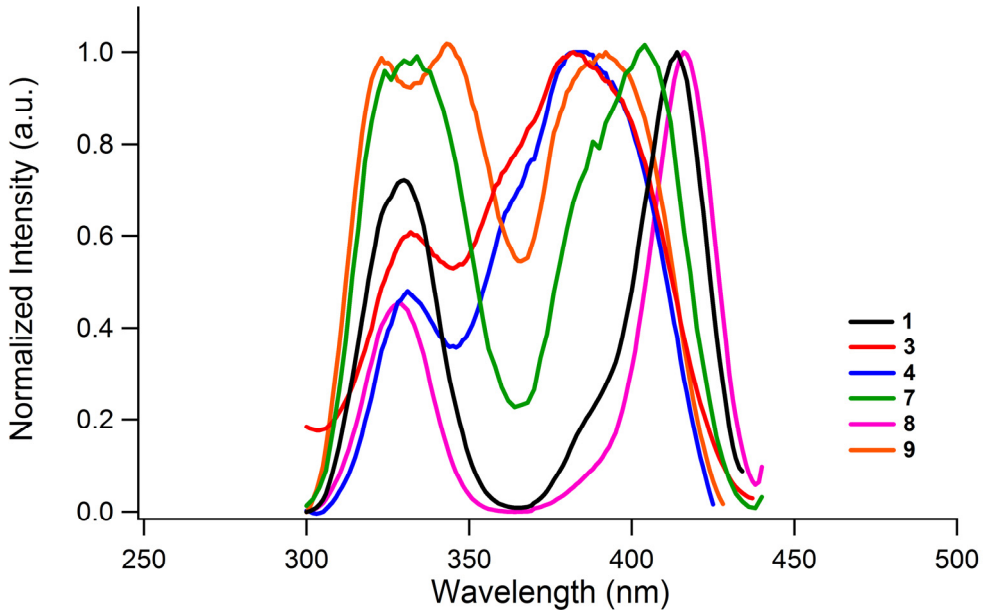

Figure S17 Excitation spectra of DMF solutions containing complexes **1**, **3**, **4**, **7**, **8** or **9**.

3 FT-IR analyses

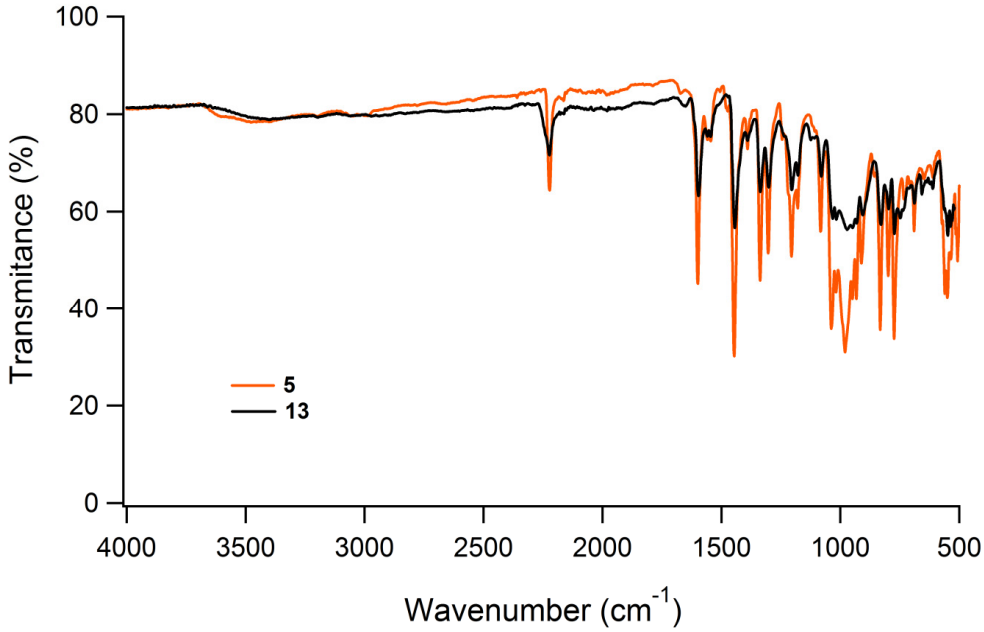

Figure S18 FT-IR spectra of **5** and CP **13**, indicating the absence of perchlorate within the CP structure.

