Supplementary Information

Strong halogen bond with guest molecules in Co(II) 2,5-diiodoterephthalate metal-organic framework

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Table 1. SCXRD Experimental details

	1	**2**
Refined Chemical formula	$C_{44.50}H_{38.25}Co_2I_4N_6O_9$	$C_{22.50}H_{20.13}CoI_2N_{2.87}O_{4.87}$
M_r	1426.52	721.28
Crystal system, space group	Orthorhombic, *Pbcn*	Orthorhombic, *Pnc*2
a, *b*, *c* (Å)	22.7381(4), 22.6517(5), 19.7113(4)	15.5617(5), 34.0855(11), 14.1496(5)
V (Å^3)	10152.4 (4)	7505.3 (4)
Z	8	12
m (mm^{-1})	3.14	3.19
Crystal size (mm)	0.15 × 0.06 × 0.06	0.11 × 0.07 × 0.02
Radiation source	Incoatec IuS3.0 microfocus X-ray tube	Incoatec IuS3.0 microfocus X-ray tube
T_{min}, T_{max}	0.656, 0.746	0.656, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	114068, 12610, 9490	78217, 14256, 10917
R_{int}	0.071	0.080
θ values (°)	θ_{max} = 28.3, θ_{min} = 1.6	θ_{max} = 25.7, θ_{min} = 1.3
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667	0.610
Range of *h*, *k*, *l*	-30 ≤ *h* ≤ 30, -30 ≤ *k* ≤ 30, -25 ≤ *l* ≤ 26	-18 ≤ *h* ≤ 18, -41 ≤ *k* ≤ 41, -17 ≤ *l* ≤ 17
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.051, 0.140, 1.06	0.077, 0.165, 1.11
No. of reflections	12610	14256
No. of parameters	610	830
No. of restraints	72	419
	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 36.7259P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0193P)^2 + 144.4646P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δ_{max}, Δ_{min} (e Å^{-3})	1.65, -1.93	2.01, -1.83
Absolute structure	–	Refined as an inversion twin.
Absolute structure parameter	–	0.57 (8)

Computer programs: *APEX3* (Bruker-AXS, 2016), *SAINT* (Bruker-AXS, 2016), *SHELXS2014*/5 (Sheldrick, 2014), *SHELXL2019*/3 (Sheldrick, 2019), ShelXle (Hübschle, 2011), CIFTAB-2014/2 (Sheldrick, 2014).

Table 2. Selected geometric parameters for **1** and **2** (Å)

1			
O3—Co2	2.120 (3)	Co2—O5	2.131 (3)
Co1—O4	2.075 (3)	Co2—O8^{i}	2.162 (4)
Co1—O5	2.293 (4)	Co1—N3	2.127 (4)
Co1—O6	2.231 (4)	Co1—N4^{ii}	2.086 (4)
Co1—O7^{i}	2.230 (4)	Co2—N1^{iii}	2.126 (4)
Co2—O2	2.044 (4)	Co2—N2	2.125 (4)
2			
O11—Co4	2.107 (16)	Co3—O13	2.065 (16)
O12—Co4	2.235 (18)	Co3—O14	2.275 (19)
Co1—O1^{iv}	2.216 (18)	Co1—N1^{iv}	2.07 (2)
Co1—O1	2.217 (18)	Co1—N1	2.07 (2)
Co1—O2	2.058 (16)	Co2—N4	2.11 (2)
Co1—O2^{iv}	2.059 (16)	Co2—N5	2.11 (2)
Co2—O3	2.117 (18)	Co3—N6	2.09 (2)
Co2—O4	2.198 (18)	Co3—N7	2.06 (2)
Co2—O5	2.334 (16)	Co4—N8B^{vi}	2.03 (4)
Co2—O6	2.062 (19)	Co4—N8B^{vii}	2.03 (4)
Co3—O7^{v}	2.176 (19)	Co4—N8A^{vi}	2.15 (18)
Co3—O8^{v}	2.151 (18)	Co4—N8A^{vii}	2.15 (16)

Symmetry code(s): (i) *x*, -*y*+1, *z*-1/2; (ii) *x*+1/2, -*y*+3/2, -*z*+1; (iii) -*x*+3/2, -*y*+1/2, *z*+1/2; (iv) -*x*, -*y*+1, *z*; (v) *x*-1, *y*, *z*-1; (vi) -*x*, -*y*, *z*-1; (vii) *x*+1, *y*, *z*-1.

