Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Replacement of the phosphodiester backbone between canonical nucleosides with dirhenium carbonyl "click" linker – a new class of luminescent organometallic dinucleoside phosphate mimics

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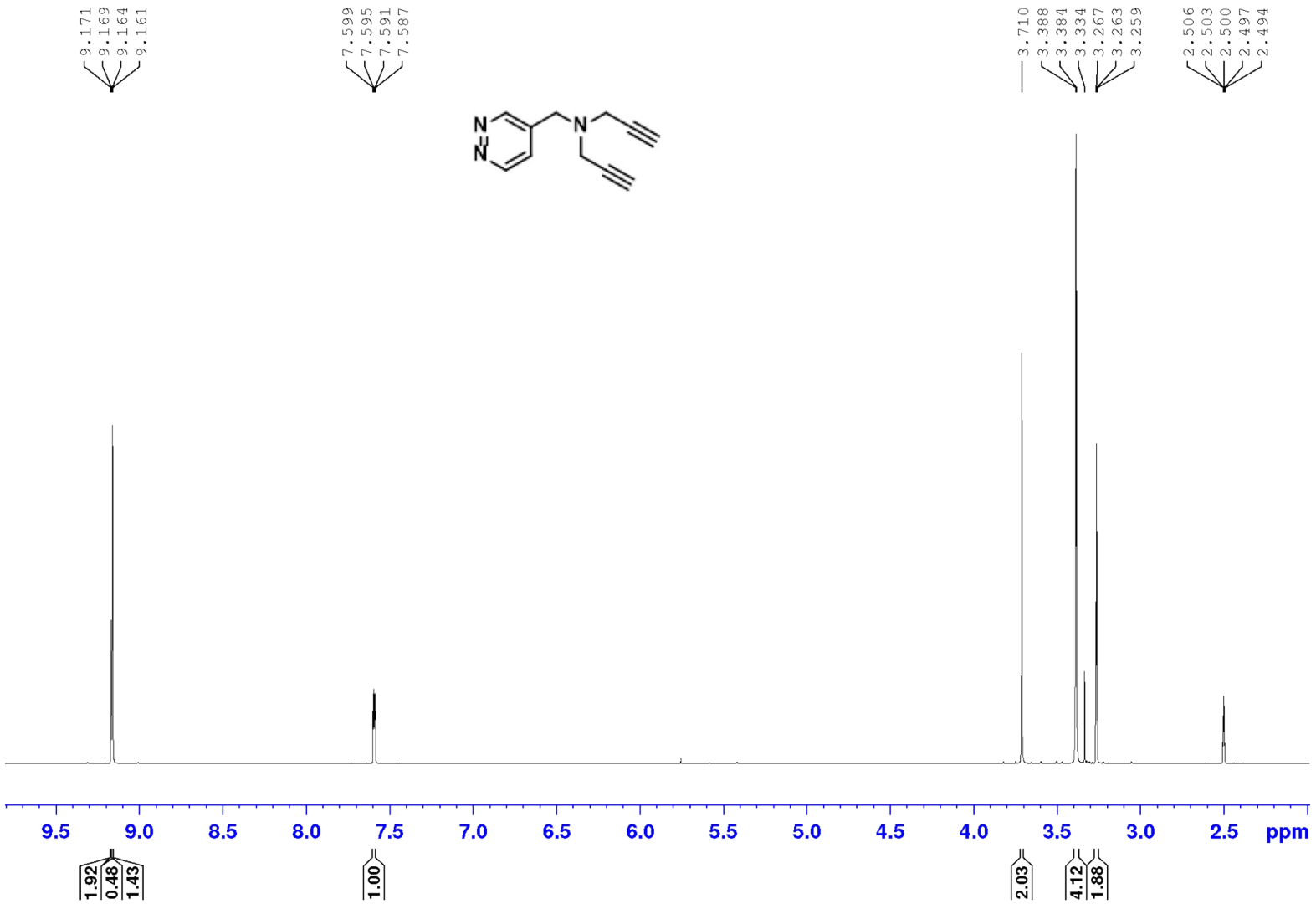

