Water driven formation of channels: unusual solid-state structural transformation of a heterometallic polymer

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Empirical formula	$C_{39}H_{70}Cl_3CoN_{13}O_2P_4Ru_2S_2$
Formula weight	1308.50
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	18.4888(13)
b/Å	15.9993(12)
c/Å	17.5570(13)
α/°	90
β/°	96.1210(10)
γ/°	90
Volume/Å^3	5163.9(7)
Z	4
ρ_{calc}g/cm^3	1.683
μ/mm^{-1}	1.304
F(000)	2676.0
Crystal size/mm^3	0.182 × 0.063 × 0.058
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.374 to 53.464
Index ranges	-23 ≤ h ≤ 20, -20 ≤ k ≤ 18, -21 ≤ l ≤ 22
Reflections collected	16361
Independent reflections	5452 [R_{int} = 0.0256, R_{sigma} = 0.0293]
Data/restraints/parameters	5452/0/301
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0254, wR_2 = 0.0562
Final R indexes [all data]	R_1 = 0.0297, wR_2 = 0.0581
Largest diff. peak/hole / e Å^{-3}	0.44/-0.27

Table S1. Crystal data and structure refinement for **1·DMSO**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	P2	2.2615(5)	N11	C16	1.494(2)
Ru1	P1	2.2552(6)	N11	C13	1.487(3)
Ru1	C1P	2.0292(19)	N12	C14	1.456(3)
Ru1	C35	2.240(2)	N12	C11	1.472(3)
Ru1	C34	2.209(2)	N12	C15	1.461(3)
Ru1	C33	2.197(2)	N13	C16	1.463(3)
Ru1	C31	2.237(2)	N13	C12	1.470(3)
Ru1	C32	2.219(2)	N13	C15	1.472(3)
Ru1	N1P	2.0292(19)	N21	C25	1.466(3)
Co2	Cl1	2.3021(8)	N21	C22	1.475(3)
Co2	Cl2	2.3063(5)	N21	C26	1.467(3)
Co2	Cl2^1	2.3063(5)	N23	C25	1.469(3)
Co2	N11	2.2831(17)	N23	C21	1.472(3)

Co2	N11[1]	2.2831(17)	N23	C24	1.467(3)
P2	C22	1.849(2)	N22	C23	1.466(3)
P2	C23	1.841(2)	N22	C26	1.472(3)
P2	C21	1.847(2)	N22	C24	1.464(3)
P1	C11	1.849(2)	C1P	C1P[2]	1.147(4)
P1	C12	1.845(2)	C35	C34	1.434(3)
P1	C13	1.844(2)	C35	C31	1.406(3)
S1D	O1D	1.5037(17)	C34	C33	1.415(3)
S1D	C1D	1.781(2)	C33	C32	1.423(4)
S1D	C2D	1.783(2)	C31	C32	1.425(4)
N11	C14	1.494(2)			

Table S2. Bond Lengths for **1·DMSO**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P1	Ru1	P2	100.42(2)	C13	P1	C11	97.90(9)
C1P	Ru1	P2	86.61(5)	C13	P1	C12	98.17(10)
C1P	Ru1	P1	88.54(6)	O1D	S1D	C1D	106.91(11)
C1P	Ru1	C35	116.64(8)	O1D	S1D	C2D	106.27(11)
C1P	Ru1	C34	154.16(8)	C1D	S1D	C2D	97.02(13)
C1P	Ru1	C33	144.13(8)	C14	N11	Co2	109.10(12)
C1P	Ru1	C31	95.14(8)	C14	N11	C16	107.87(15)
C1P	Ru1	C32	107.68(9)	C16	N11	Co2	108.12(12)
C35	Ru1	P2	94.07(6)	C13	N11	Co2	111.32(12)
C35	Ru1	P1	151.73(6)	C13	N11	C14	110.13(15)
C34	Ru1	P2	95.83(6)	C13	N11	C16	110.21(16)
C34	Ru1	P1	116.09(6)	C14	N12	C11	111.76(16)
C34	Ru1	C35	37.59(8)	C14	N12	C15	109.13(16)
C34	Ru1	C31	62.25(9)	C15	N12	C11	110.72(16)
C34	Ru1	C32	62.68(9)	C16	N13	C12	110.94(17)
C33	Ru1	P2	128.81(7)	C16	N13	C15	108.82(16)
C33	Ru1	P1	89.83(6)	C12	N13	C15	111.33(16)
C33	Ru1	C35	62.36(9)	C25	N21	C22	111.17(17)
C33	Ru1	C34	37.47(8)	C25	N21	C26	108.35(18)
C33	Ru1	C31	62.35(9)	C26	N21	C22	111.16(18)
C33	Ru1	C32	37.60(9)	C25	N23	C21	110.18(18)
C31	Ru1	P2	124.06(6)	C24	N23	C25	107.96(17)
C31	Ru1	P1	135.49(6)	C24	N23	C21	111.11(17)
C31	Ru1	C35	36.60(8)	C23	N22	C26	110.79(17)
C32	Ru1	P2	155.61(7)	C24	N22	C23	111.14(17)
C32	Ru1	P1	99.62(7)	C24	N22	C26	108.17(18)
C32	Ru1	C35	62.03(8)	C1P[2]	C1P	Ru1	179.0(3)
C32	Ru1	C31	37.29(9)	N12	C14	N11	114.43(16)
N1P	Ru1	P2	86.61(5)	N12	C11	P1	112.76(14)
N1P	Ru1	P1	88.54(6)	N13	C16	N11	114.46(16)

N1P	Ru1	C35	116.64(8)	N13	C12	P1	112.84(14)
N1P	Ru1	C34	154.16(8)	N11	C13	P1	113.07(14)
N1P	Ru1	C33	144.13(8)	N12	C15	N13	113.99(17)
N1P	Ru1	C31	95.14(8)	N21	C25	N23	114.83(18)
N1P	Ru1	C32	107.68(9)	N21	C22	P2	112.50(15)
Cl1	Co2	Cl2	119.594(16)	N22	C23	P2	113.42(15)
Cl1	Co2	$Cl2^1$	119.593(16)	C34	C35	Ru1	70.04(12)
Cl2	Co2	$Cl2^1$	120.81(3)	C31	C35	Ru1	71.60(13)
N11	Co2	Cl1	88.89(4)	C31	C35	C34	108.1(2)
$N11^1$	Co2	Cl1	88.89(4)	N23	C21	P2	113.39(14)
N11	Co2	Cl2	90.24(4)	C35	C34	Ru1	72.37(12)
$N11^1$	Co2	$Cl2^1$	90.24(4)	C33	C34	Ru1	70.81(13)
N11	Co2	$Cl2^1$	90.86(4)	C33	C34	C35	107.5(2)
$N11^1$	Co2	Cl2	90.86(4)	N21	C26	N22	114.19(17)
$N11^1$	Co2	N11	177.78(9)	N22	C24	N23	114.89(18)
C22	P2	Ru1	127.17(7)	C34	C33	Ru1	71.72(13)
C23	P2	Ru1	116.65(7)	C34	C33	C32	108.5(2)
C23	P2	C22	97.37(10)	C32	C33	Ru1	72.02(14)
C23	P2	C21	97.36(10)	C35	C31	Ru1	71.79(12)
C21	P2	Ru1	115.49(7)	C35	C31	C32	108.5(2)
C21	P2	C22	97.23(10)	C32	C31	Ru1	70.64(12)
C11	P1	Ru1	113.81(7)	C33	C32	Ru1	70.39(12)
C12	P1	Ru1	120.08(7)	C33	C32	C31	107.4(2)
C12	P1	C11	96.70(10)	C31	C32	Ru1	72.07(12)
C13	P1	Ru1	124.74(7)				

Table S3. Bond Angles for **1·DMSO**.

Empirical formula	$C_{105}H_{234}Cl_7Co_2N_{39}O_{30}P_{12}Ru_6$
Formula weight	3807.29
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7090(9)
b/Å	16.0946(12)
c/Å	44.352(3)
α/°	90

β/°	91.6510(10)
γ/°	90
Volume/Å^3	8354.8(11)
Z	2
ρ_{calc}g/cm^3	1.513
μ/mm^{-1}	1.019
F(000)	3868.0
Crystal size/mm^3	0.051 × 0.019 × 0.015
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.128 to 52.04
Index ranges	-14 ≤ h ≤ 6, -19 ≤ k ≤ 19, -54 ≤ l ≤ 53
Reflections collected	45999
Independent reflections	16422 [R_{int} = 0.0471]
Data/restraints/parameters	16422/39/951
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0599, wR_2 = 0.1299
Final R indexes [all data]	R_1 = 0.0768, wR_2 = 0.1419
Largest diff. peak/hole / e Å^{-3}	1.14/-0.61

Table S4. Crystal data and structure refinement for **2·15H$_2$O**.

Note about the chloride position in the crystal structure of 2·15H$_2$O. More than one crystallographic position containing water molecules that could be a good candidate for the Cl atom. The possible alternative positions should be those in which: a) water molecules are not bonded by hydrogen bonds to PTA-N and b) are close to the cationic moiety. Additionally, changing the clusters of disordered water for Cl should cause in all the cases the instability of the refinement and/or an increase of the R factor. Thus we focused on the fully occupied water molecules that agree with the premises, being found three possible positions: position "A": Xfrac, Yfrac, Zfrac = 0.3386(6), 0.4898(4), 0.10347(18), which was finally assigned to O4; position "B": Xfrac, Yfrac, Zfrac = 0.9924(5), 0.3764(3), 0.15362(12), finally assigned O7; position "C": Xfrac, Yfrac, Zfrac = 0.8646(5), 0.3244(4), 0.10408(15), finally assigned to Cl4. The three possible crystallographic positions were assigned, two of them to 1 O and the remained possition to ½ Cl. The three possible different combinations display the next Uiso:

Entry 1: Cl4 in position C (final structure). Uiso: Cl4 = 0.092; O4 = 0.082; O7 = 0.055.
Entry 2: Cl4 in position A, O4 in position C. Uiso: Cl4 = 0.106; O4 = 0.068; O7 = 0.055.
Entry 3: Cl4 in position B, O7 in position C. Uiso: Cl4 = 0.079; O4 = 0.082; O7 = 0.068.

At this point it is important to stress that for each combination the R factor and the GooF remained always unaltered. After this evaluation we considered to discard position Entry 2 due to the high Uiso value when ½ Cl was locted in it. For what concern Entries 1 and 3, the Uiso are comparable, thus we decided to check the untied spatial occupancy factors:

Entry 1: Cl4 in position C, O7 in position B. sof: Cl4 = 0.4987; O7 = 1.1086.
Entry 3: Cl4 in position B, O7 in position C. sof: Cl4 = 0.5458; O7 = 1.0150.

Looking to these results we were inclined to assign the ½ Cl to position C but before to do it, we tried also to test the refinement with tied occupancy factors on Cl4 and O7 and riding hydrogens on O7.