4 Single-Crystal X-Ray Analyses

Single crystals of coordination polymers **10-13** were obtained from nitromethane/methanol (**10**–**12**) and 1,2-dichlorobenzene/DMF/methanol (**13**) mixtures at ambient conditions. Intensity data for CP **10** was collected on a RigakuSuperNova dual system in combination with an Atlas CCD detector using Cu-$K_\alpha$radiation (λ = 1.54178 Å) at 100(2) K. Intensity data for CP **11** was collected on a Bruker APEX II CCD system, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 100(2) K. Intensity data for CP **12** was collected on a marμx system using a Genix micro-source sealed tube with Mo-K_α radiation (λ = 0.71073 Å) at 140(2) K. Intensity data for CP **13** was collected at the Swiss Norwegian beamline BM01A at the ESRF in Grenoble (France) using synchrotron radiation (λ = 0.69710 Å) on the Pilatus@SNBL kappa goniometer from Huber Diffraktionstechnik GmbH equipped with a Pilatus2M pixel detector from Dectris Ltd.[1] Data collection was performed at low temperature (100 K) using a Cryostream 700 Series from Oxford Cryosystems Ltd.

The solutions of **10**–**12** were obtained by *SHELXT*[2] and that of **13** was performed by *SIR2014*.[3] The refinements were carried out by *SHELXL-2014*[4] and OLEX2.[5] The crystal structures were refined using full-matrix least-squares based on F^2 with anisotropically refined non hydrogen atoms (except some disordered *tert*-butyl, -CN fragments and solvent molecules which were refined in isotropic approximation). Hydrogen atoms were placed in calculated positions by means of the "riding" model. Additional electron density found in the difference Fourier map of compound **13** was treated by the SQUEEZE algorithm of *PLATON*[6] and refined using ABIN instruction because of presence of a twinned component. Intense disorder affected solvent molecules of **10** and **11** and several moieties of crystal structures **12** and **13** and tough restraints/constraints (involving SHELX commands: DFIX, EADP, SIMU, RIGU, ISOR and SADI) were used to handle it. Crystallographic data have been deposited with the CCDC no. 1481126−1481129. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internet.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk) or via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data of coordination polymers **10** and **11**

Structure, CCDC no.	**Coordination Polymer 10, 1481126**	**Coordination Polymer 11, 1481127**
Empirical formula	$C_{53.5}H_{60}AgB_2N_9O_{13.5}Zn_2$	$C_{53.75}H_{60.5}AgB_2Co_2N_{9.5}O_{14.25}$
Mol. weight / g mol^{-1}	1305.33	1314.96
Temperature / *K*	100(2)	100(2)
Wavelength / Å	1.54178	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å	12.3180(2)	12.3035(11)
b / Å	19.2910(4)	19.295(4)
c / Å	27.0609(5)	27.164(3)
α / °	90	90
β / °	96.918(2)	97.324(7)
γ / °	90	90
Volume / $Å^3$	6383.6(2)	6395.9(15)
Z	4	4
Density / g cm^{-3}	1.358	1.366
Absorption coeff. / mm^{-1}	3.846	0.882
Crystal size / mm^3	0.8 x 0.2 x 0.1	0.7 x 0.2 x 0.1
Θ range / °	4.01 to 73.08	3.10 to 30.00
Index ranges	$-15 \le h \le 14$ $-23 \le k \le 23$ $-33 \le l \le 25$	$-17 \le h \le 17$ $-25 \le k \le 27$ $-38 \le l \le 38$
Reflections collected	46094	106504
Independent reflections	12520 [*R*(int) = 0.036]	18526 [*R*(int) = 0.031]
Observed reflections	11432	14988
Completeness	99.5 % (to Θ = 67.5°)	99.2 % (to Θ = 26.00°)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. & min. transmission	1.00 and 0.38	0.75 and 0.64
Data / restraints / parameters	12520 / 53 / 813	18526 / 48 / 815
Goodness-of-fit on F^2	1.01	1.08
Final *R* indices [I > 2 s (I)]	*R*1 = 0.083, w*R*2 = 0.179	*R*1 = 0.065, w*R*2 = 0.140
R indices (all data)	*R*1 = 0.088, w*R*2 = 0.181	*R*1 = 0.083, w*R*2 = 0.152
Extinction coefficient	-	-
Larg. diff. peak/hole / $eÅ^{-3}$	1.61 and -2.53	3.11 and -2.11
Flack x (Parsons)	-	-