Fig. S1 ^{1}H-NMR spectrum of **1** in DMSO-d_6 (600 MHz)

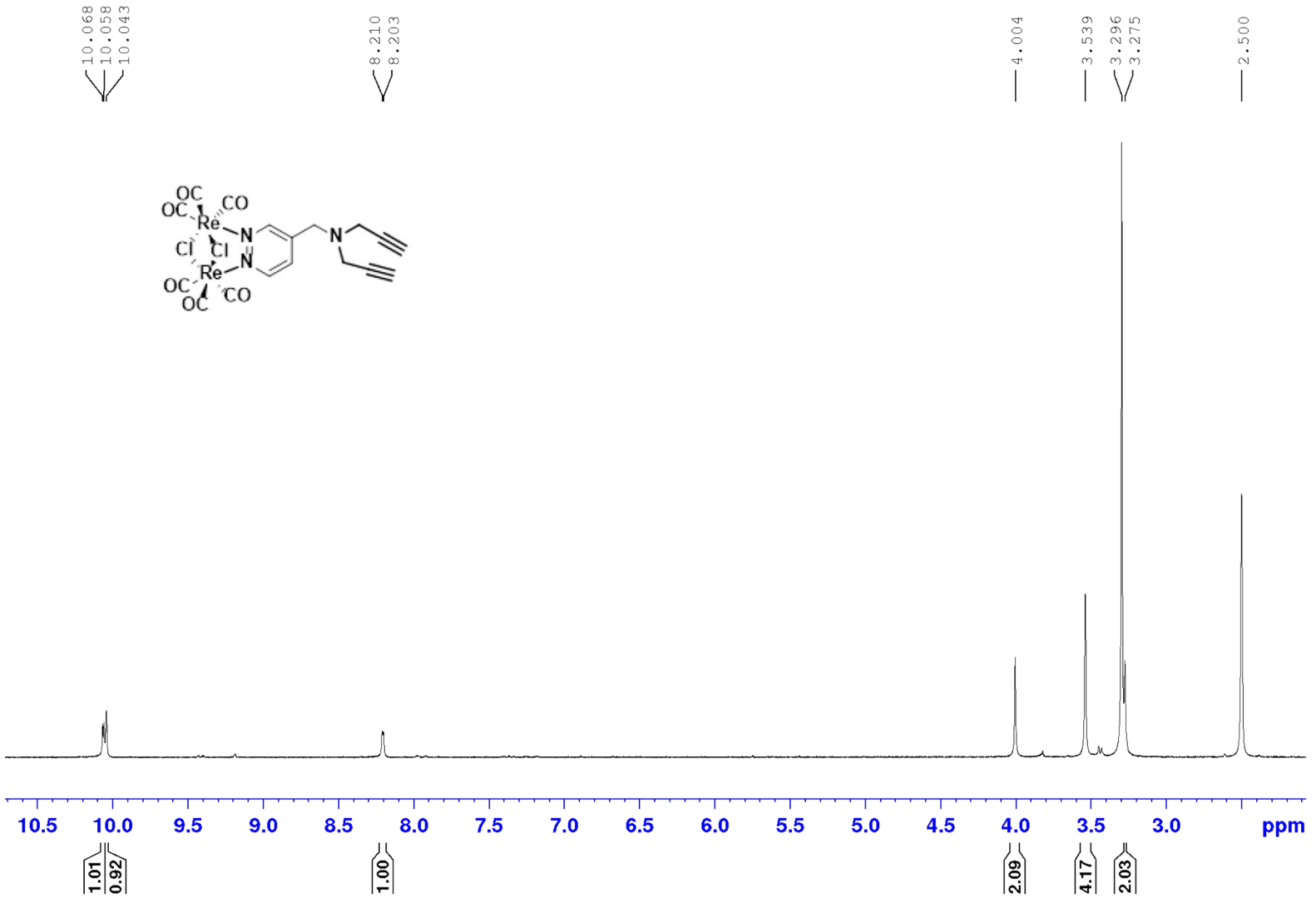

Fig. S2 ^{1}H-NMR spectrum of **2** in DMSO-d_6 (600 MHz)