Entry 1: Cl4 in position C, (H_2)O7 in position B. R% = 5.96.
Entry 3: Cl4 in position B, (H_2)O7 in position C. R% = 5.98.

The slight variation of the R factor let us to choose Entry 1, with O4 in position A, O7 in position B and Cl4 in position C (final structure).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	P4	2.2547(14)	N10	C27	1.466(7)
Ru1	P3	2.2552(14)	N10	C24	1.483(7)
Ru1	CCN	2.020(5)	N10	C29	1.464(7)
Ru1	C32	2.230(5)	NCN	CCN	1.140(7)
Ru1	C30	2.224(5)	N2	C4	1.467(7)
Ru1	C34	2.220(6)	N2	C3	1.484(7)
Ru1	C31	2.235(5)	N2	C6	1.458(8)
Ru1	C33	2.207(6)	N12	C28	1.463(7)
Ru1	NCN1	2.020(5)	N12	C27	1.465(7)
Ru2	P2	2.2641(14)	N12	C26	1.473(7)
Ru2	P1	2.2562(15)	N8	C19	1.481(7)
Ru2	NCN	2.025(5)	N8	C23	1.479(7)
Ru2	C15	2.219(6)	N8	C21	1.475(7)
Ru2	C13	2.205(6)	N3	C5	1.480(7)
Ru2	C17	2.230(6)	N3	C2	1.475(7)
Ru2	C14	2.209(6)	N3	C6	1.473(7)
Ru2	C16	2.225(6)	N5	C7	1.476(7)
Ru2	CCN1	2.025(5)	N5	C12	1.458(9)
Ru3	P5	2.2549(15)	N5	C10	1.455(8)
Ru3	P6	2.2619(15)	N6	C8	1.479(7)
Ru3	CCNM	2.013(5)	N6	C11	1.457(8)
Ru3	C49	2.236(6)	N6	C10	1.479(8)
Ru3	C50	2.223(6)	CCNM	$CCNM^3$	1.159(10)
Ru3	C51	2.209(6)	N14	C35	1.480(8)
Ru3	C47	2.245(6)	N14	C40	1.479(8)
Ru3	C48	2.233(6)	N14	C39	1.463(9)
Ru3	NCNM	2.013(5)	N16	C44	1.463(8)
Co1	Cl2	2.3311(14)	N16	C42	1.487(7)
Co1	Cl3	2.3433(14)	N16	C46	1.465(8)

Co1	Cl1	2.3220(14)	N15	C36	1.484(7)
Co1	N7[1]	2.283(4)	N15	C40	1.455(8)
Co1	N1	2.260(4)	N15	C38	1.459(8)
P4	C26	1.854(5)	N17	C41	1.489(8)
P4	C24	1.848(5)	N17	C44	1.451(8)
P4	C25	1.844(5)	N17	C45	1.446(9)
P3	C20	1.841(5)	N4	C9	1.483(7)
P3	C19	1.833(5)	N4	C12	1.474(8)
P3	C18	1.840(5)	N4	C11	1.462(8)
P2	C7	1.852(6)	N13	C37	1.486(8)
P2	C8	1.852(6)	N13	C38	1.460(8)
P2	C9	1.840(6)	N13	C39	1.479(9)
P5	C36	1.844(6)	N18	C43	1.490(8)
P5	C35	1.836(6)	N18	C46	1.469(9)
P5	C37	1.847(6)	N18	C45	1.468(10)
P6	C41	1.844(6)	C32	C31	1.435(8)
P6	C42	1.839(6)	C32	C33	1.415(8)
P6	C43	1.848(6)	C49	C50	1.428(9)
P1	C1	1.835(5)	C49	C48	1.396(9)
P1	C2	1.837(6)	C30	C34	1.429(9)
P1	C3	1.846(6)	C30	C31	1.393(8)
N7	Co1[2]	2.283(4)	C15	C14	1.422(9)
N7	C22	1.490(7)	C15	C16	1.417(9)
N7	C20	1.489(6)	C50	C51	1.406(9)
N7	C21	1.485(6)	C13	C17	1.407(10)
N11	C28	1.472(7)	C13	C14	1.411(9)
N11	C29	1.483(7)	C34	C33	1.416(9)
N11	C25	1.483(7)	C17	C16	1.401(9)
N1	C4	1.488(6)	C51	C47	1.422(9)
N1	C1	1.496(7)	C47	C48	1.428(10)
N1	C5	1.487(7)	O14C	O14D	1.81(4)
N9	C22	1.471(6)	CCN1	NCN1	1.140(7)
N9	C23	1.470(7)	NCNM	NCNM[3]	1.159(10)
N9	C18	1.478(7)			

Table S5. Bond Lengths for **2·15H$_2$O**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P4	Ru1	P3	94.04(5)	C2	P1	C3	97.3(3)

CCN	Ru1	P4	89.08(14)	C3	P1	Ru2	116.51(18)
CCN	Ru1	P3	85.89(14)	C22	N7	Co1[2]	113.4(3)
CCN	Ru1	C32	154.2(2)	C20	N7	Co1[2]	107.2(3)
CCN	Ru1	C30	93.9(2)	C20	N7	C22	109.5(4)
CCN	Ru1	C34	104.5(2)	C21	N7	Co1[2]	108.5(3)
CCN	Ru1	C31	117.2(2)	C21	N7	C22	107.8(4)
CCN	Ru1	C33	140.4(2)	C21	N7	C20	110.4(4)
C32	Ru1	P4	115.40(15)	C28	N11	C29	108.1(4)
C32	Ru1	P3	99.55(17)	C28	N11	C25	110.6(4)
C32	Ru1	C31	37.5(2)	C25	N11	C29	110.3(4)
C30	Ru1	P4	142.71(17)	C4	N1	Co1	110.5(3)
C30	Ru1	P3	123.24(16)	C4	N1	C1	109.6(4)
C30	Ru1	C32	61.9(2)	C1	N1	Co1	108.1(3)
C30	Ru1	C31	36.4(2)	C5	N1	Co1	109.9(3)
C34	Ru1	P4	105.98(17)	C5	N1	C4	108.4(4)
C34	Ru1	P3	157.40(16)	C5	N1	C1	110.4(4)
C34	Ru1	C32	62.6(2)	C22	N9	C18	112.4(4)
C34	Ru1	C30	37.5(2)	C23	N9	C22	108.4(4)
C34	Ru1	C31	62.1(2)	C23	N9	C18	110.6(4)
C31	Ru1	P4	152.60(15)	C27	N10	C24	109.6(4)
C31	Ru1	P3	95.26(15)	C29	N10	C27	109.0(4)
C33	Ru1	P4	93.31(15)	C29	N10	C24	111.6(4)
C33	Ru1	P3	133.15(18)	CCN	NCN	Ru2	176.2(5)
C33	Ru1	C32	37.2(2)	C4	N2	C3	111.4(4)
C33	Ru1	C30	61.8(2)	C6	N2	C4	108.9(4)
C33	Ru1	C34	37.3(2)	C6	N2	C3	112.0(4)
C33	Ru1	C31	61.9(2)	NCN	CCN	Ru1	177.5(5)
NCN1	Ru1	P4	89.08(14)	C28	N12	C27	108.3(4)
NCN1	Ru1	P3	85.89(14)	C28	N12	C26	111.7(4)
NCN1	Ru1	C32	154.2(2)	C27	N12	C26	111.5(4)
NCN1	Ru1	C30	93.9(2)	C23	N8	C19	111.9(4)
NCN1	Ru1	C34	104.5(2)	C21	N8	C19	110.4(4)
NCN1	Ru1	C31	117.2(2)	C21	N8	C23	108.7(4)
NCN1	Ru1	C33	140.4(2)	C2	N3	C5	111.7(4)
P1	Ru2	P2	96.28(5)	C6	N3	C5	108.3(4)
NCN	Ru2	P2	83.63(14)	C6	N3	C2	111.4(4)
NCN	Ru2	P1	90.25(14)	C12	N5	C7	111.1(5)
NCN	Ru2	C15	111.2(2)	C10	N5	C7	111.7(5)
NCN	Ru2	C13	146.8(2)	C10	N5	C12	109.4(5)
NCN	Ru2	C17	109.9(2)	C8	N6	C10	110.2(5)
NCN	Ru2	C14	148.6(2)	C11	N6	C8	110.6(5)
NCN	Ru2	C16	93.0(2)	C11	N6	C10	108.6(5)
C15	Ru2	P2	159.66(17)	CCNM[3]	CCNM	Ru3	178.4(7)
C15	Ru2	P1	97.51(17)	C40	N14	C35	110.5(5)
C15	Ru2	C17	62.0(2)	C39	N14	C35	110.2(5)
C15	Ru2	C16	37.2(2)	C39	N14	C40	108.9(5)

C13	Ru2	P2	97.79(17)	C44	N16	C42	110.5(5)
C13	Ru2	P1	122.29(19)	C44	N16	C46	109.0(5)
C13	Ru2	C15	62.1(2)	C46	N16	C42	110.4(5)
C13	Ru2	C17	37.0(3)	C40	N15	C36	111.0(5)
C13	Ru2	C14	37.3(2)	C40	N15	C38	109.1(5)
C13	Ru2	C16	61.5(2)	C38	N15	C36	111.0(5)
C17	Ru2	P2	100.43(18)	C44	N17	C41	110.2(5)
C17	Ru2	P1	154.97(18)	C45	N17	C41	110.9(5)
C14	Ru2	P2	126.96(17)	C45	N17	C44	109.0(5)
C14	Ru2	P1	92.81(17)	N9	C22	N7	114.0(4)
C14	Ru2	C15	37.5(2)	C12	N4	C9	110.6(5)
C14	Ru2	C17	62.2(2)	C11	N4	C9	111.5(5)
C14	Ru2	C16	62.1(2)	C11	N4	C12	109.0(5)
C16	Ru2	P2	132.22(18)	N7	C20	P3	114.3(3)
C16	Ru2	P1	131.46(18)	N2	C4	N1	114.0(4)
C16	Ru2	C17	36.7(2)	N1	C1	P1	113.7(3)
CCN1	Ru2	P2	83.63(14)	N12	C28	N11	114.5(4)
CCN1	Ru2	P1	90.25(14)	N12	C27	N10	114.3(4)
CCN1	Ru2	C15	111.2(2)	C38	N13	C37	111.5(5)
CCN1	Ru2	C13	146.8(2)	C38	N13	C39	108.3(5)
CCN1	Ru2	C17	109.9(2)	C39	N13	C37	110.5(5)
CCN1	Ru2	C14	148.6(2)	N12	C26	P4	112.4(4)
CCN1	Ru2	C16	93.0(2)	N8	C19	P3	112.3(3)
P5	Ru3	P6	96.41(6)	N10	C24	P4	112.9(4)
CCNM	Ru3	P5	87.75(15)	N10	C29	N11	114.7(4)
CCNM	Ru3	P6	86.43(15)	N9	C23	N8	114.0(4)
CCNM	Ru3	C49	112.2(2)	N8	C21	N7	114.6(4)
CCNM	Ru3	C50	149.5(2)	N3	C5	N1	113.7(4)
CCNM	Ru3	C51	147.7(2)	N15	C36	P5	112.7(4)
CCNM	Ru3	C47	110.7(2)	N9	C18	P3	112.9(4)
CCNM	Ru3	C48	94.4(2)	C46	N18	C43	110.9(6)
C49	Ru3	P5	98.15(18)	C45	N18	C43	110.4(6)
C49	Ru3	P6	156.72(17)	C45	N18	C46	109.1(5)
C49	Ru3	C47	62.0(2)	N11	C25	P4	113.3(4)
C50	Ru3	P5	94.59(18)	C31	C32	Ru1	71.4(3)
C50	Ru3	P6	123.37(17)	C33	C32	Ru1	70.5(3)
C50	Ru3	C49	37.4(2)	C33	C32	C31	106.6(5)
C50	Ru3	C47	62.1(2)	N5	C7	P2	112.1(4)
C50	Ru3	C48	61.4(2)	N3	C2	P1	112.7(4)
C51	Ru3	P5	123.97(17)	C50	C49	Ru3	70.8(3)
C51	Ru3	P6	94.78(17)	C48	C49	Ru3	71.6(3)
C51	Ru3	C49	62.0(2)	C48	C49	C50	107.4(6)
C51	Ru3	C50	37.0(2)	N6	C8	P2	113.4(4)
C51	Ru3	C47	37.2(2)	N4	C9	P2	112.2(4)
C51	Ru3	C48	61.6(2)	C34	C30	Ru1	71.1(3)
C47	Ru3	P5	156.54(17)	C31	C30	Ru1	72.2(3)

