Supplementary Materials

Contents

Table S1. Bond lengths of **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	Cl1[1]	2.3598(5)	P1	C23	1.7927(18)
Ru1	Cl1	2.3598(5)	P1	C29	1.8010(18)
Ru1	O1[1]	2.0153(12)	C11	C12	1.401(2)
Ru1	O1	2.0152(12)	C11	C16	1.403(2)
Ru1	O2	2.0121(12)	C12	C13	1.388(3)
Ru1	O2[1]	2.0121(12)	C13	C14	1.391(3)
O1	C1	1.283(2)	C14	C15	1.387(3)
O2	C3	1.278(2)	C15	C16	1.390(3)
C1	C2	1.395(2)	C17	C18	1.396(2)
C1	C4	1.508(3)	C17	C22	1.403(2)
C2	C3	1.402(3)	C18	C19	1.391(3)
C3	C5	1.500(2)	C19	C20	1.391(3)
Ru2	Cl2	2.3633(5)	C20	C21	1.382(3)
Ru2	Cl2[2]	2.3633(5)	C21	C22	1.389(3)
Ru2	O3[2]	2.0183(13)	C23	C24	1.397(2)
Ru2	O3	2.0183(13)	C23	C28	1.399(3)
Ru2	O4	2.0110(12)	C24	C25	1.388(2)
Ru2	O4[2]	2.0110(12)	C25	C26	1.392(3)
O3	C6	1.276(2)	C26	C27	1.388(3)
O4	C8	1.282(2)	C27	C28	1.391(2)
C6	C7	1.407(3)	C29	C30	1.395(3)
C6	C9	1.505(3)	C29	C34	1.398(3)
C7	C8	1.391(3)	C30	C31	1.388(3)
C8	C10	1.511(3)	C31	C32	1.389(3)
P1	C11	1.7980(18)	C32	C33	1.394(3)
P1	C17	1.7937(18)	C33	C34	1.387(3)

[1] -x, 1-y, 2-z; [2] 2-x, 2-y, 1-z

Table S2. Bond angles of **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Ru1	Cl1[1]	180.0	C7	C6	C9	118.16(16)
O1	Ru1	Cl1	88.46(4)	C8	C7	C6	126.78(16)
O1[1]	Ru1	Cl1	91.54(4)	O4	C8	C7	126.36(17)
O1[1]	Ru1	Cl1[1]	88.46(4)	O4	C8	C10	114.11(16)
O1	Ru1	Cl1[1]	91.54(4)	C7	C8	C10	119.52(16)
O1	Ru1	O1[1]	180.00(7)	C11	P1	C29	110.90(8)
O2[1]	Ru1	Cl1[1]	89.43(4)	C17	P1	C11	110.83(8)
O2	Ru1	Cl1[1]	90.57(4)	C17	P1	C29	110.31(9)
O2[1]	Ru1	Cl1	90.57(4)	C23	P1	C11	110.53(8)
O2	Ru1	Cl1	89.43(4)	C23	P1	C17	107.74(8)
O2[1]	Ru1	O1[1]	94.21(5)	C23	P1	C29	106.40(8)
O2	Ru1	O1	94.21(5)	C12	C11	P1	120.21(14)
O2[1]	Ru1	O1	85.79(5)	C12	C11	C16	120.12(16)
O2	Ru1	O1[1]	85.79(5)	C16	C11	P1	119.63(13)
O2	Ru1	O2[1]	180.0	C13	C12	C11	119.62(17)
C1	O1	Ru1	122.40(11)	C12	C13	C14	119.97(17)
C3	O2	Ru1	122.72(11)	C15	C14	C13	120.70(18)
O1	C1	C2	126.52(17)	C14	C15	C16	119.99(17)
O1	C1	C4	114.29(16)	C15	C16	C11	119.58(16)
C2	C1	C4	119.19(16)	C18	C17	P1	120.82(14)
C1	C2	C3	127.05(17)	C18	C17	C22	119.94(16)
O2	C3	C2	126.45(16)	C22	C17	P1	119.23(14)
O2	C3	C5	114.96(16)	C19	C18	C17	119.95(17)
C2	C3	C5	118.58(16)	C18	C19	C20	119.70(17)
Cl2	Ru2	Cl2[2]	180.0	C21	C20	C19	120.64(17)
O3[2]	Ru2	Cl2	87.95(4)	C20	C21	C22	120.27(17)
O3[2]	Ru2	Cl2[2]	92.05(4)	C21	C22	C17	119.50(17)
O3	Ru2	Cl2[2]	87.95(4)	C24	C23	P1	117.70(13)
O3	Ru2	Cl2	92.05(4)	C24	C23	C28	120.13(16)
O3	Ru2	O3[2]	180.0	C28	C23	P1	122.00(14)
O4	Ru2	Cl2	93.22(4)	C25	C24	C23	119.82(17)
O4[2]	Ru2	Cl2	86.78(4)	C24	C25	C26	119.93(17)
O4[2]	Ru2	Cl2[2]	93.22(4)	C27	C26	C25	120.35(17)
O4	Ru2	Cl2[2]	86.78(4)	C26	C27	C28	120.18(17)

O4[2]	Ru2	O3[2]	93.37(5)	C27	C28	C23	119.53(17)
O4[2]	Ru2	O3	86.63(5)	C30	C29	P1	121.28(14)
O4	Ru2	O3[2]	86.63(5)	C30	C29	C34	120.12(17)
O4	Ru2	O3	93.37(5)	C34	C29	P1	118.03(14)
O4	Ru2	O4[2]	180.00(7)	C31	C30	C29	119.35(17)
C6	O3	Ru2	122.60(12)	C30	C31	C32	120.77(18)
C8	O4	Ru2	122.41(11)	C31	C32	C33	119.70(18)
O3	C6	C7	126.14(17)	C34	C33	C32	120.09(18)
O3	C6	C9	115.69(16)	C33	C34	C29	119.92(18)