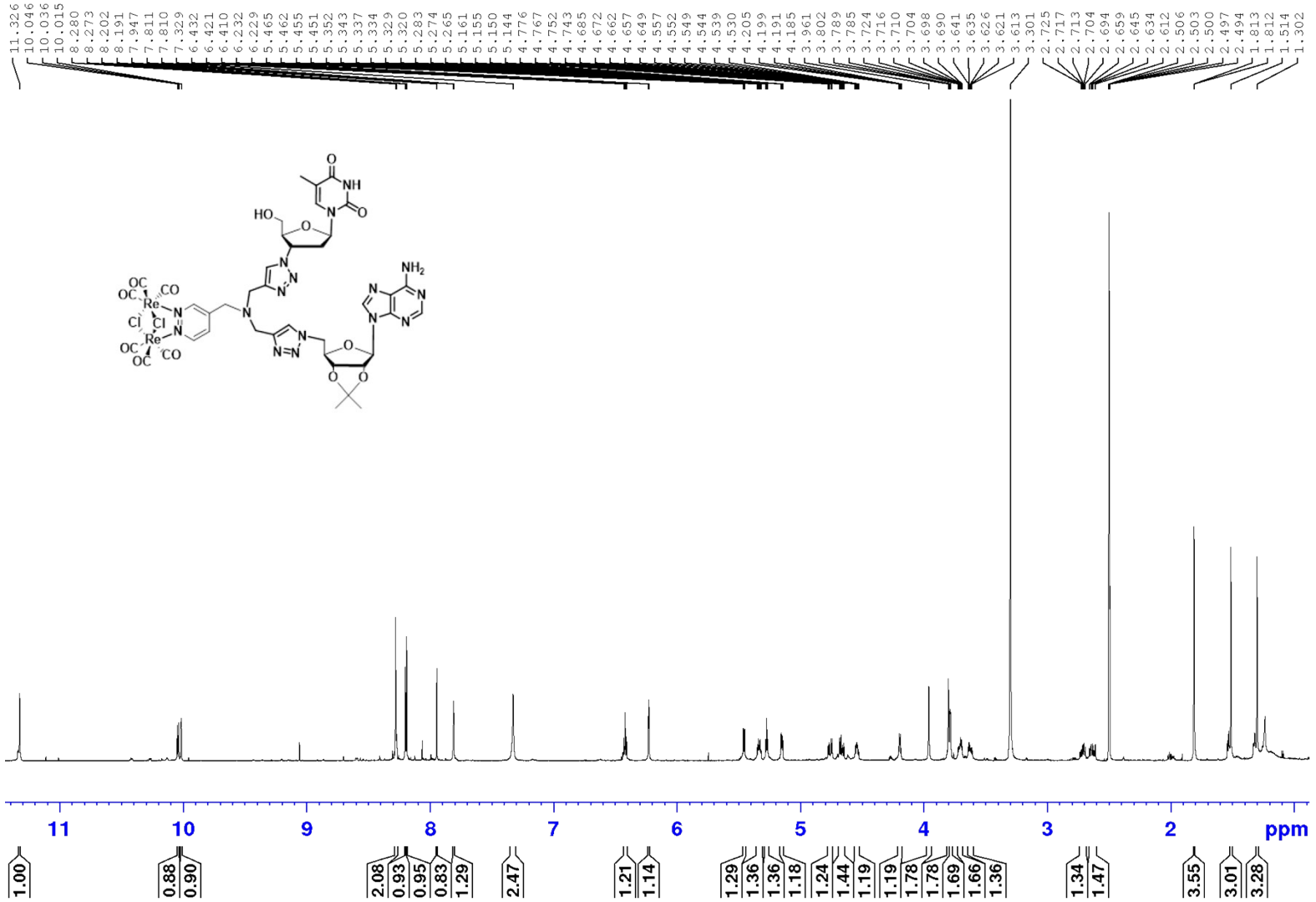

Fig. S3 ^{1}H-NMR spectrum of **4** in DMSO-d_6 (600 MHz)