C47	Ru3	P6	99.04(17)	C31	C30	C34	109.2(5)
C48	Ru3	P5	130.75(19)	C14	C15	Ru2	70.9(3)
C48	Ru3	P6	132.84(19)	C16	C15	Ru2	71.6(3)
C48	Ru3	C49	36.4(2)	C16	C15	C14	107.4(6)
C48	Ru3	C47	37.2(2)	N17	C41	P6	112.9(4)
NCNM	Ru3	P5	87.75(15)	N2	C3	P1	112.1(4)
NCNM	Ru3	P6	86.43(15)	C49	C50	Ru3	71.8(3)
NCNM	Ru3	C49	112.2(2)	C51	C50	Ru3	71.0(3)
NCNM	Ru3	C50	149.5(2)	C51	C50	C49	107.8(6)
NCNM	Ru3	C51	147.7(2)	C17	C13	Ru2	72.5(3)
NCNM	Ru3	C47	110.7(2)	C17	C13	C14	109.0(6)
NCNM	Ru3	C48	94.4(2)	C14	C13	Ru2	71.5(3)
Cl2	Co1	Cl3	120.48(6)	C30	C34	Ru1	71.4(3)
Cl1	Co1	Cl2	114.36(6)	C33	C34	Ru1	70.9(3)
Cl1	Co1	Cl3	125.16(6)	C33	C34	C30	106.4(5)
$N7^{1}$	Co1	Cl2	90.35(11)	C13	C17	Ru2	70.5(3)
$N7^{1}$	Co1	Cl3	89.68(11)	C16	C17	Ru2	71.5(3)
$N7^{1}$	Co1	Cl1	90.04(11)	C16	C17	C13	107.5(6)
N1	Co1	Cl2	91.66(12)	N14	C35	P5	113.6(4)
N1	Co1	Cl3	87.97(11)	C15	C14	Ru2	71.7(3)
N1	Co1	Cl1	90.54(12)	C13	C14	Ru2	71.2(3)
N1	Co1	$N7^{1}$	177.47(16)	C13	C14	C15	107.3(6)
C26	P4	Ru1	117.77(18)	N17	C44	N16	115.1(5)
C24	P4	Ru1	121.53(17)	C32	C31	Ru1	71.1(3)
C24	P4	C26	96.4(3)	C30	C31	Ru1	71.4(3)
C25	P4	Ru1	119.96(18)	C30	C31	C32	108.3(5)
C25	P4	C26	97.0(2)	N5	C12	N4	113.8(5)
C25	P4	C24	98.9(2)	C50	C51	Ru3	72.1(3)
C20	P3	Ru1	122.81(17)	C50	C51	C47	109.2(6)
C19	P3	Ru1	118.63(17)	C47	C51	Ru3	72.8(3)
C19	P3	C20	98.1(2)	N2	C6	N3	113.7(5)
C19	P3	C18	98.8(3)	C32	C33	Ru1	72.3(3)
C18	P3	Ru1	117.26(18)	C32	C33	C34	109.5(5)
C18	P3	C20	96.3(2)	C34	C33	Ru1	71.8(3)
C7	P2	Ru2	122.4(2)	C15	C16	Ru2	71.2(3)
C8	P2	Ru2	113.91(19)	C17	C16	Ru2	71.9(3)
C8	P2	C7	96.9(3)	C17	C16	C15	108.8(6)
C9	P2	Ru2	122.59(19)	C51	C47	Ru3	70.0(3)
C9	P2	C7	98.1(3)	C51	C47	C48	105.8(6)
C9	P2	C8	97.5(3)	C48	C47	Ru3	70.9(4)
C36	P5	Ru3	121.7(2)	N16	C42	P6	113.1(4)
C36	P5	C37	97.8(3)	N6	C11	N4	114.6(5)
C35	P5	Ru3	115.3(2)	N13	C37	P5	112.3(4)
C35	P5	C36	97.1(3)	N15	C40	N14	113.9(5)
C35	P5	C37	97.7(3)	N5	C10	N6	113.9(5)
C37	P5	Ru3	122.0(2)	N15	C38	N13	114.7(5)

C41	P6	Ru3	114.3(2)	N18	C43	P6	112.5(4)
C41	P6	C43	97.5(3)	C49	C48	Ru3	71.9(4)
C42	P6	Ru3	122.6(2)	C49	C48	C47	109.8(6)
C42	P6	C41	97.3(3)	C47	C48	Ru3	71.9(3)
C42	P6	C43	97.5(3)	N14	C39	N13	114.4(5)
C43	P6	Ru3	122.3(2)	N16	C46	N18	113.7(5)
C1	P1	Ru2	119.99(17)	N17	C45	N18	114.8(5)
C1	P1	C2	98.5(2)	NCN1	CCN1	Ru2	176.2(5)
C1	P1	C3	97.6(2)	CCN1	NCN1	Ru1	177.5(5)
C2	P1	Ru2	121.99(18)	NCNM	NCNM	Ru3	178.4(7)

Table S6. Bond Angles for **2·15H_2O**.

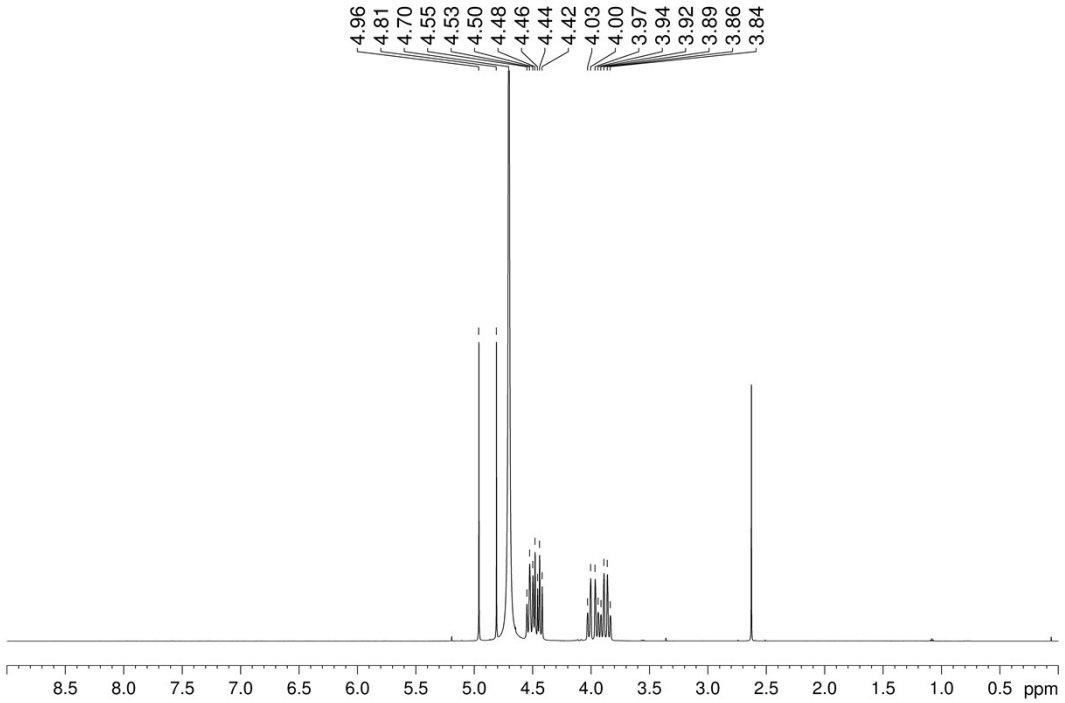

Figure S1. ^{1}H NMR spectrum of **1·DMSO** in D_2O.

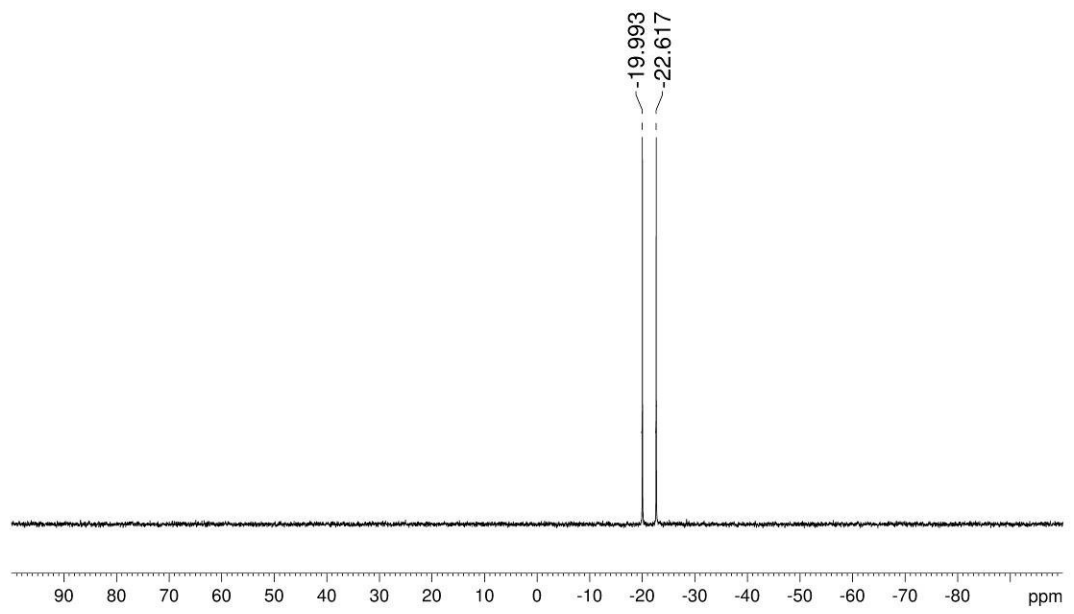

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **1·DMSO** in D_2O.