[1] -x, 1-y, 2-z; [2] 2-x, 2-y, 1-z

Table S3. Bond lengths of **2**·H_2O.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	Ru2	2.66606(19)	C11	C12	1.400(3)
Ru1	Cl3	2.3667(4)	C11	C16	1.391(3)
Ru1	Cl1	2.3395(4)	C29	C30	1.397(3)
Ru1	Cl5	2.3678(4)	C29	C34	1.399(3)
Ru1	Cl4	2.3586(4)	C17	C18	1.386(3)
Ru1	O2	1.9908(13)	C17	C22	1.395(3)
Ru1	O1	1.9949(13)	C12	C13	1.386(3)
Ru2	Cl3	2.3640(5)	C13	C14	1.387(3)
Ru2	Cl5	2.3780(4)	C16	C15	1.389(3)
Ru2	Cl4	2.3586(4)	C3	C5	1.505(3)
Ru2	Cl2	2.3313(5)	C3	C2	1.383(3)
Ru2	O3	2.0013(15)	C8	C10	1.507(4)
Ru2	O4	2.0010(14)	C8	C7	1.387(4)
P1	C11	1.7927(19)	C14	C15	1.390(3)
P1	C23	1.7913(18)	C30	C31	1.388(3)
P1	C29	1.7910(19)	C6	C7	1.395(4)
P1	C17	1.7877(18)	C6	C9	1.498(3)
O2	C3	1.281(2)	C34	C33	1.393(3)
O3	C8	1.280(3)	C2	C1	1.394(3)
O1	C1	1.280(2)	C4	C1	1.501(3)
O4	C6	1.273(3)	C18	C19	1.392(3)
C27	C26	1.387(3)	C22	C21	1.385(3)
C27	C28	1.390(3)	C21	C20	1.389(3)
C24	C23	1.400(3)	C19	C20	1.381(3)
C24	C25	1.388(3)	C33	C32	1.387(4)
C26	C25	1.385(3)	C31	C32	1.378(4)
C28	C23	1.392(2)			

Table S4. Bong angles of **2**·H_2O.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl3	Ru1	Ru2	55.648(12)	O4	Ru2	Cl3	87.82(5)	C15	C16	C11	119.13(19)
Cl3	Ru1	Cl5	91.201(15)	O4	Ru2	Cl5	89.68(4)	O2	C3	C5	114.07(19)
Cl1	Ru1	Ru2	129.265(13)	O4	Ru2	Cl4	177.95(4)	O2	C3	C2	126.39(19)
Cl1	Ru1	Cl3	91.514(16)	O4	Ru2	Cl2	86.08(4)	C2	C3	C5	119.49(19)
Cl1	Ru1	Cl5	92.224(16)	O4	Ru2	O3	93.80(7)	O3	C8	C10	113.8(2)
Cl1	Ru1	Cl4	174.933(16)	Ru2	Cl3	Ru1	68.605(12)	O3	C8	C7	126.2(2)
Cl5	Ru1	Ru2	56.002(11)	Ru1	Cl5	Ru2	68.356(12)	C7	C8	C10	120.0(2)
Cl4	Ru1	Ru2	55.586(11)	C23	P1	C11	110.72(8)	C13	C14	C15	120.24(19)
Cl4	Ru1	Cl3	90.839(16)	C29	P1	C11	106.89(9)	C31	C30	C29	119.7(2)
Cl4	Ru1	Cl5	92.213(15)	C29	P1	C23	109.10(9)	O4	C6	C7	126.8(2)
O2	Ru1	Ru2	122.95(4)	C17	P1	C11	109.10(9)	O4	C6	C9	113.9(2)
O2	Ru1	Cl3	178.43(4)	C17	P1	C23	107.59(9)	C7	C6	C9	119.2(2)
O2	Ru1	Cl1	89.06(4)	C17	P1	C29	113.47(9)	C16	C15	C14	120.6(2)
O2	Ru1	Cl5	87.32(4)	C3	O2	Ru1	121.77(13)	C33	C34	C29	118.7(2)
O2	Ru1	Cl4	88.71(4)	C8	O3	Ru2	123.36(15)	C3	C2	C1	126.27(18)
O2	Ru1	O1	93.60(6)	C1	O1	Ru1	121.92(13)	C17	C18	C19	119.3(2)
O1	Ru1	Ru2	123.14(4)	C6	O4	Ru2	122.74(16)	C21	C22	C17	119.89(18)
O1	Ru1	Cl3	87.88(4)	C26	C27	C28	120.34(18)	O1	C1	C2	126.15(18)
O1	Ru1	Cl1	88.10(4)	C25	C24	C23	119.72(18)	O1	C1	C4	114.8(2)
O1	Ru1	Cl5	179.03(4)	C25	C26	C27	120.00(19)	C2	C1	C4	119.02(19)
O1	Ru1	Cl4	87.51(4)	C27	C28	C23	119.78(18)	C22	C21	C20	119.86(19)
Cl3	Ru2	Ru1	55.746(11)	C12	C11	P1	118.68(14)	C20	C19	C18	120.5(2)
Cl3	Ru2	Cl5	91.019(15)	C16	C11	P1	120.96(15)	C32	C33	C34	120.3(2)
Cl5	Ru2	Ru1	55.641(11)	C16	C11	C12	120.35(17)	C19	C20	C21	120.12(19)
Cl4	Ru2	Ru1	55.585(11)	C24	C23	P1	119.36(14)	C32	C31	C30	119.8(2)
Cl4	Ru2	Cl3	90.906(16)	C28	C23	P1	120.76(14)	C31	C32	C33	120.8(2)
Cl4	Ru2	Cl5	91.956(16)	C28	C23	C24	119.87(17)	C8	C7	C6	126.6(2)
Cl2	Ru2	Ru1	130.347(14)	C26	C25	C24	120.29(19)				
Cl2	Ru2	Cl3	93.050(18)	C30	C29	P1	119.87(16)				

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Ru2	Cl5	174.010(18)	C30	C29	C34	120.60(19)				
Cl2	Ru2	Cl4	92.373(17)	C34	C29	P1	119.27(16)				
O3	Ru2	Ru1	122.45(4)	C18	C17	P1	121.11(15)				
O3	Ru2	Cl3	178.13(5)	C18	C17	C22	120.31(17)				
O3	Ru2	Cl5	88.08(4)	C22	C17	P1	118.44(14)				
O3	Ru2	Cl4	87.49(5)	C13	C12	C11	119.96(18)				
O3	Ru2	Cl2	87.98(4)	C12	C13	C14	119.72(19)				