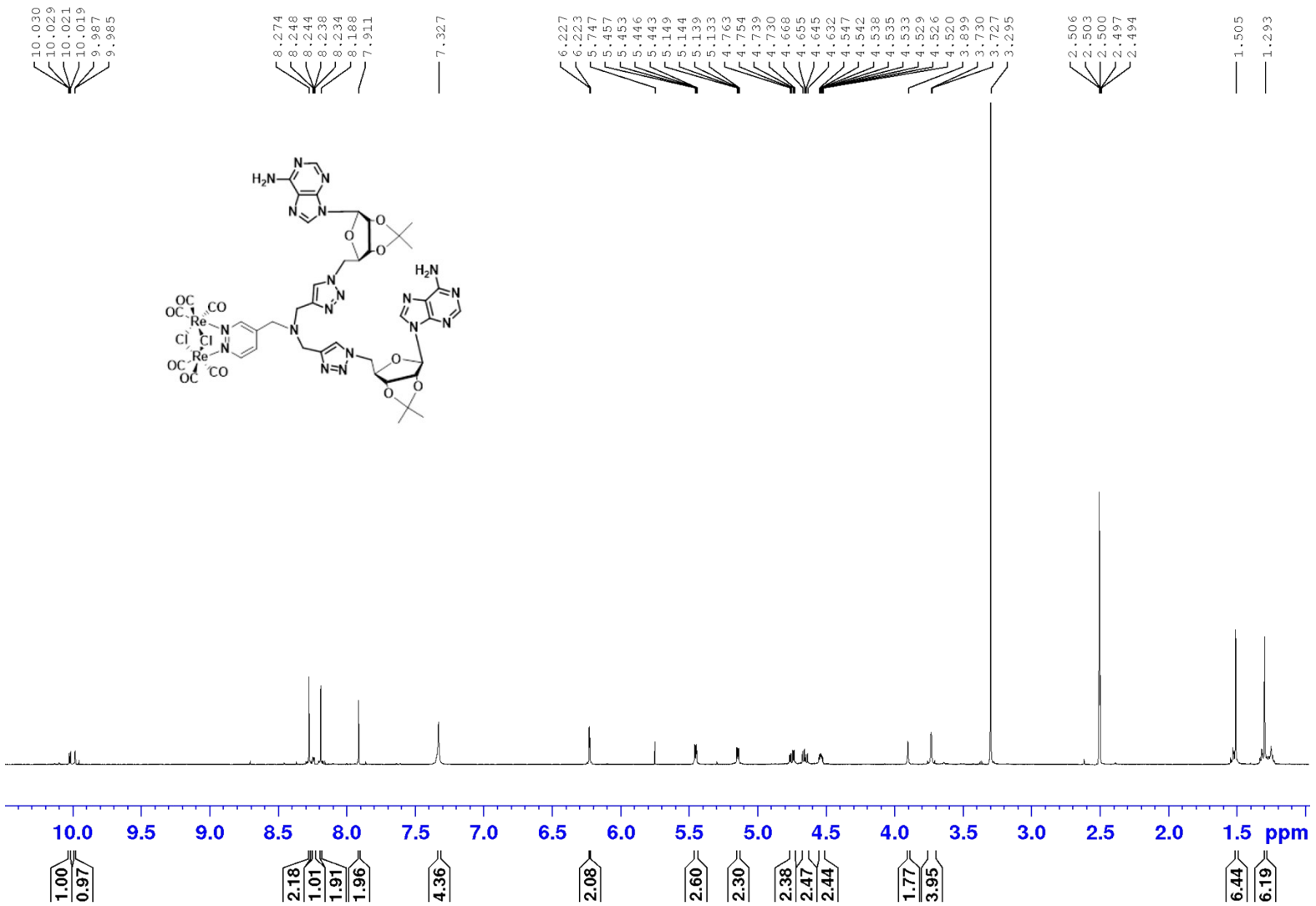

Fig. S4 ^{1}H-NMR spectrum of **5** in DMSO-d_6 (600 MHz)