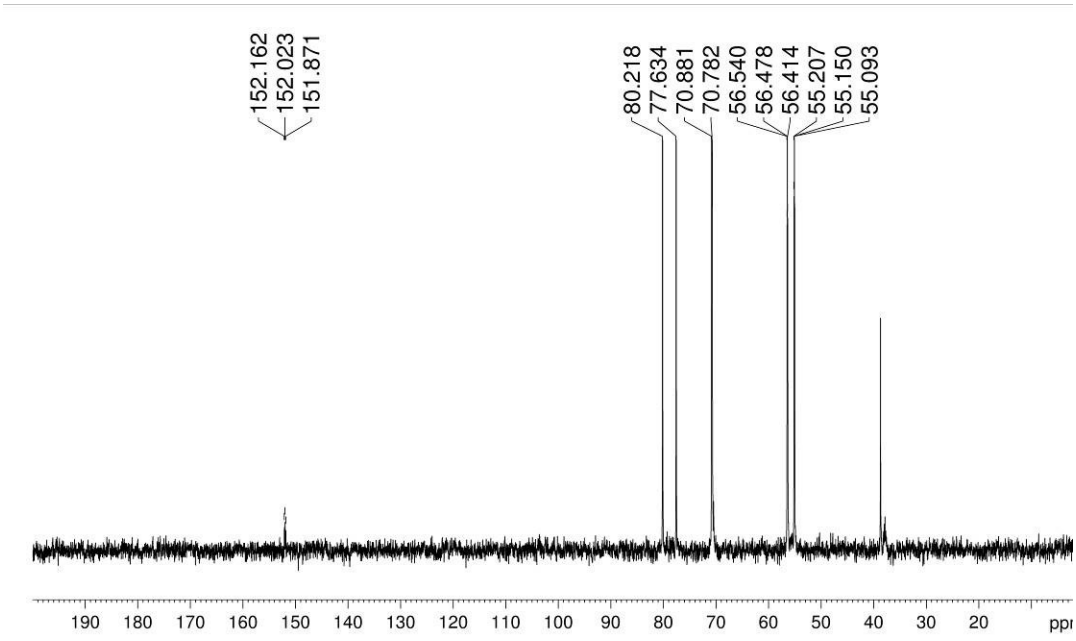

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1·DMSO** in D_2O.

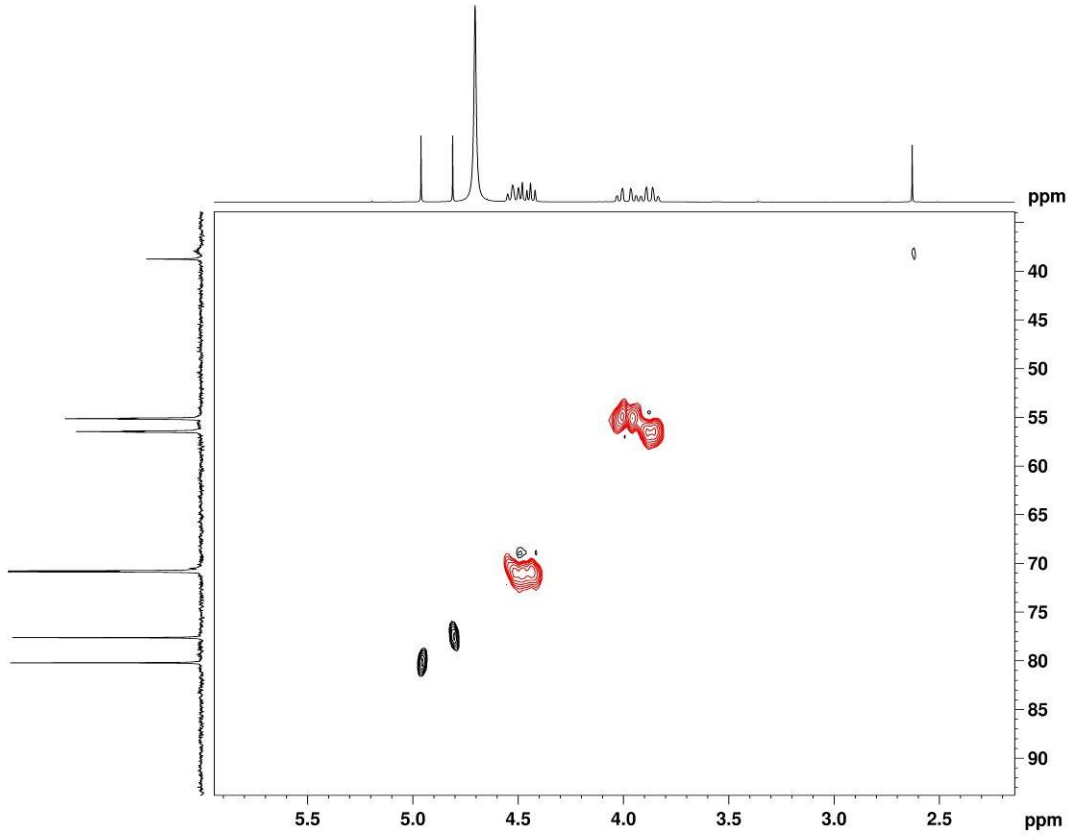

Figure S4. ^{1}H-^{13}C NMR HSQC-DEPT spectrum of **1·DMSO** in D_2O.

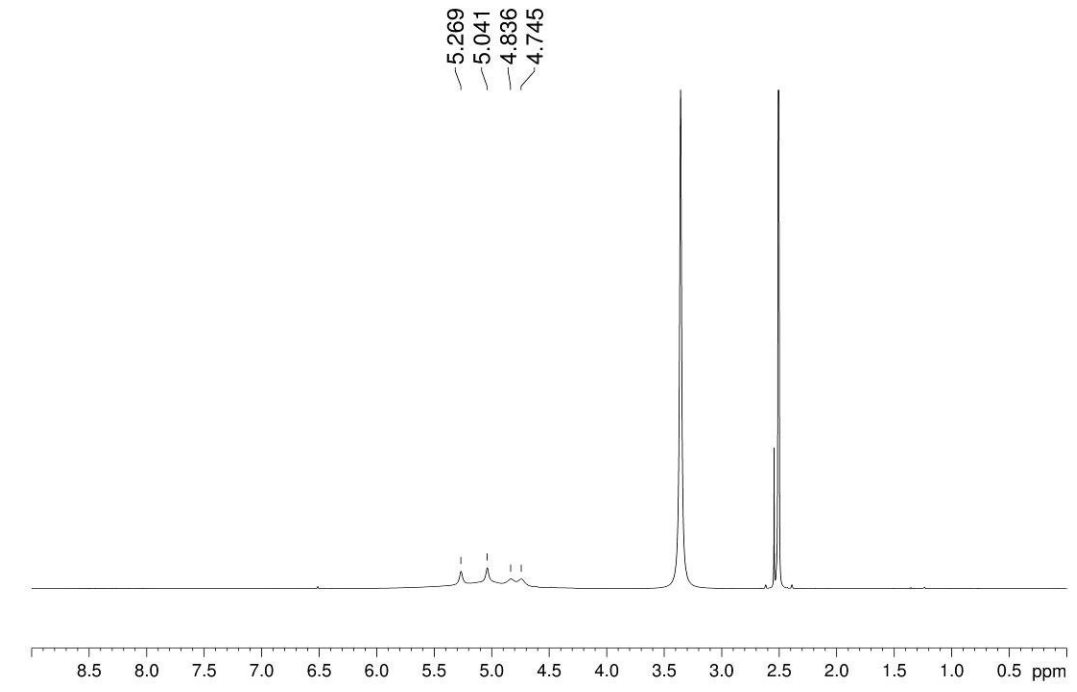

Figure S5. ^{1}H NMR spectrum of **1·DMSO** in DMSO-d6.

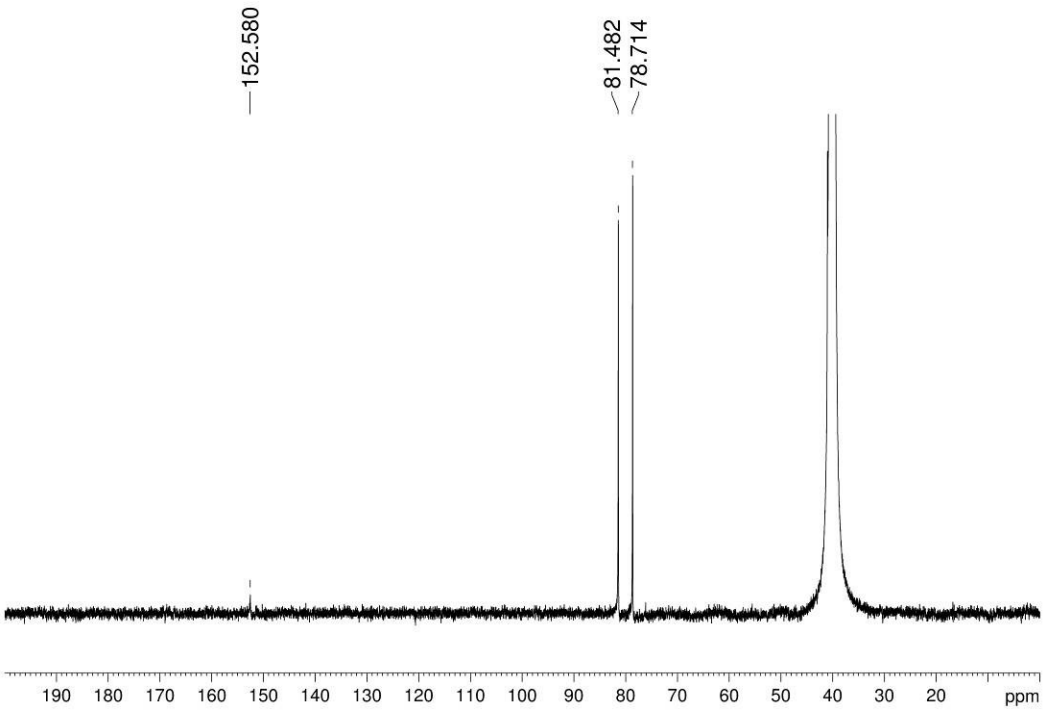

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1·DMSO** in DMSO-d6.