Table S5. Bond lengths of **3**·CH_3CN.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru(1)	O(1)	2.0020(12)	C(13)	C(14)	1.396(2)
Ru(1)	O(2)	2.0085(12)	C(13)	C(18)	1.401(2)
Ru(1)	O(3)	2.0114(11)	C(14)	C(15)	1.387(2)
Ru(1)	O(4)	2.0123(11)	C(15)	C(16)	1.388(3)
Ru(1)	N(1)	2.0163(15)	C(16)	C(17)	1.388(3)
Ru(1)	N(2)	2.0069(15)	C(17)	C(18)	1.384(2)
S(1)	C(11)	1.6315(18)	C(19)	C(20)	1.398(2)
S(2)	C(12)	1.6267(18)	C(19)	C(24)	1.399(2)
O(1)	C(1)	1.282(2)	C(20)	C(21)	1.393(2)
O(2)	C(3)	1.279(2)	C(21)	C(22)	1.388(2)
O(3)	C(6)	1.2765(19)	C(22)	C(23)	1.388(3)
O(4)	C(8)	1.280(2)	C(23)	C(24)	1.386(2)
N(1)	C(11)	1.160(2)	C(25)	C(26)	1.397(2)
N(2)	C(12)	1.159(2)	C(25)	C(30)	1.400(2)
C(1)	C(2)	1.390(2)	C(26)	C(27)	1.390(2)
C(1)	C(4)	1.508(2)	C(27)	C(28)	1.389(3)
C(2)	C(3)	1.392(2)	C(28)	C(29)	1.386(3)
C(3)	C(5)	1.506(2)	C(29)	C(30)	1.386(2)
C(6)	C(7)	1.400(2)	C(31)	C(32)	1.402(2)
C(6)	C(9)	1.504(2)	C(31)	C(36)	1.395(2)
C(7)	C(8)	1.394(2)	C(32)	C(33)	1.384(2)
C(8)	C(10)	1.504(2)	C(33)	C(34)	1.382(3)
P(1)	C(13)	1.7874(16)	C(34)	C(35)	1.391(3)
P(1)	C(19)	1.7925(16)	C(35)	C(36)	1.387(2)
P(1)	C(25)	1.7931(16)	N(3)	C(38)	1.131(3)
P(1)	C(31)	1.7925(16)	C(37)	C(38)	1.443(3)

Table S6. Bond angles of **3**·CH_3CN.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O(1)	Ru(1)	O(2)	93.71(5)	C(13)	P(1)	C(25)	106.27(7)
O(1)	Ru(1)	O(3)	85.99(5)	C(13)	P(1)	C(31)	110.71(7)
O(1)	Ru(1)	O(4)	179.07(5)	C(19)	P(1)	C(25)	110.84(7)
O(1)	Ru(1)	N(1)	92.10(5)	C(31)	P(1)	C(19)	107.03(8)
O(1)	Ru(1)	N(2)	89.62(5)	C(31)	P(1)	C(25)	110.78(7)
O(2)	Ru(1)	O(3)	179.69(5)	C(14)	C(13)	P(1)	121.93(13)
O(2)	Ru(1)	O(4)	87.03(5)	C(14)	C(13)	C(18)	120.24(15)
O(2)	Ru(1)	N(1)	89.62(5)	C(18)	C(13)	P(1)	117.83(12)
O(3)	Ru(1)	O(4)	93.28(5)	C(15)	C(14)	C(13)	119.54(16)
O(3)	Ru(1)	N(1)	90.43(5)	C(14)	C(15)	C(16)	119.97(16)
O(4)	Ru(1)	N(1)	87.34(5)	C(17)	C(16)	C(15)	120.63(16)
N(2)	Ru(1)	O(2)	88.50(6)	C(18)	C(17)	C(16)	119.94(17)
N(2)	Ru(1)	O(3)	91.46(5)	C(17)	C(18)	C(13)	119.61(16)
N(2)	Ru(1)	O(4)	90.97(5)	C(20)	C(19)	P(1)	121.54(12)
N(2)	Ru(1)	N(1)	177.54(6)	C(20)	C(19)	C(24)	120.24(15)
C(1)	O(1)	Ru(1)	122.33(11)	C(24)	C(19)	P(1)	118.21(12)
C(3)	O(2)	Ru(1)	122.57(11)	C(21)	C(20)	C(19)	119.39(15)
C(6)	O(3)	Ru(1)	122.59(11)	C(22)	C(21)	C(20)	120.18(16)
C(8)	O(4)	Ru(1)	121.74(11)	C(23)	C(22)	C(21)	120.29(16)
C(11)	N(1)	Ru(1)	170.90(14)	C(24)	C(23)	C(22)	120.20(16)
C(12)	N(2)	Ru(1)	173.04(14)	C(23)	C(24)	C(19)	119.66(16)
O(1)	C(1)	C(2)	126.41(15)	C(26)	C(25)	P(1)	122.66(12)
O(1)	C(1)	C(4)	114.72(15)	C(26)	C(25)	C(30)	120.01(15)
C(2)	C(1)	C(4)	118.87(15)	C(30)	C(25)	P(1)	117.26(12)
C(1)	C(2)	C(3)	127.07(16)	C(27)	C(26)	C(25)	119.40(16)
O(2)	C(3)	C(2)	126.01(15)	C(28)	C(27)	C(26)	120.35(16)
O(2)	C(3)	C(5)	115.61(15)	C(29)	C(28)	C(27)	120.31(16)
C(2)	C(3)	C(5)	118.38(15)	C(28)	C(29)	C(30)	119.99(16)
O(3)	C(6)	C(7)	125.92(15)	C(29)	C(30)	C(25)	119.92(16)
O(3)	C(6)	C(9)	114.86(15)	C(32)	C(31)	P(1)	118.08(12)
C(7)	C(6)	C(9)	119.22(15)	C(36)	C(31)	P(1)	121.60(12)
C(8)	C(7)	C(6)	126.61(15)	C(36)	C(31)	C(32)	120.32(15)
O(4)	C(8)	C(7)	126.49(15)	C(33)	C(32)	C(31)	119.56(16)
O(4)	C(8)	C(10)	114.88(15)	C(34)	C(33)	C(32)	120.16(17)