Table S2. Crystallographic data of coordination polymers **12** and **13**

Structure, CCDC no.	**Coordination Polymer 12, 1481128**	**Coordination Polymer 13, 1481129**
Empirical formula	$C_{78.25}H_{68.5}AgB_2N_{11.5}O_{12.75}Zn_2$	$C_{125}H_{71}Ag_3B_4Cl_2Co_4N_{22}O_{19}$
Mol. Weight / g mol^{-1}	1634.17	2858.50
Temperature / *K*	140(2)	120(2)
Wavelength / Å	0.71073	0.69791
Crystal system	Triclinic	Orthorhombic
Space group	*P*1	$Pna2_1$
a / Å	15.6943(3)	40.6211(2)
b / Å	17.8805(5)	14.7220(1)
c / Å	18.0418(4)	34.9798(3)
α / °	67.658(2)	90
β / °	78.0034(17)	90
γ / °	65.410(2)	90
Volume / $Å^3$	4250.72(19)	20918.8(3)
Z	2	4
Density / g cm^{-3}	1.277	0.908
Absorption Coeff. / mm^{-1}	0.850	0.626
Crystal size / mm^3	0.7 x 0.5 x 0.1	0.50 x 0.03 x 0.02
Θ range / °	3.60 to 29.48	1.51 to 23.04
Index ranges	$-20 \le h \le 21$ $-23 \le k \le 24$ $-23 \le l \le 19$	$-43 \le h \le 45$ $-11 \le k \le 15$ $-38 \le l \le 38$
Reflections collected	55999	89199
Independent reflections	32067 [*R*(int) = 0.031]	25055
Observed reflections	28082	21882
Completeness	99.6 % (to Θ = 26.00°)	68.0 % (to Θ = 24.725°)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. & min. transmission	0.75 and 0.50	1.00 and 0.40
Data / restraints / parameters	32067 / 209 /2059	25055 / 397 / 1558
Goodness-of-fit on F^2	1.01	1.29
Final *R* indices [I > 2 s (I)]	*R*1 = 0.061, w*R*2 = 0.151	*R*1 = 0.088, w*R*2 = 0.201
R indices (all data)	*R*1 = 0.072, w*R*2 = 0.159	*R*1 = 0.095, w*R*2 = 0.204
Extinction coefficient	-	-
Larg. diff. peak/hole / $eÅ^{-3}$	2.18 and -0.95	0.95 and -0.75
Flack x (Parsons)	0.011(6)	0.31(3)

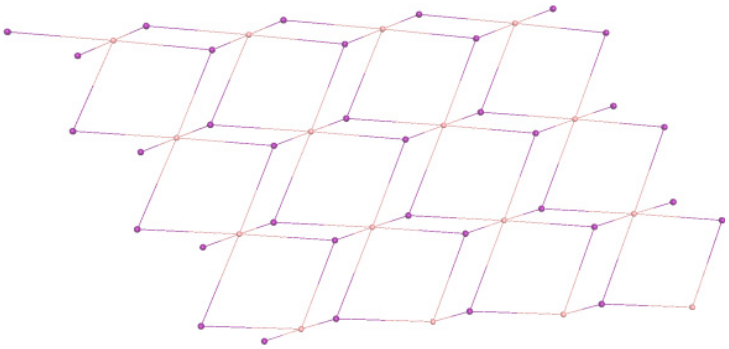

Figure S19 The underlying **kgd** net of the two-dimensional coordination polymer **12**. Purple spheres: Ag(I); orange spheres: centers of metalloligands.