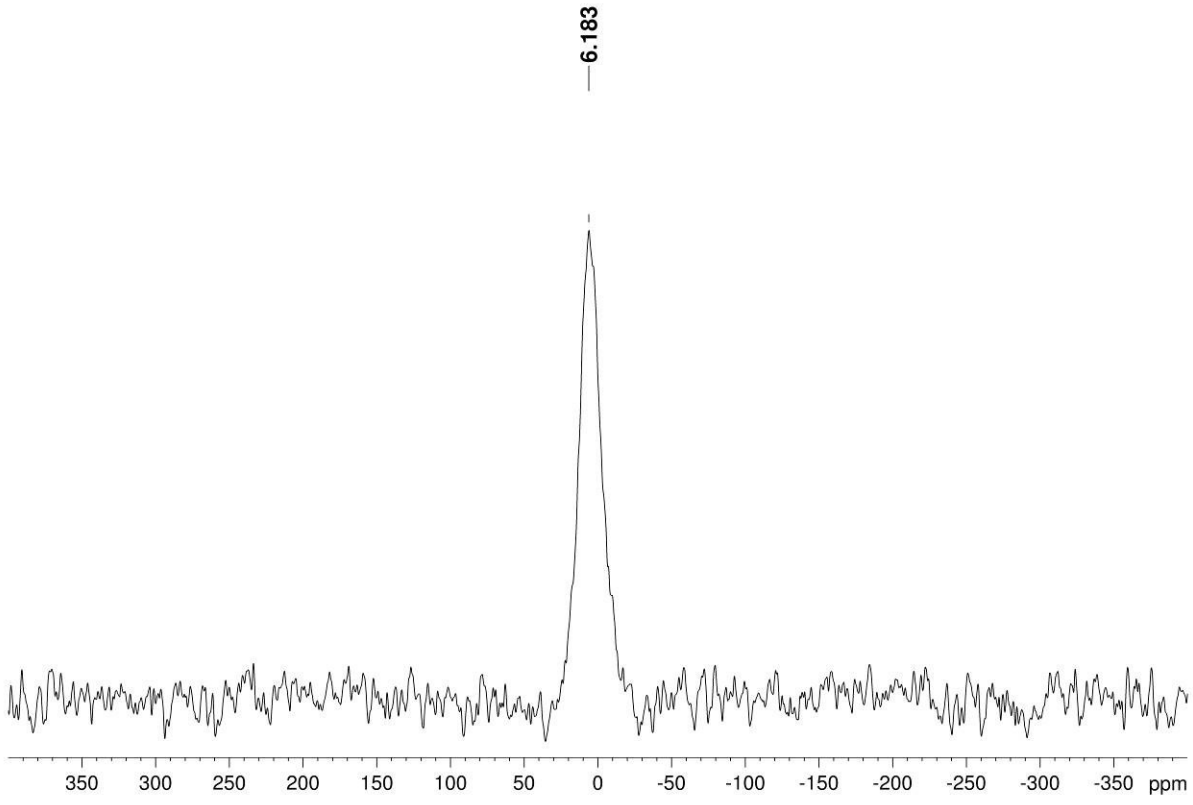

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **1·DMSO** in DMSO-d6.

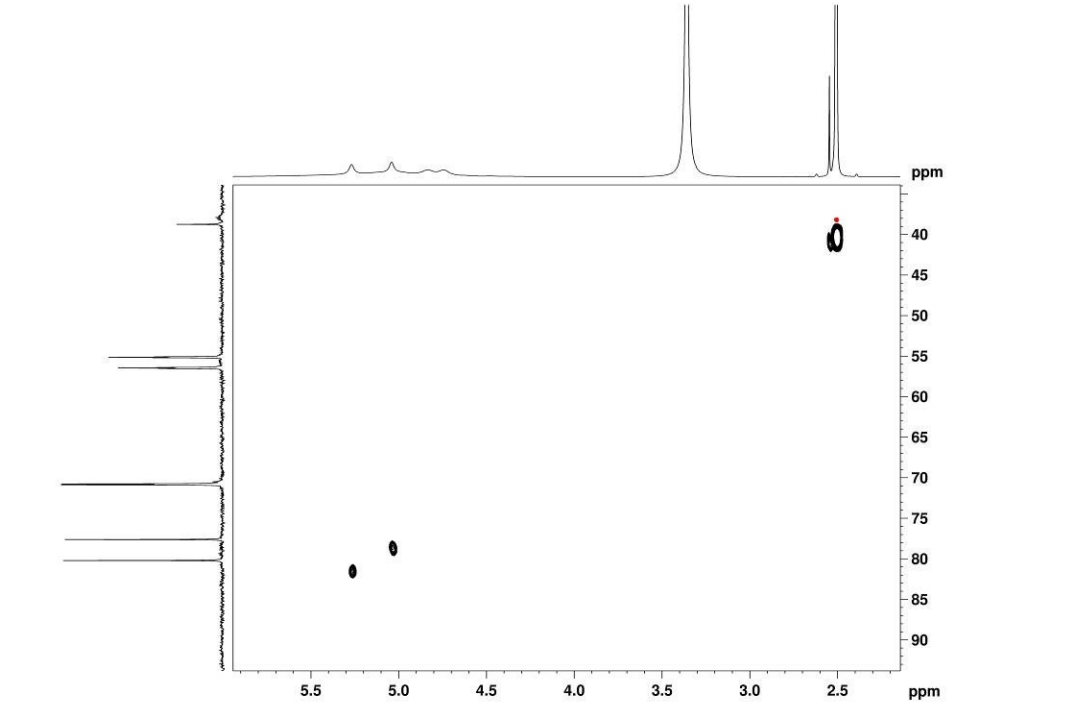

Figure S8. ^{1}H-^{13}C NMR HSQC-DEPT spectrum of **1·DMSO** in DMSO-d6.

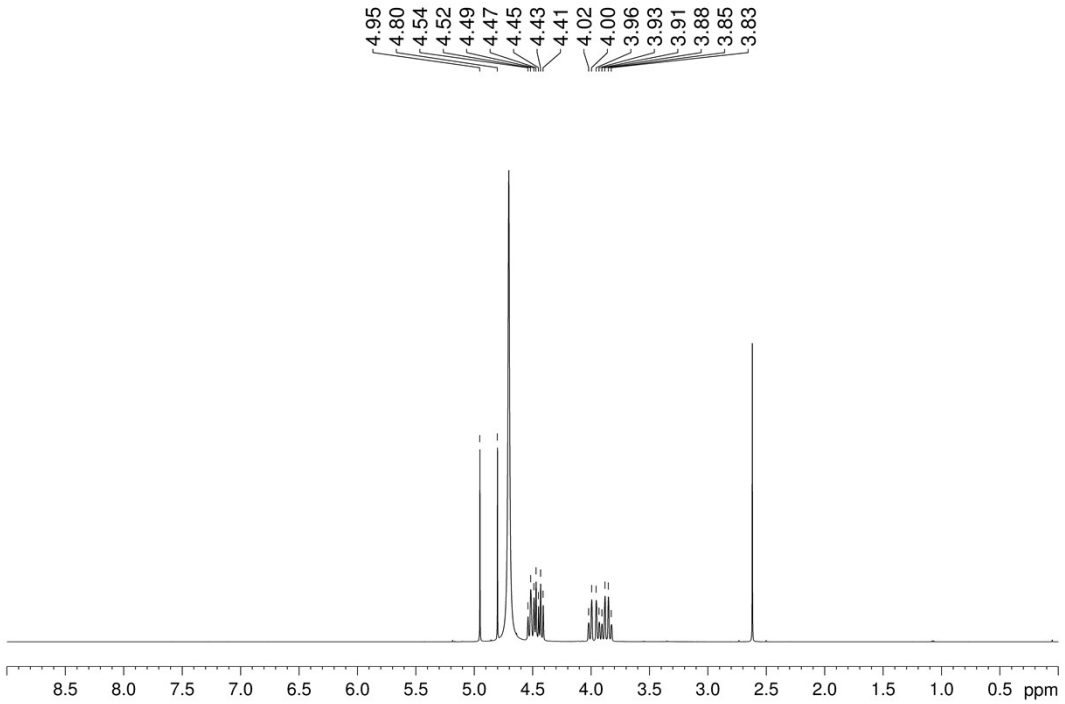

Figure S9. ^{1}H NMR spectrum of **2·15H$_2$O** in D_2O.

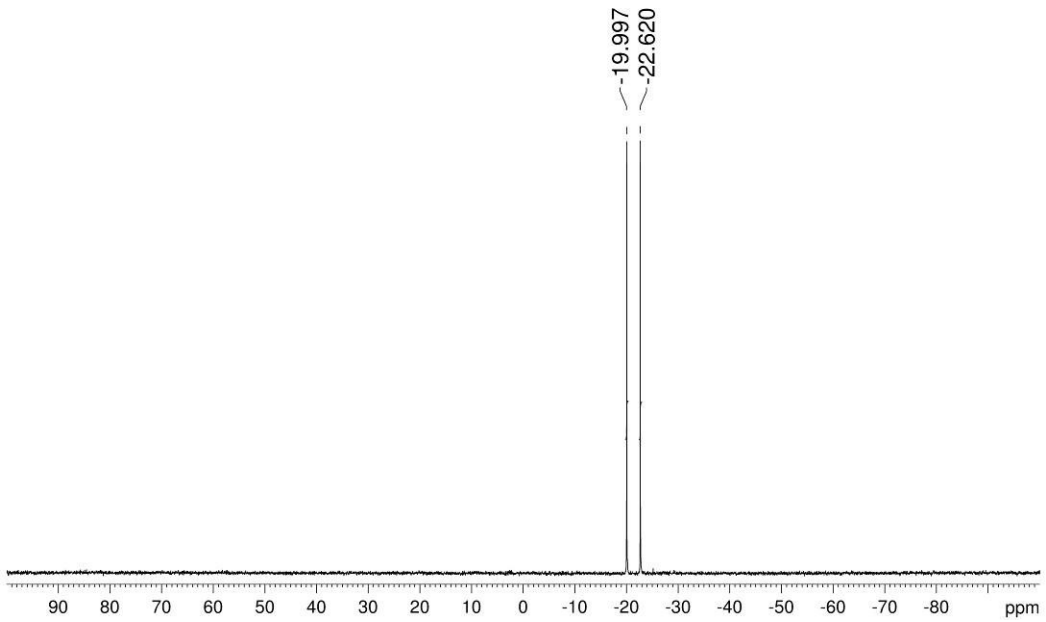

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **2·15H$_2$O** in D_2O.