C(7)	C(8)	C(10)	118.59(15)	C(33)	C(34)	C(35)	120.42(17)
N(1)	C(11)	S(1)	178.94(16)	C(36)	C(35)	C(34)	120.21(17)
N(2)	C(12)	S(2)	177.92(16)	C(35)	C(36)	C(31)	119.32(16)
C(13)	P(1)	C(19)	111.26(7)	N(3)	C(38)	C(37)	178.5(3)

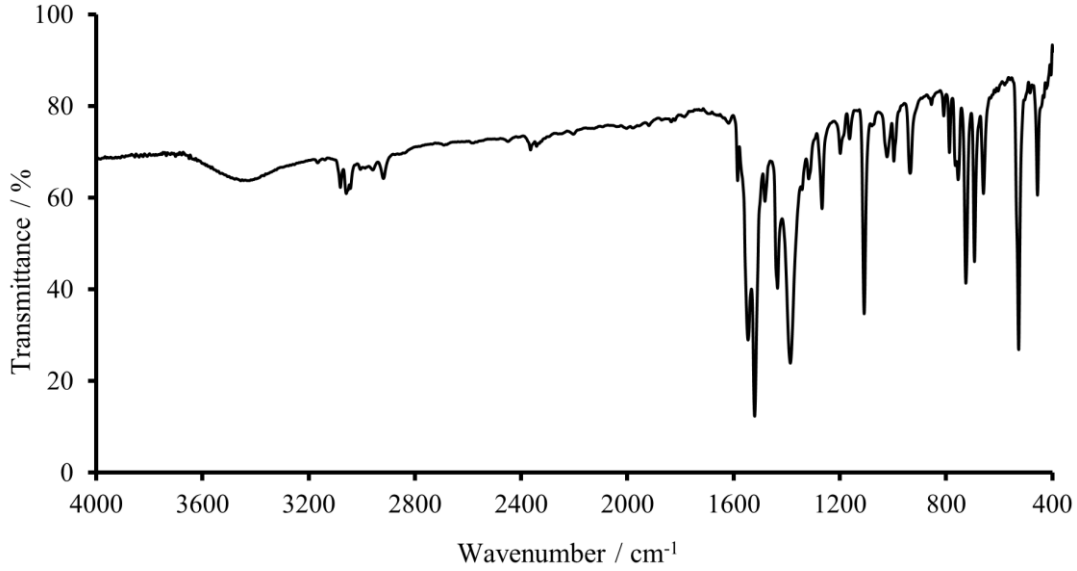

Figure S1. IR spectrum of **1**.

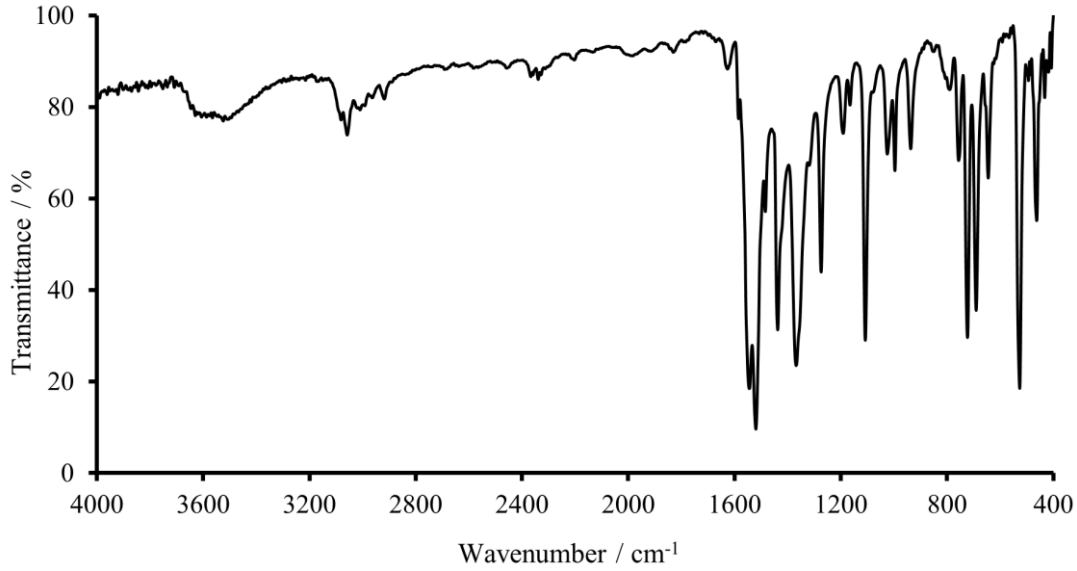

Figure S2. IR spectrum of **2**.

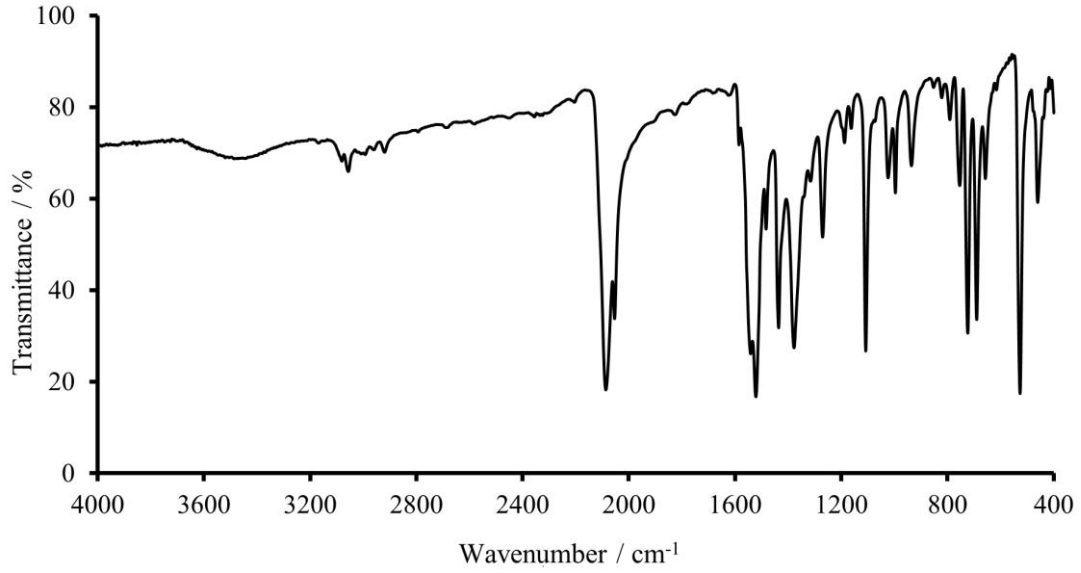

Figure S3. IR spectrum of **3**·0.5C_6H_{14}.