Powder X-ray diffractometry (PXRD)

Analysis of polycrystals was performed on Bruker D8 Advance (CuKα radiation, LYNXEYE XE-T linear detector, 4 – 50° 2θ range, 0.03° 2θ step, 0.5s per step). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspensions were deposited on the polished side of a standard quartz sample holder, and a smooth thin layer being formed after drying.

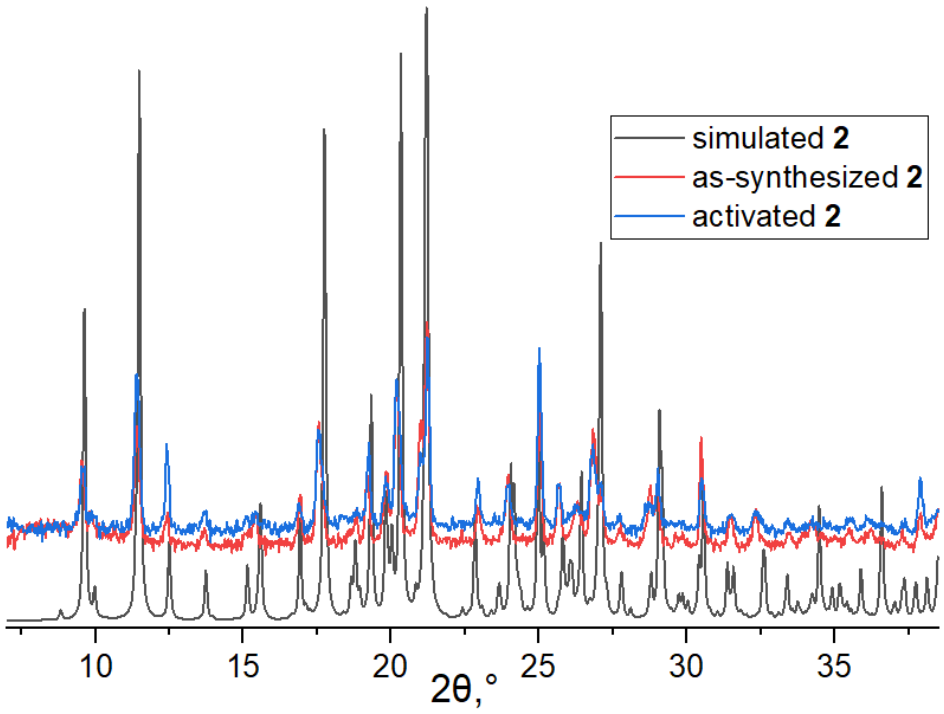

Figure S1. PXRD data for **2**

Thermogravimetric analysis (TGA) was carried out on a TG 209 F1 Iris thermobalance (NETZSCH, Germany). The measurements were made in a helium flow in the temperature range of 30–450 °C using the heating rate of 10 °C/min the gas flow rate of 60 mL/min and open Al crucibles.