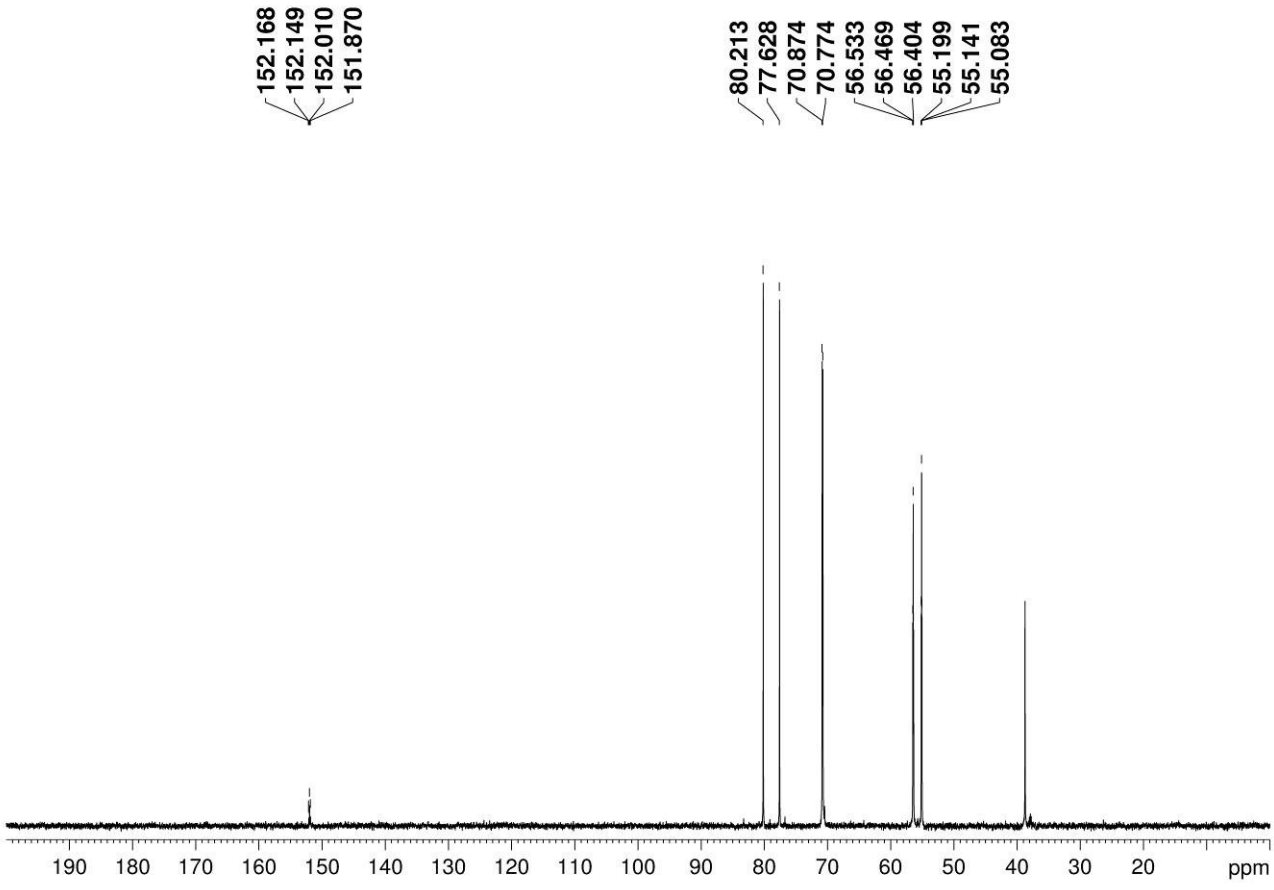

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2·15H$_2$O** in D_2O.

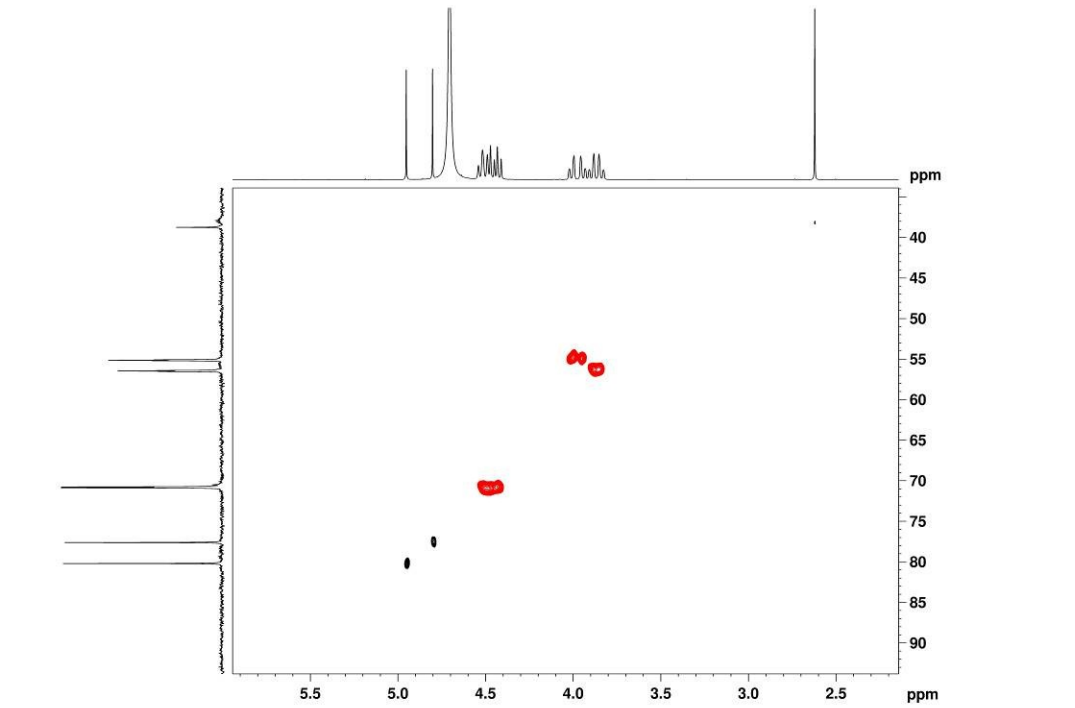

Figure S12. ^{1}H-^{13}C NMR HSQC-DEPT spectrum of **2·15H$_2$O** in D_2O

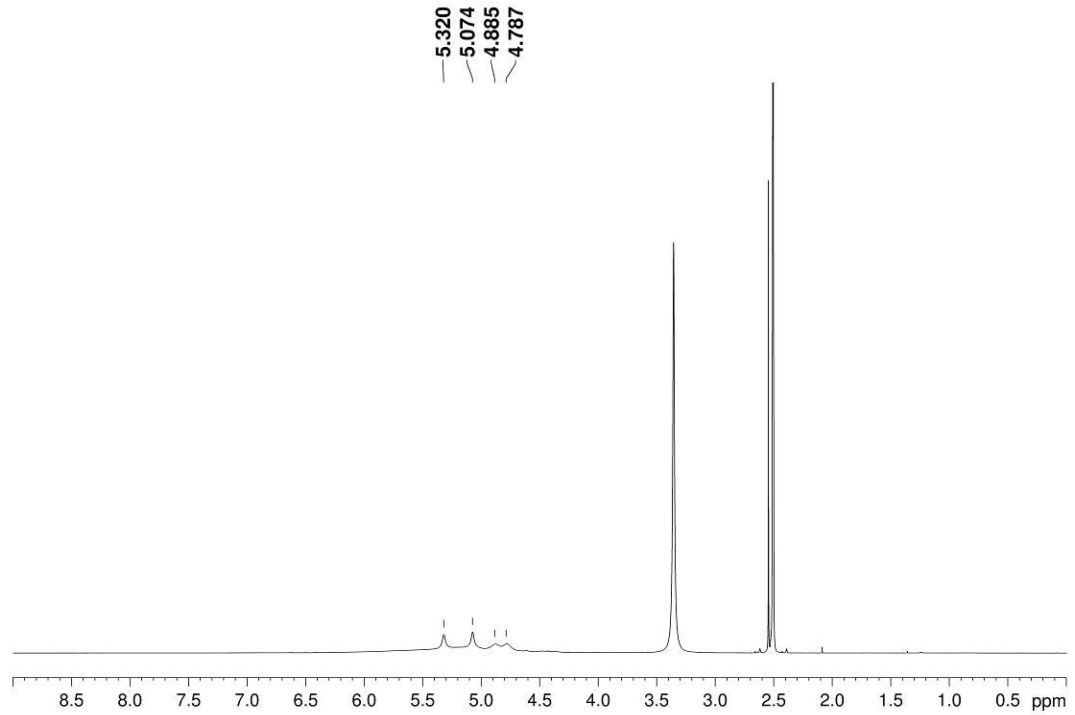

Figure S13. ^{1}H NMR spectrum of **2·15H$_2$O** in DMSO-d6.

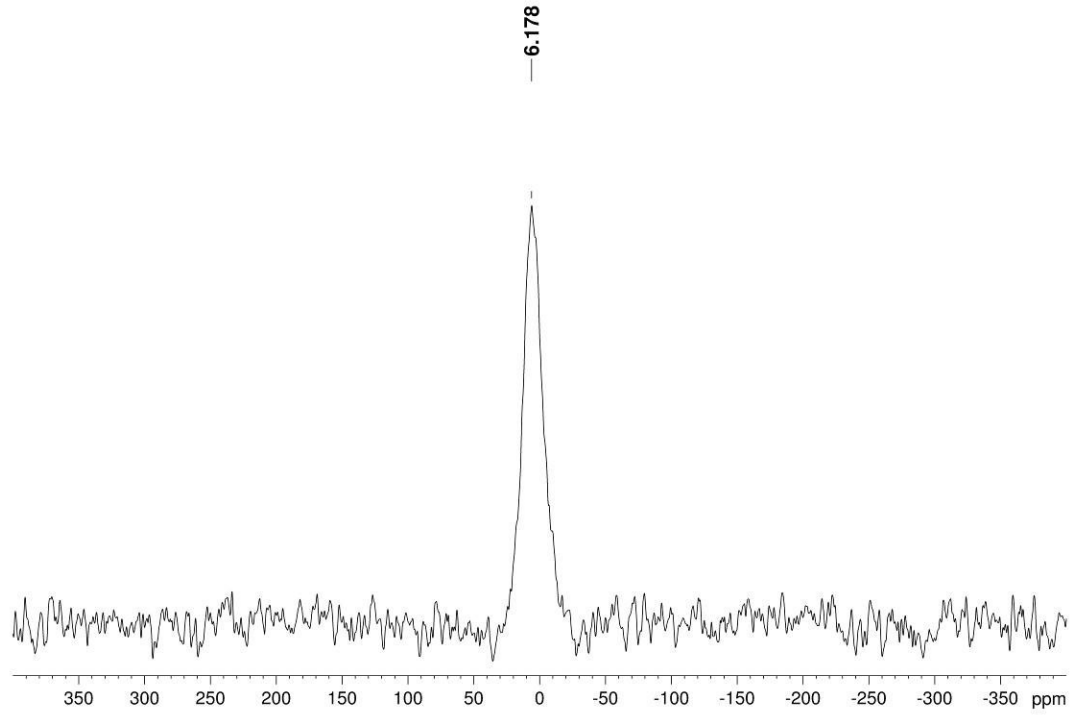

Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of **2·15H$_2$O** in DMSO-d6.