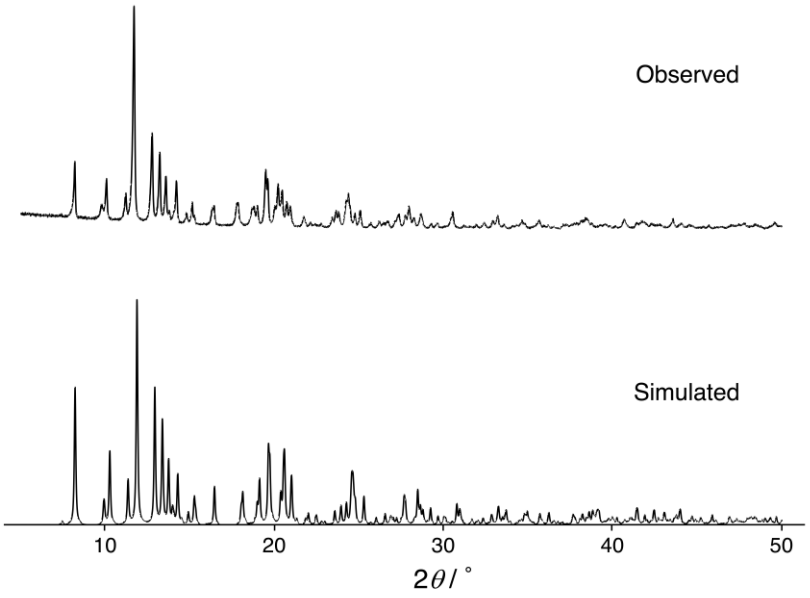

Figure S4. Observed (top) and simulated (bottom) XRD patterns of **1**.

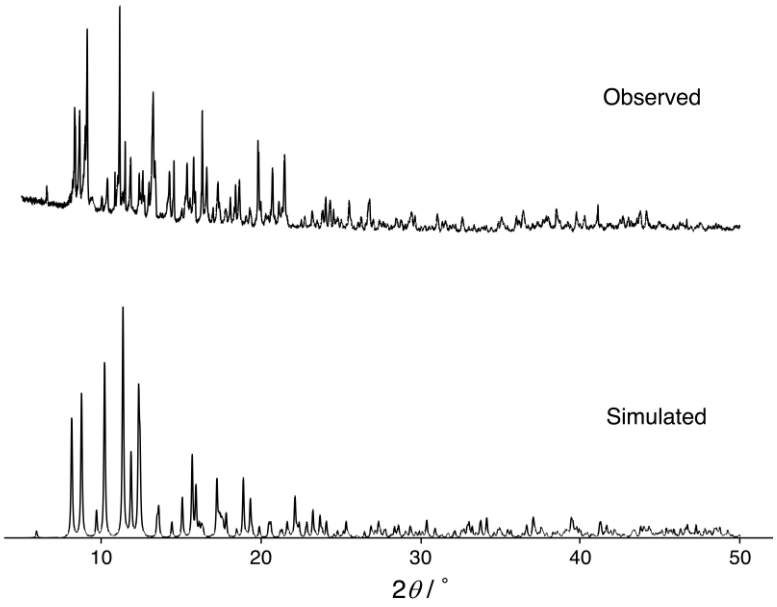

Figure S5. Observed (top for **2**) and simulated (bottom for **2**·H_2O) XRD patterns.

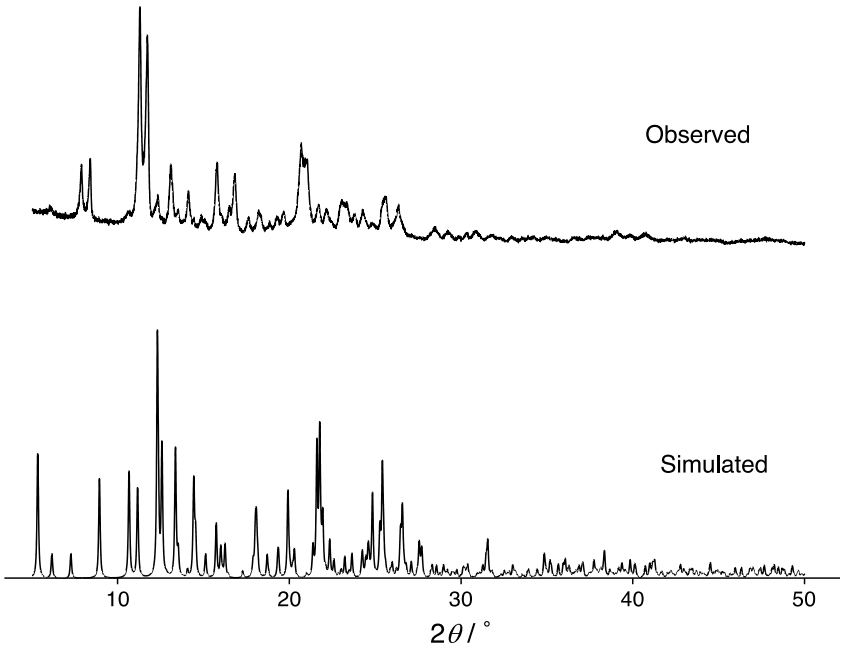

Figure S6. Observed (top for **3**·0.5C_6H_{14}) and simulated (bottom for **3**·CH_3CN) XRD patterns.