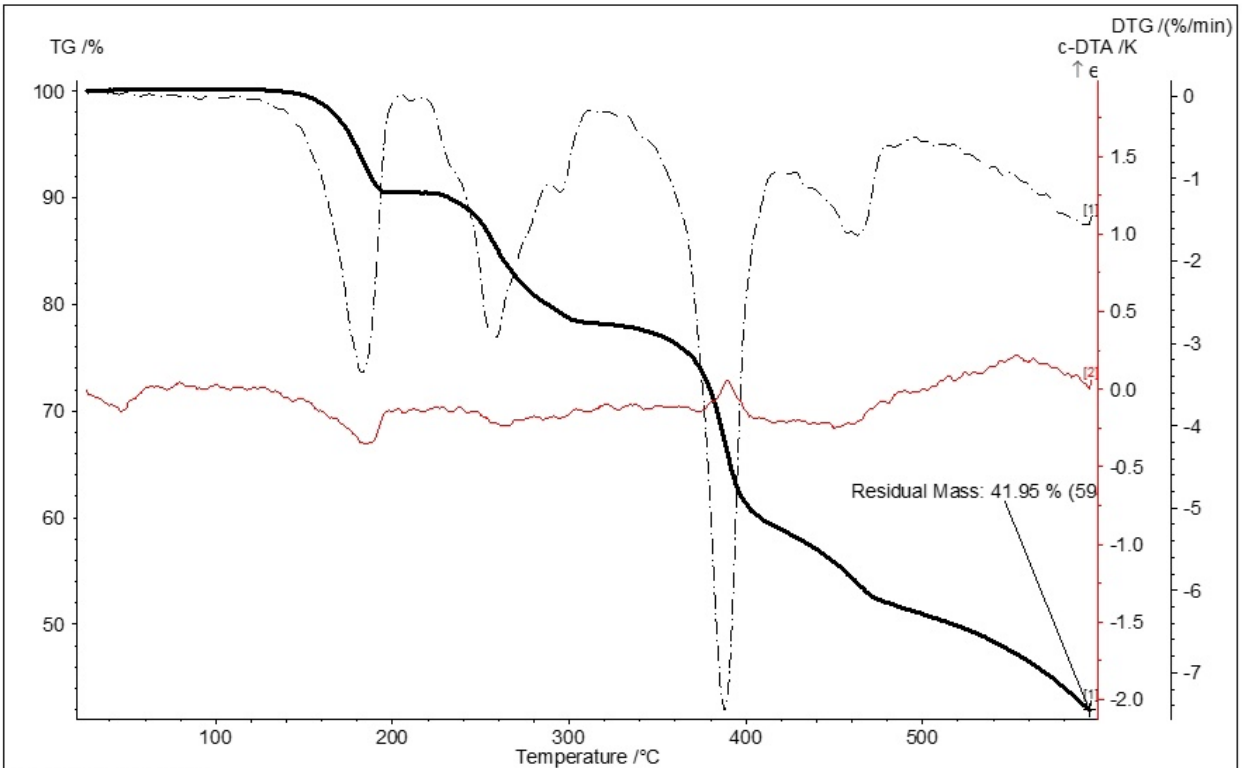

Figure S2. TGA data for **2**

Sorption experiments

An activated sample of MOF (see main article text) was placed into the glass vial. The latter was placed to another (bigger) vial containing an equimolar mixture of liquid organic substrates. The bigger vial was closed and kept at room temperature for 24 h.

After that, the sample of MOF was removed, filtered of, rapidly washed with 1-2 portions of DMSO and then into an excess of d6:DMSO for another 48 hours to achieve extraction of guest molecules. After that, the d6-DMSO solution was used for ^{1}H NMR spectra measurements to analyze the ratio of absorbed substrates. The NMR spectra were recorded on Bruker Advance 500 spectrometer. The spectra are shown below on Figs S4-S7.

Computational details

The single point calculations based on the experimental X-ray geometries in **2** carried out at the DFT level of theory using the dispersion-corrected hybrid functional ωB97XD [Phys. Chem. Chem. Phys. 2008, 10, 6615.] with the help of Gaussian-09 [M. J. Frisch et al., Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [Mol. Phys. 2010, 108, 1965. || J. Chem. Phys. 2009, 130, 064108. || Chem. Phys. Lett. 2013, 582, 158. || J. Mol. Struct. - Theochem 2010, 961, 107.] for all atoms. The topological analysis of the electron density distribution (QTAIM) was performed using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Cartesian atomic coordinates for model supramolecular associates are presented in **Table S4.**