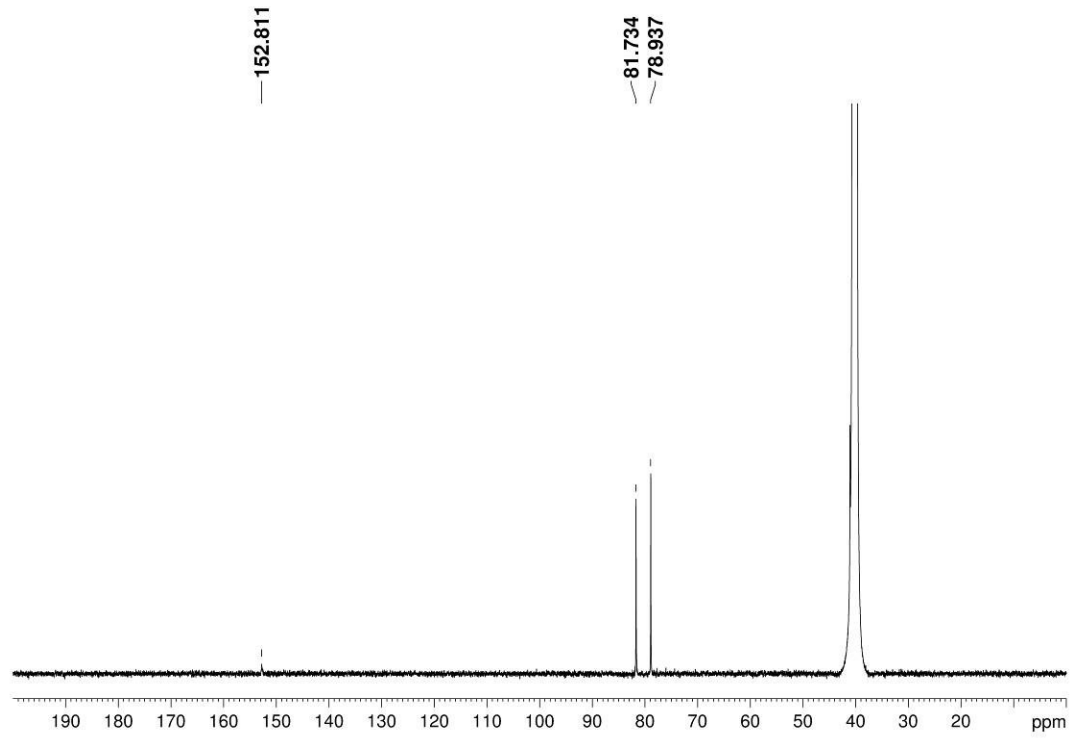

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **2·15H$_2$O** in DMSO-d6

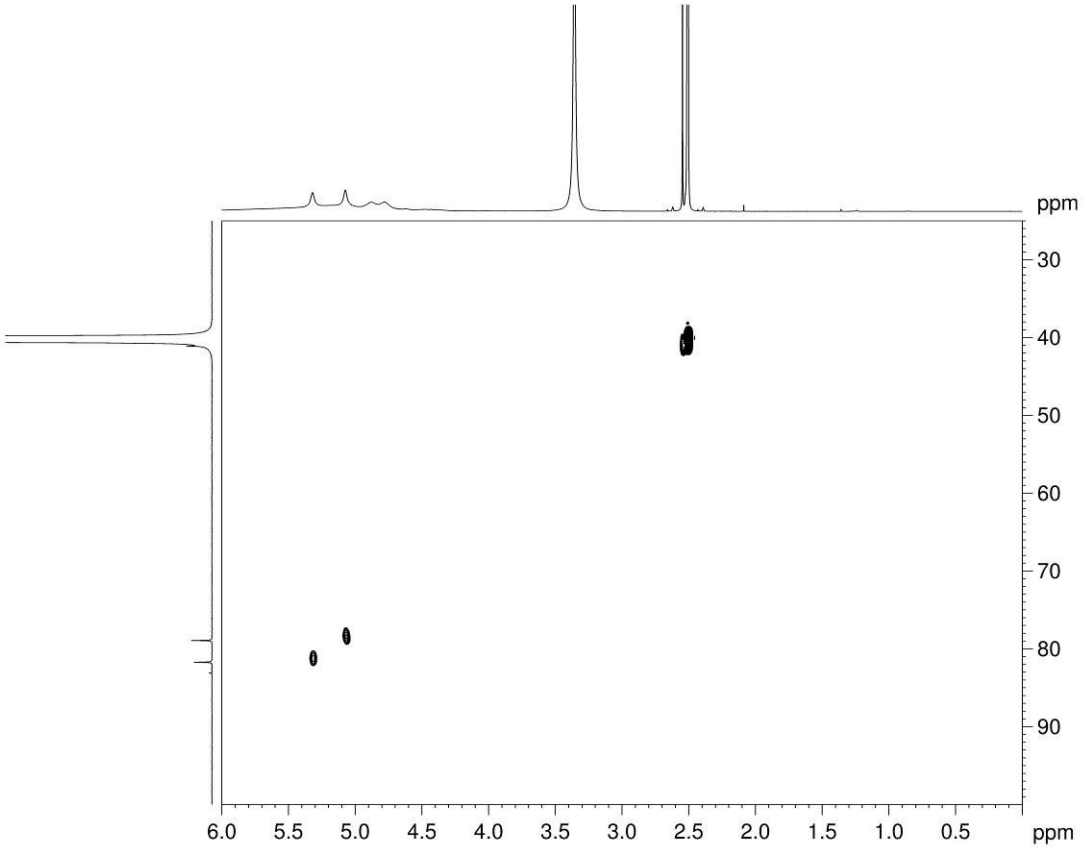

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Figure S16. ^{1}H-^{13}C NMR HSQC-DEPT spectrum of **2·15H$_2$O** in DMSO-d6.

NMR diffusion measurements. Diffusion-Order Spectroscopy (DOSY) measurements have been carried out on a Bruker AV500 spectrometer operating at 500.13 MHz for ^{1}H, using Δ = 3.6 - 4.0 msec and δ = 83.9 - 99.9 msec. The observed diffusion coefficients were calibrated against the residual solvent. The shape of the gradient pulse was rectangular and its strength varied automatically in the course of the experiments. The diffusion coefficients (D) was determined from the slope of the regression line ln(I/I0) versus G^2 according to $\ln(I/I_0) = -D(\mu G\delta)^2(\Delta-\delta/3)$, in which: I and I_0 are the observed spin echo intensity with and without gradients, respectively; G is the gradient strength; Δ is the delay between the mid-points of the gradients; D is the diffusion coefficient; δ is the gradient length. The calibration of the gradients was carried out by a diffusion measurement of HDO in D_2O. The experimental error in the D values was estimated to be ±2%.[1] All the data leading to the reported D values afforded lines with correlation coefficients of >0.999 and 64 points were used for regression analysis. The gradient strength was increased in 1.5 % steps

from 2%. A measurement of ^{1}H NMR spectrum and T_1 was carried out before each diffusion experiment and the recovery delay (ca. 5-8 sec) set to five times T_1. The number of scans was set to 16 per increment. Typical experiment duration is 1.5-3 h.[2]

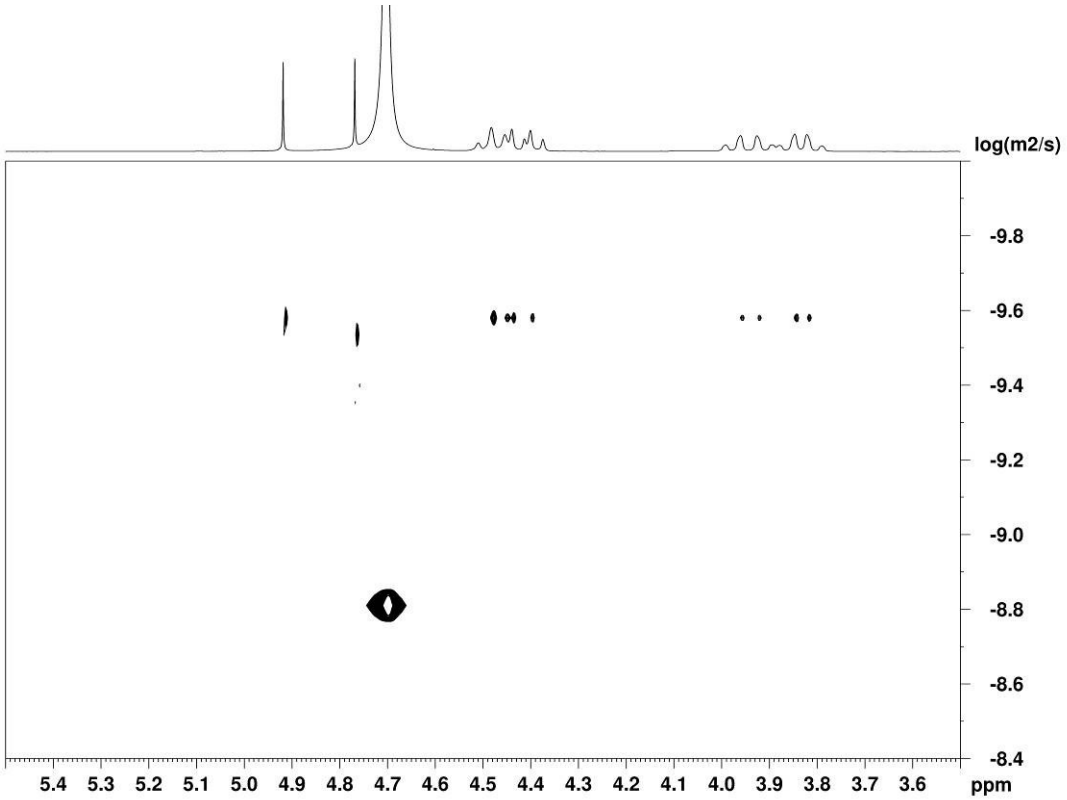

Figure S17. ^{1}H DOSY spectrum of **1·DMSO** in D_2O.