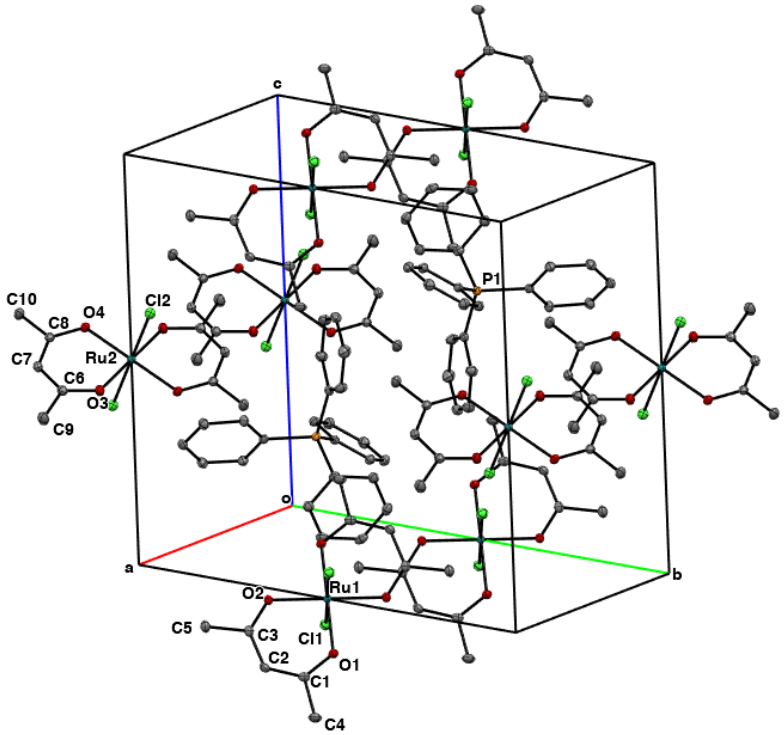

Figure S7. Crystal packing diagram of **1** without hydrogen atoms for clarity.

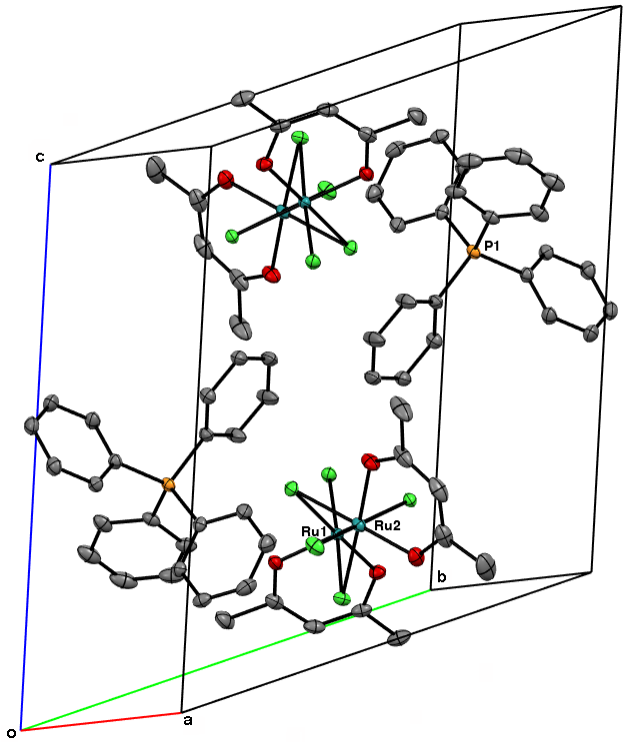

Figure S8. Packing diagram of **2**·H_2O without hydrogen atoms for clarity.

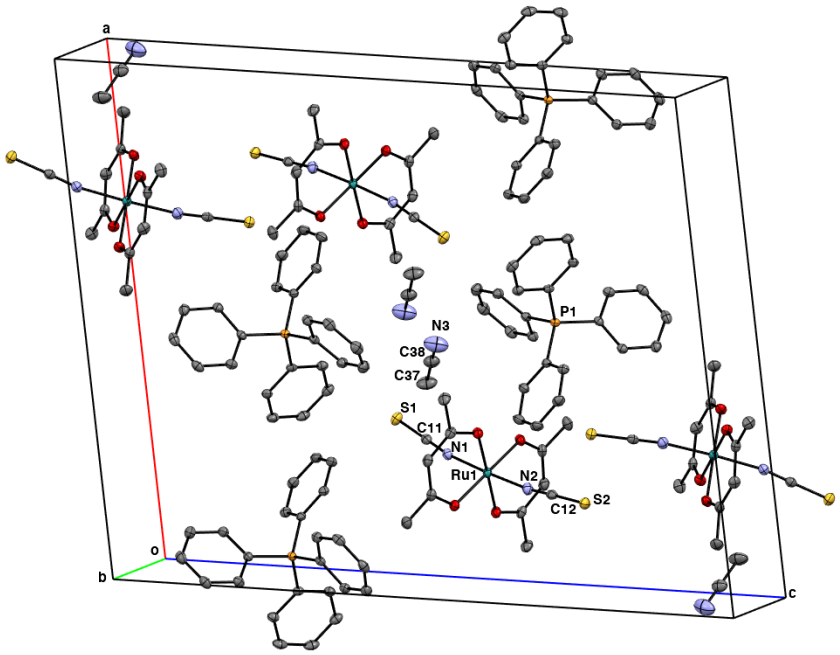

Figure S9. Packing diagram of **3**·CH_3CN without hydrogen atoms for clarity.