Figure S20 The underlying net of the three-dimensional coordination polymer **13**. Interpenetrating **utp** nets are shown in green and fuchsia, and the connections by Ag(2) atoms are depicted with dashed lines.

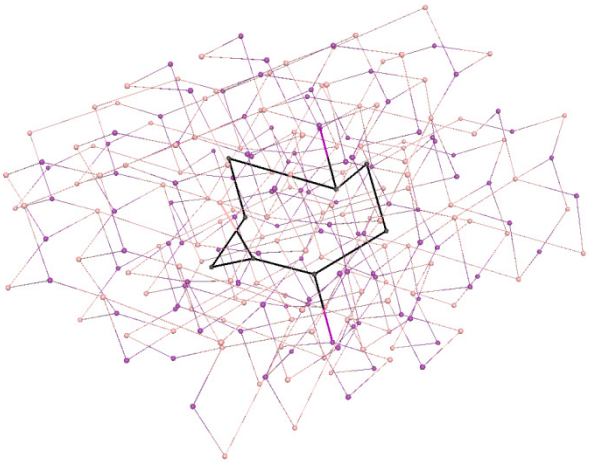

Figure S21 The 8-membered ring (black) catenated by 42 other 8- and 10-rings in the underlying net of coordination polymer **13**.

4 References

[1] V. Dyadkin, P. Pattison, V. Dmitriev and D. Chernyshov, *J. Synchrotron Rad*., 2016, **23**, 825.

[2] G. M. Sheldrick, *Acta Cryst., Sect. A*., 2015, **A71**, 3.

[3] M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori, *J. Apll. Cryst.*, 2015, **48**, 306.

[4] G. M. Sheldrick, *Acta Cryst., Sect. C.*, 2015, **C71**, 3.

[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howarda and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

[6] A. L. Spek, *Acta Cryst., Sect C.*, 2015, **C71**, 9.

5 Input Systre files for CP 12 and 13

crystal

name 12

cell 15.6943 17.8805 18.0418 67.658 78.003 65.410

group P1

atom 1 6 0.64048 0.07161 0.51671

edge 1 0.9233 0.2168 0.2525

edge 1 0.3669 -0.0791 0.8192

edge 1 0.3669 0.9209 -0.1808

edge 1 1.3669 -0.0791 -0.1808

edge 1 0.9233 -0.7832 1.2525

edge 1 -0.0767 0.2168 1.2525

atom 2 3 0.36690 0.92093 0.81919

edge 2 0.6405 1.0716 0.5167

edge 2 0.6405 0.0716 1.5167

edge 2 -0.3595 1.0716 1.5167

atom 3 3 0.92328 0.21684 0.25252

edge 3 0.6405 0.0716 0.5167

edge 3 0.6405 1.0716 -0.4833

edge 3 1.6405 0.0716 -0.4833

end

crystal

name 13

cell 40.6211 14.7220 34.9798 90.000 90.000 90.000

group Pna21

atom 1 4 0.38836 0.09992 0.21053

edge 1 0.8660 -1.1004 0.4092

edge 1 0.1568 0.7110 0.1304

edge 1 0.3432 0.2110 0.6304

edge 1 0.6568 0.7890 0.1304

atom 2 4 0.86603 0.89964 0.40915

edge 2 0.3884 2.0999 0.2105

edge 2 1.0694 0.1744 0.4857

edge 2 0.9306 0.8256 -0.0143

edge 2 0.5694 0.3256 0.4857

atom 3 3 0.34319 0.21100 0.63043

edge 3 0.6116 0.9001 0.7105

edge 3 0.1116 -0.4001 0.7105

edge 3 0.3884 0.0999 0.2105

atom 4 3 0.06943 0.17440 0.48570

edge 4 -0.1340 0.8996 0.4092

edge 4 0.1340 0.1004 0.9092

edge 4 0.3660 -0.3996 0.4092

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