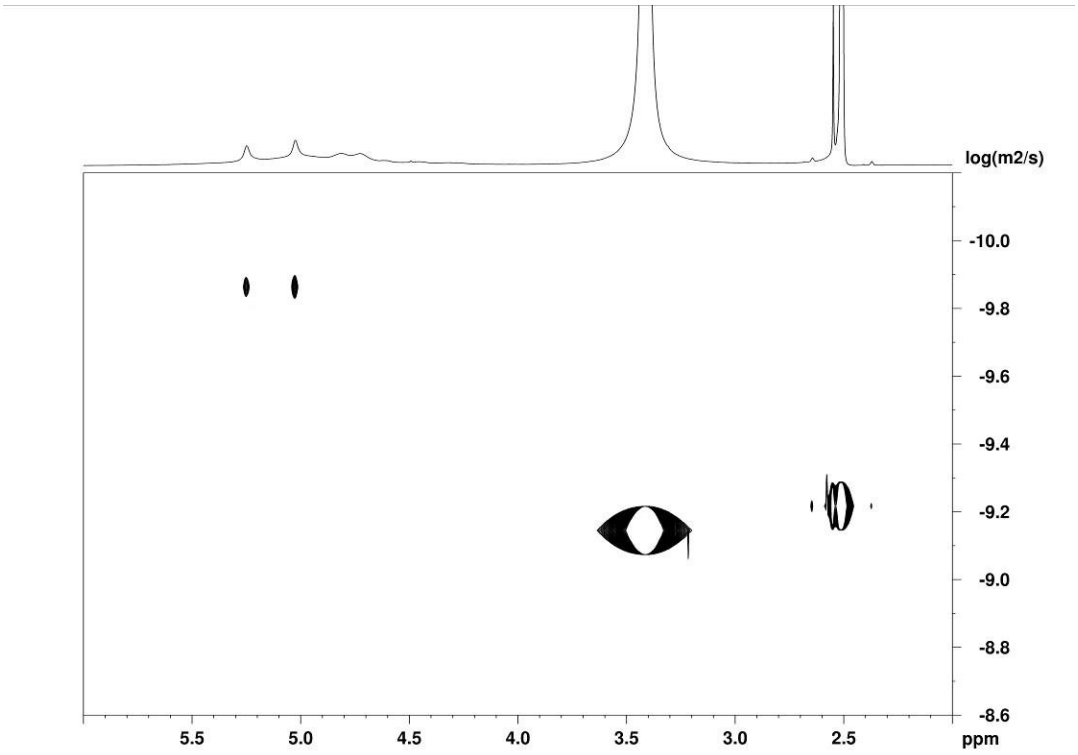

Figure S18. ^{1}H DOSY spectrum of **1·DMSO** in DMSO-d6.

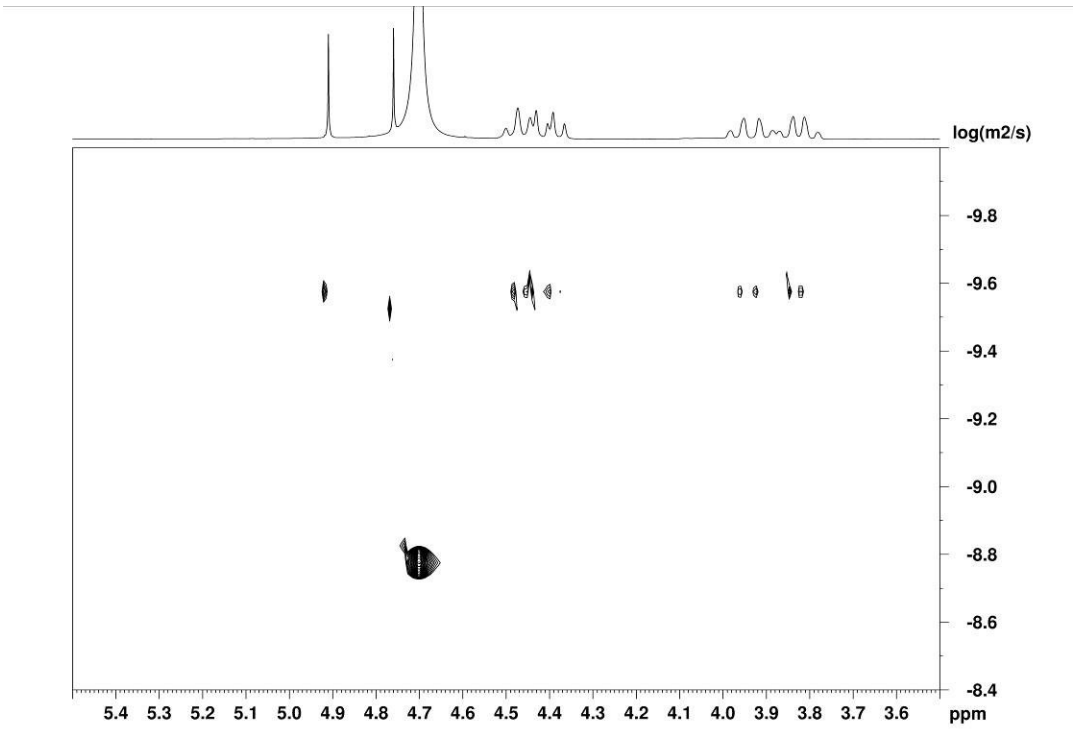

Figure S19. ^{1}H DOSY spectrum of **2·15H_2O** in D_2O.

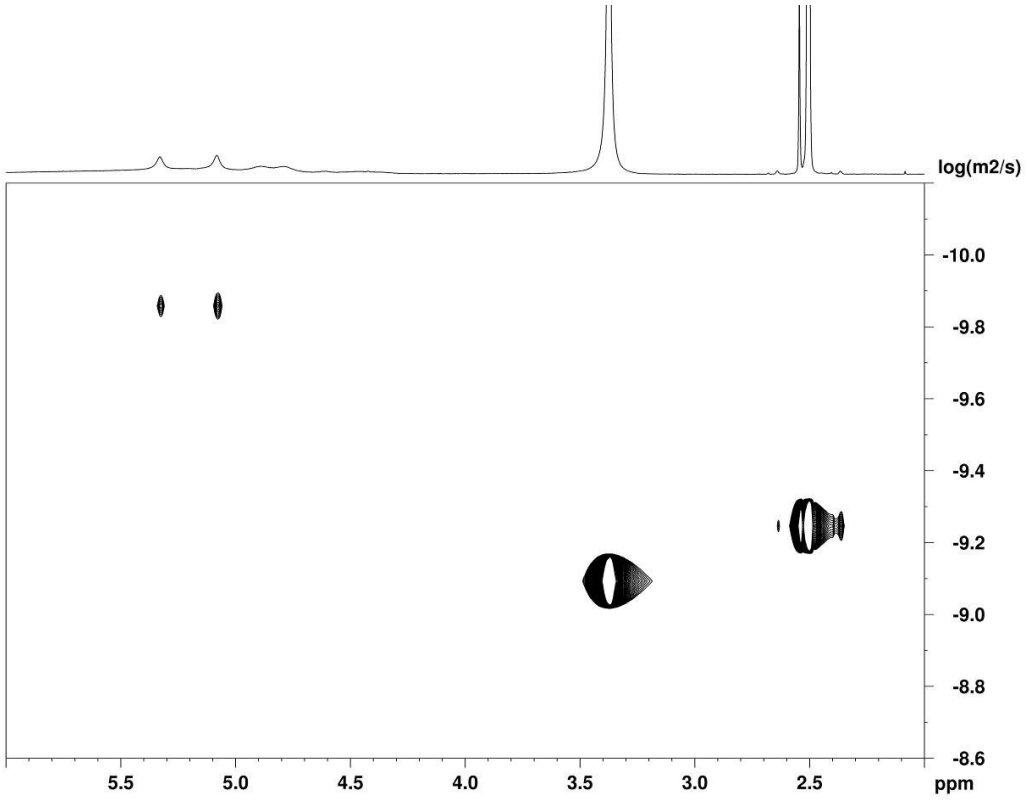

Figure S20. ^{1}H DOSY spectrum of **2·15H$_2$O** in DMSO-d6.

TG analysis: TGA was run with a TGA Q50 (TA Instruments) setting a temperature ramp of 5 ºC/min from 23 to 140 ºC under a nitrogen flux of 50.0 ml/min.

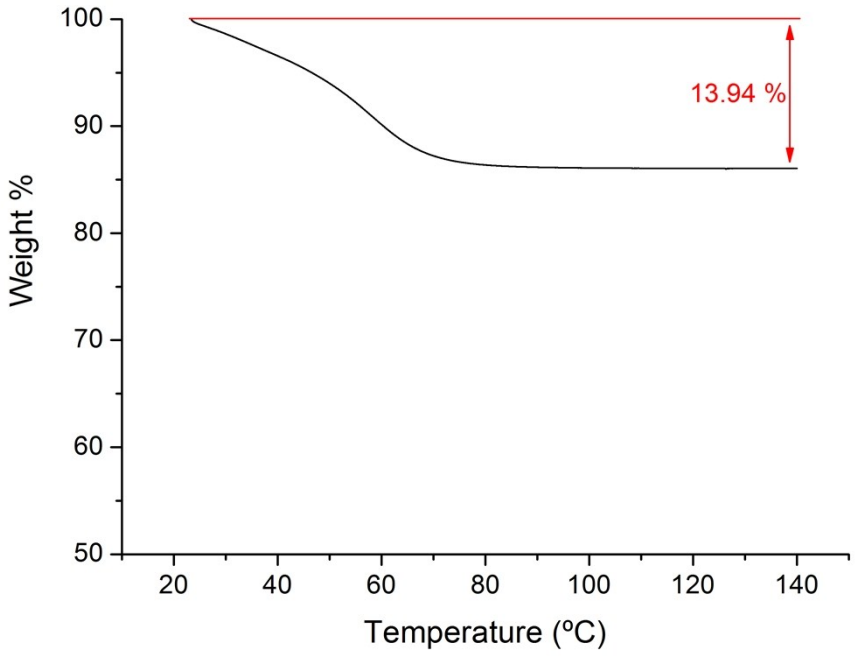

Figure S21. TGA of **2·15H_2O**.

(1) Casas-Solvas, J. M.; Ortiz-Salmerón, E.; Fernández, I.; García-Fuentes, L.; Santoyo-González, F.; Vargas-Berenguel, A.; *Chem. Eur. J.* **2009**, *15*, 8146-8162: D = (kBT)/(6πηrH), in which *D* is the diffusion coefficient, *kB* is the Boltzman constant, *T* is the temperature, and η is the viscosity of the solvent.

(2) a) Serrano-Ruiz, M.; Aguilera-Sáez, L. M.; Lorenzo-Luis, P.; Padrón, J. N.; Romerosa, A.; *Dalton Trans.*, **2013**, *42*, 11212-11219; b) Mena-Cruz, A.; Lorenzo-Luis, P.; Passarelli, V.; Romerosa, A.; Serrano-Ruiz, M.; *Dalton Trans.* **2011**, *40*, 3237-3250.