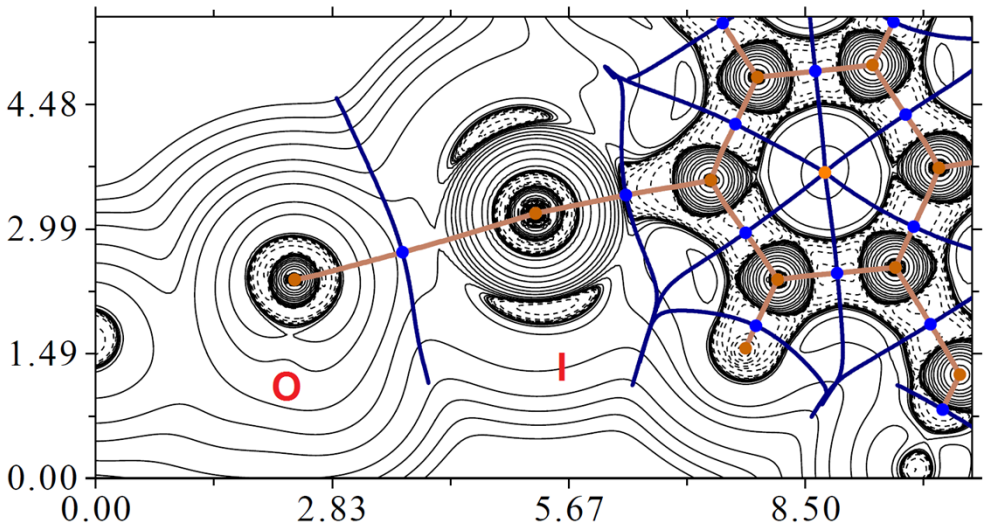

Figure S3. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces for intermolecular interactions I···O (halogen bonds, 2.995 Å) in **2**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å.

Table S3. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues, energy density – H_b, potential energy density – $V(\mathbf{r})$, Lagrangian kinetic energy – $G(\mathbf{r})$ at the bond critical points (3, –1), corresponding to intermolecular interactions I···O (halogen bonds) in **1**, and estimated strength for these interactions E_{int} (kcal/mol).

$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	Interatomic distances	E^a	E^b
0.020	0.075	0.001	-0.016	0.017	2.916	6.8	7.1
0.018	0.065	0.001	-0.014	0.015	2.995	6.0	6.3
0.013	0.053	0.001	-0.010	0.011	3.096	4.3	4.6
0.010	0.042	0.002	-0.007	0.009	3.231	3.0	3.8

a) E = 0.68(-V(r)), b) E = 0.67G(r) (see Bartashevich et al., Russ. Chem. Rev. 2014, 83,1181)

Table S4

Atom	X	Y	Z
N	7.93802300	11.70155200	18.01244100
C	8.48112700	10.49151700	18.36618100
H	8.18215500	9.80288800	17.73929700
H	8.17611700	10.25735000	19.27373600
H	9.45365500	10.55345000	18.35654500
O	7.02143900	10.83237200	16.07253100
C	7.98315200	12.81614800	18.97461400
H	8.85801500	13.25343100	18.93080600
H	7.84140100	12.46694200	19.88422100
H	7.28021500	13.46278400	18.76418100
C	7.15838200	11.72200300	16.83802400
H	6.69518800	12.52768200	16.65256500
I	2.19435500	16.19538400	9.35161200
I	5.64251700	12.27827900	13.94811000
I	9.64311900	10.25666800	14.27454100
I	13.63687300	6.76051800	9.74129200

I	6.05708000	1.22810100	-0.29926400
I	1.68517600	4.38373600	-4.71889200
O	1.55928200	17.03934100	12.38514500
O	1.05663900	15.32824900	13.52984800
O	6.85959700	13.28311900	9.60757800
O	6.43009400	11.55839300	10.97443000
O	9.50353000	11.44591100	11.22629300
O	9.00400000	9.73822700	9.76746900
O	14.12068700	5.84225500	12.85066700
O	14.55019000	7.52948700	14.05055300
O	6.64017700	1.76222000	-4.73021100
O	6.26825300	0.12270800	-3.27846200
O	1.23871100	4.05617500	-0.39477400
O	1.68222000	5.70591300	-1.62154400
C	1.74602300	15.85998300	12.73464000
C	2.86024000	15.02829700	12.11064300
C	3.24617100	15.05897400	10.71124700
C	4.30436600	14.36022100	10.33203800
H	4.58189400	14.43623200	9.42736900
C	5.04510300	13.51149200	11.17676900
C	4.66539800	13.42968700	12.51815100
C	3.57763500	14.19661100	12.96103400
H	3.32298300	14.14834600	13.87860700
C	6.21845500	12.73434300	10.63200900
C	9.61401800	10.22905900	10.90934200
C	10.66598900	9.37692100	11.56446800
C	11.45808000	8.60999700	10.67162800
H	11.30000400	8.63464100	9.73488200