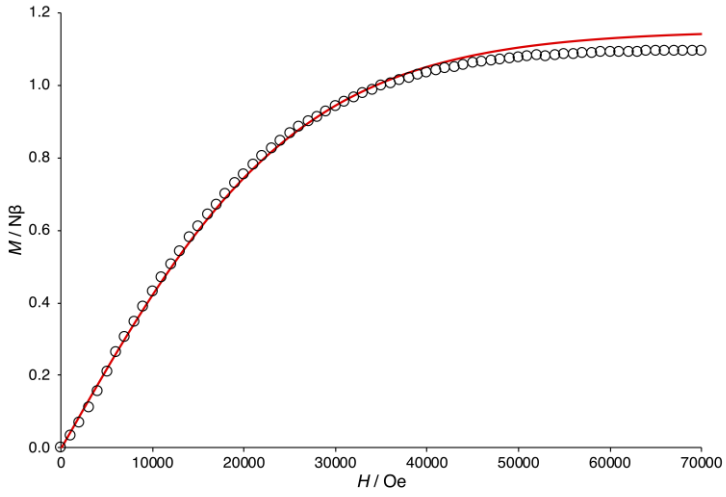

Figure S10. Field dependence of magnetization for **1** at 2 K. The red solid line represents the Brillouin function with g = 2.3.

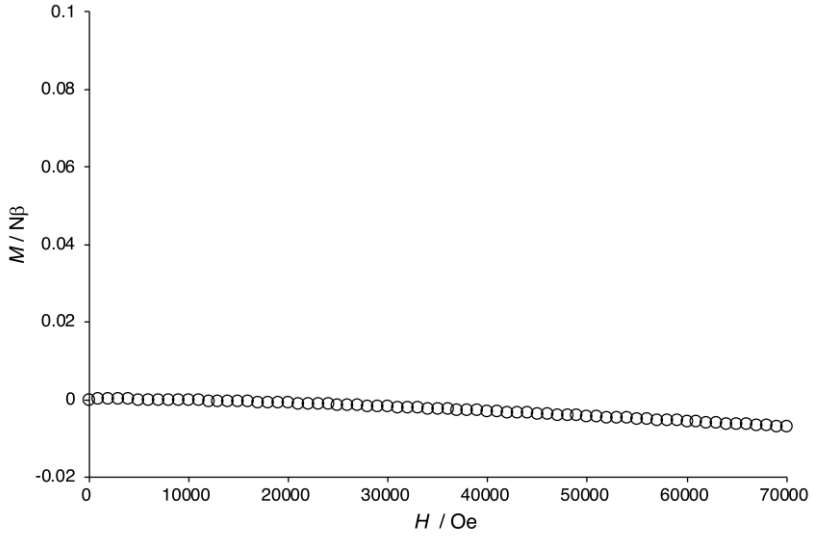

Figure S11. Field dependence of magnetization for **2** at 2 K.

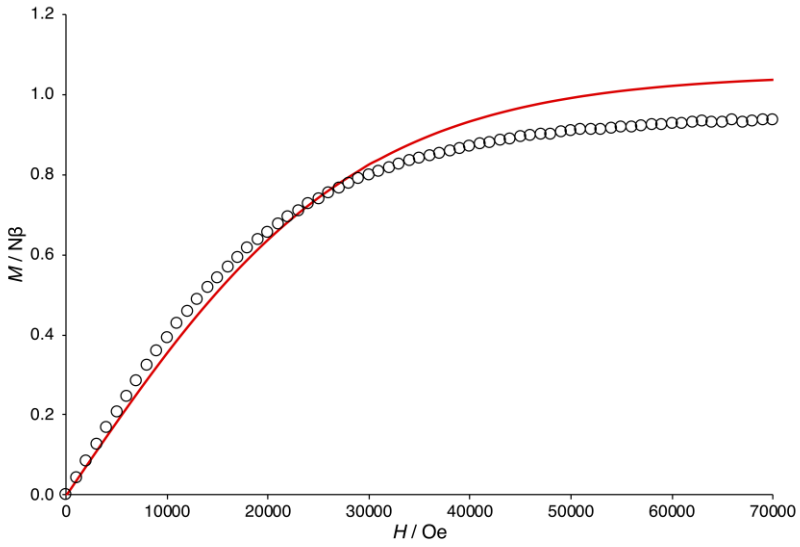

Figure S12. Field dependence of magnetization for **3**·0.5C_6H_{14} at 2 K. The red solid line represents the Brillouin function with g = 2.1.

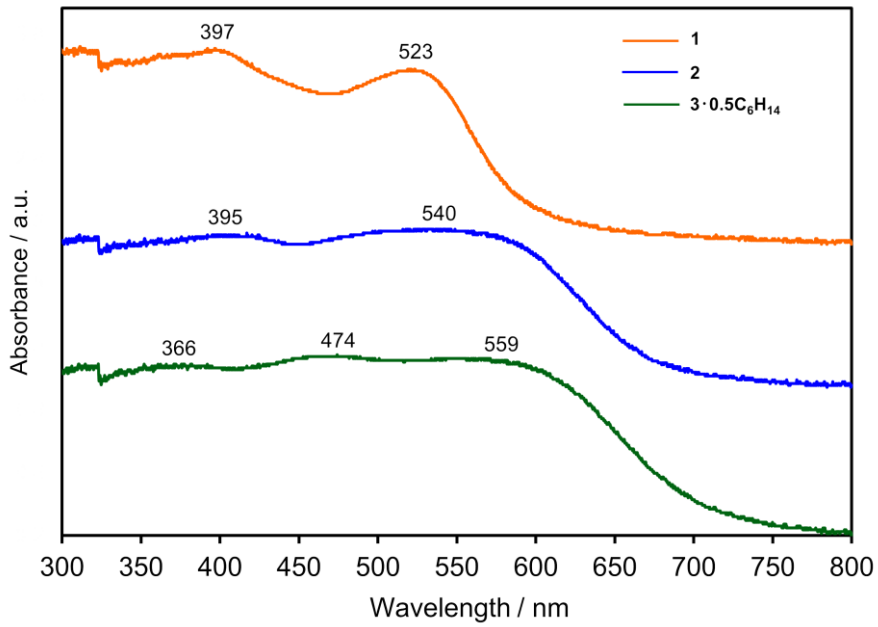

Figure S13. Diffuse reflectance spectra of **1** (orange solid line), **2** (blue solid line) and **3**·0.5C_6H_{14} (green solid line).