C	12.50538200	7.80217100	11.22770800
C	10.92898200	9.34965300	12.83934700
C	11.98095300	8.51455800	13.43787500
H	12.10191400	8.46152100	14.37858300
C	12.79327400	7.81239700	12.55211000
C	13.87636800	7.02161300	13.15912800
C	1.87518500	4.53678000	-1.26214400
C	2.88980800	3.66078300	-1.94840000
C	3.07343600	3.58579500	-3.36760500
C	4.11295700	2.83250500	-3.83454200
H	4.25859900	2.80554300	-4.77774000
C	4.98130000	2.09285000	-3.01245000
C	4.77433000	2.17124600	-1.62720400
C	3.75348200	2.91771900	-1.09659400
H	3.62349500	2.93731800	-0.15625400
C	6.08306900	1.26798100	-3.67182100
O	15.01237200	5.32074700	7.50353300
N	15.91183800	6.13879900	5.59333700
C	15.08240000	6.20015200	6.59229900
H	14.49454100	6.94614800	6.64182200
C	15.99120300	7.30452300	4.74011600
H	16.61907100	7.13320900	4.01129800
H	16.30548700	8.07042400	5.27001900
H	15.10536900	7.50242300	4.37661300
C	16.75995100	5.10259900	5.37684800
H	17.53567100	5.18341600	5.96032100
H	17.05023900	5.11429100	4.43694700
H	16.29386200	4.25782400	5.55742500

O	-0.54932800	5.32074700	-6.64606700
N	0.35013800	6.13879900	-8.55626300
C	-0.47930000	6.20015200	-7.55730100
H	-1.06715900	6.94614800	-7.50777800
C	0.42950300	7.30452300	-9.40948400
H	1.05737100	7.13320900	-10.13830200
H	0.74378700	8.07042400	-8.87958100
H	-0.45633100	7.50242300	-9.77298700
C	1.19825100	5.10259900	-8.77275200
H	1.97397100	5.18341600	-8.18927900
H	1.48853900	5.11429100	-9.71265300
H	0.73216200	4.25782400	-8.59217500

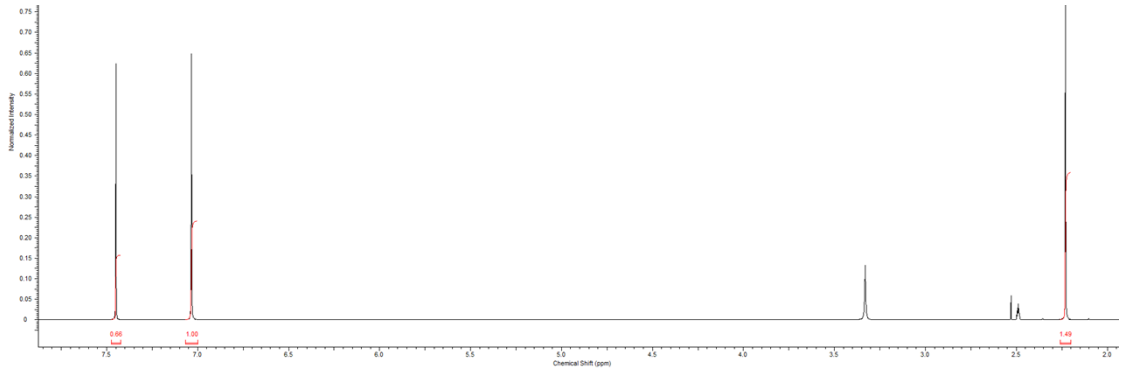

Figure S4. ^{1}H NMR spectrum for the d^{6}-DMSO extract after sorption of 1,4-dichlorobenzene: p-xylene mixture by activated sample of **2.**