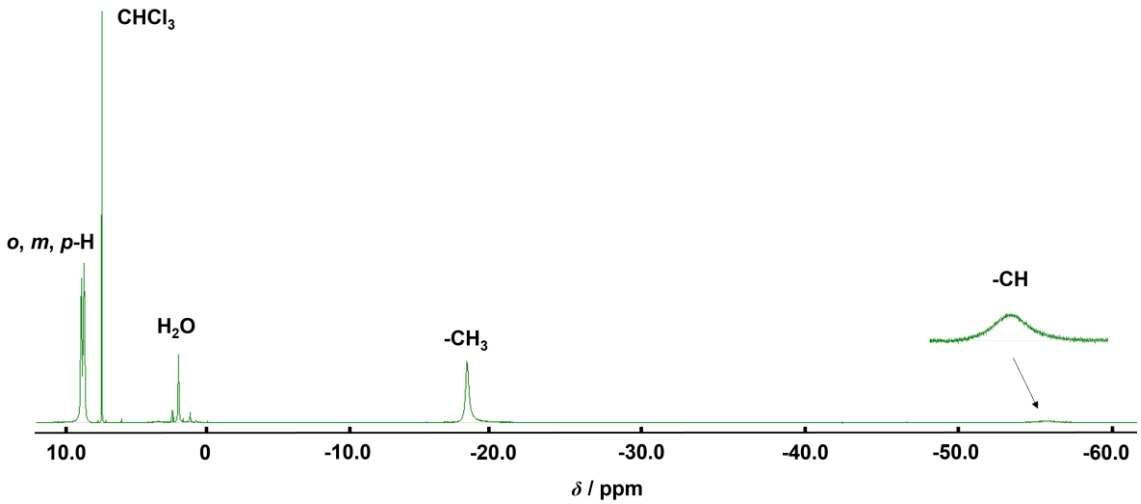

Figure S14. ^{1}H NMR spectrum of **1** in chlrooform-d_1 at 298 K.

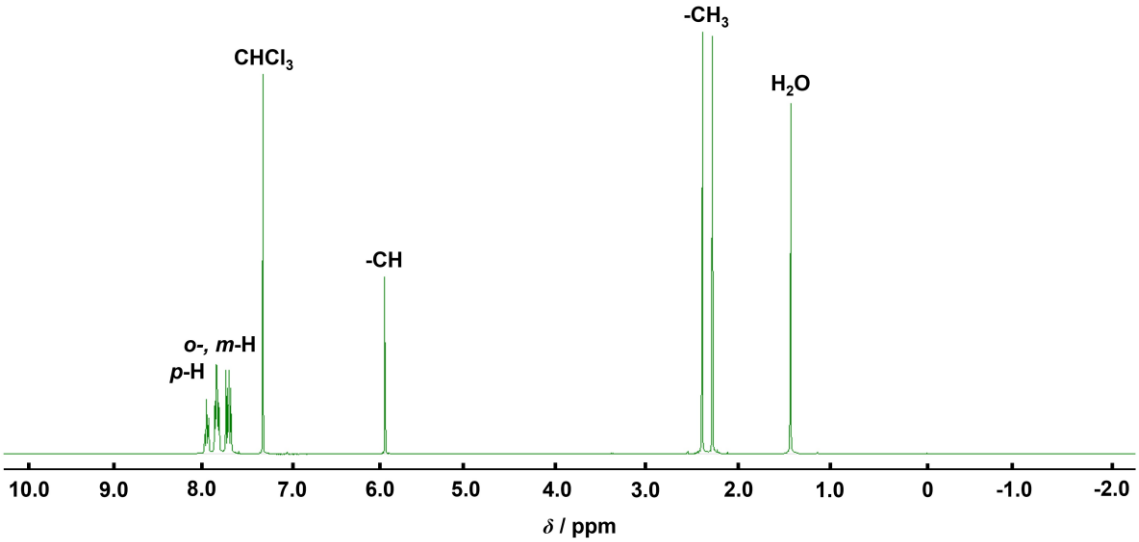

Figure S15. ^{1}H NMR spectrum of **2** in chlroform-d_1 at 298 K.

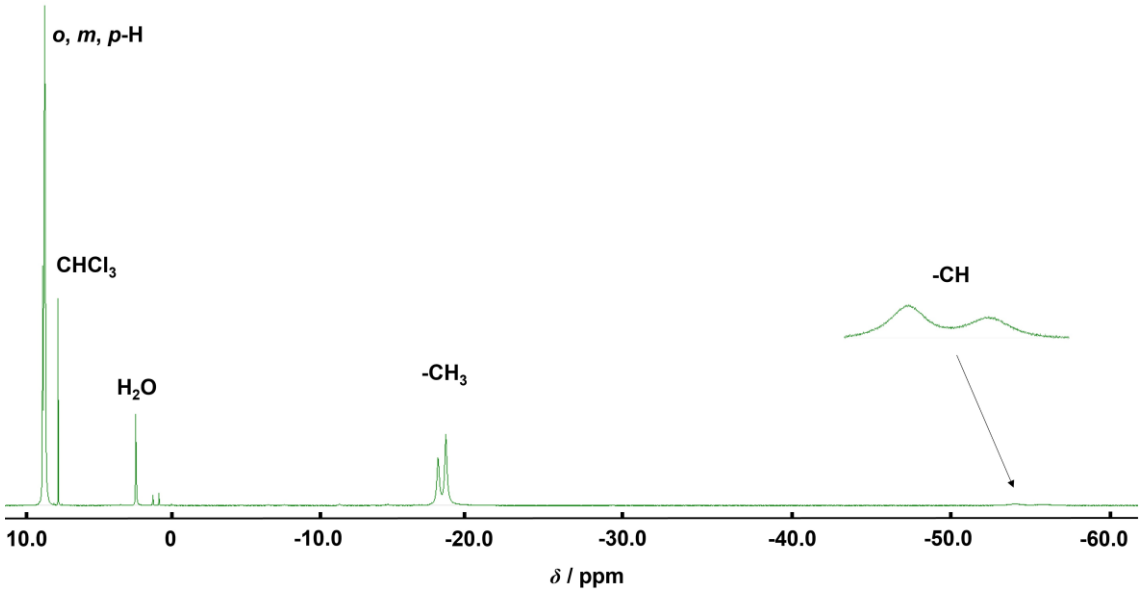

Figure S16. ^{1}H NMR spectrum of **3**·0.5C_6H_{14} in chloroform-d_1 at 298 K.