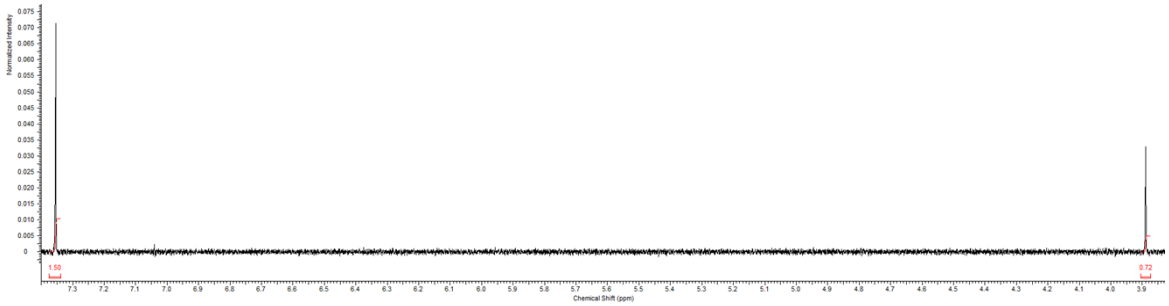

Figure S5. ^{1}H NMR spectrum for the d^{6}-DMSO extract after sorption of 1,2-dichloroethane: benzene mixture by activated sample of **2.**

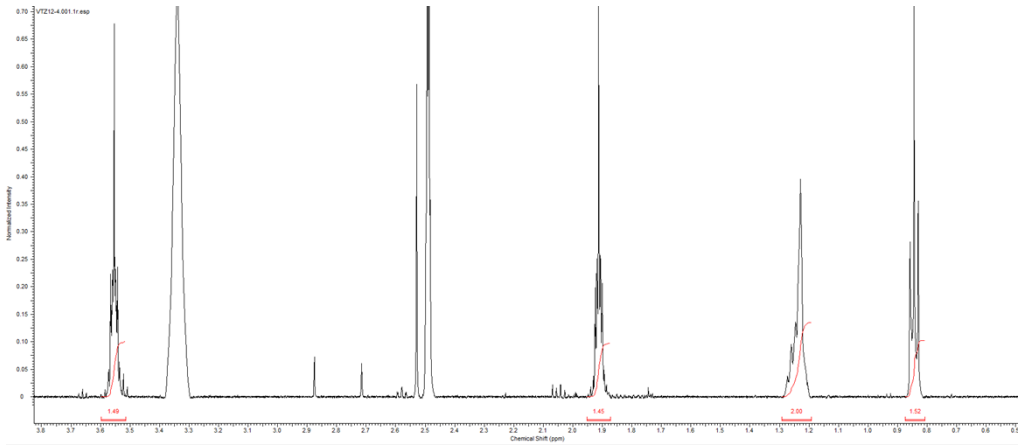

Figure S6. ^{1}H NMR spectrum for the d^{6}-DMSO extract after sorption of 1,4-dibromobutane: n-hexane mixture by activated sample of **2.**

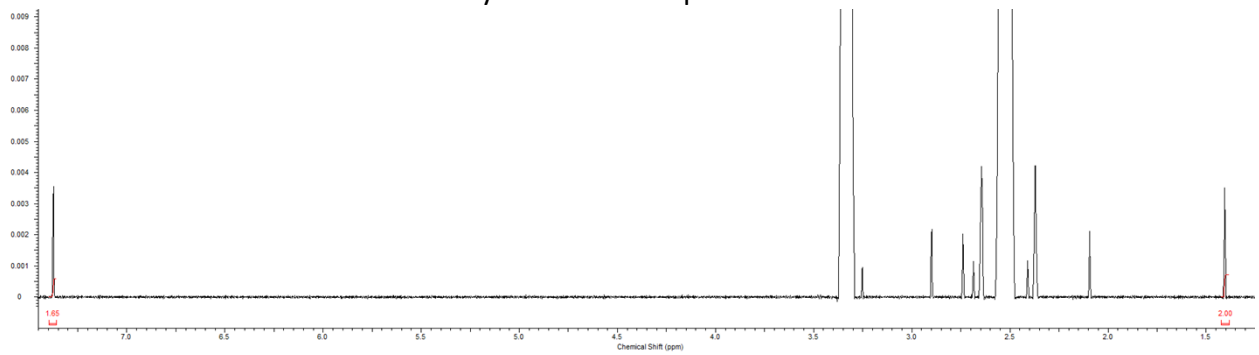

Figure S7. ^{1}H NMR spectrum for the d^{6}-DMSO extract after sorption of benzene: cyclohexane mixture by activated sample of **2.**