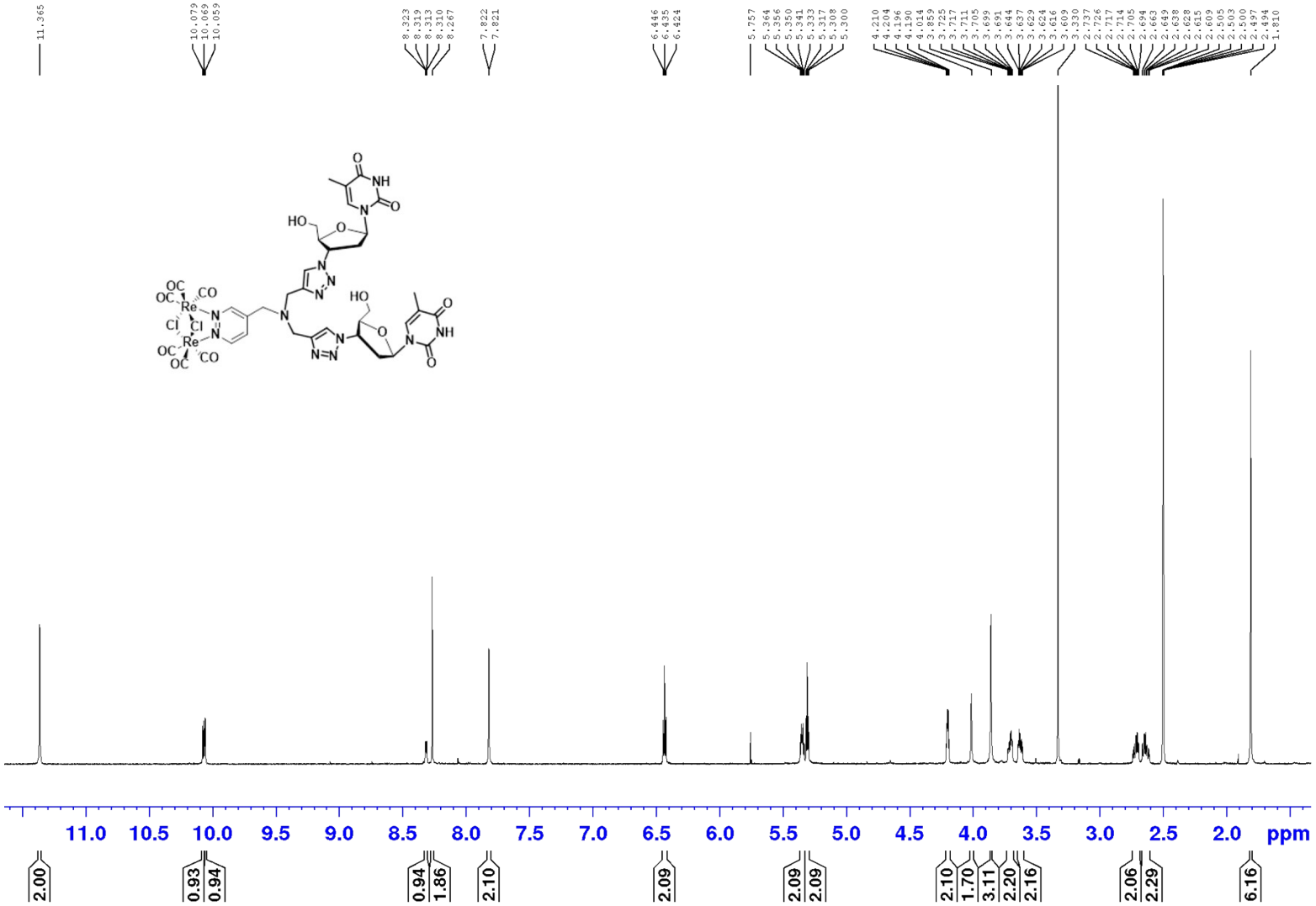

Fig. S5 ^{1}H-NMR spectrum of **6** in DMSO-d_6 (600 MHz)

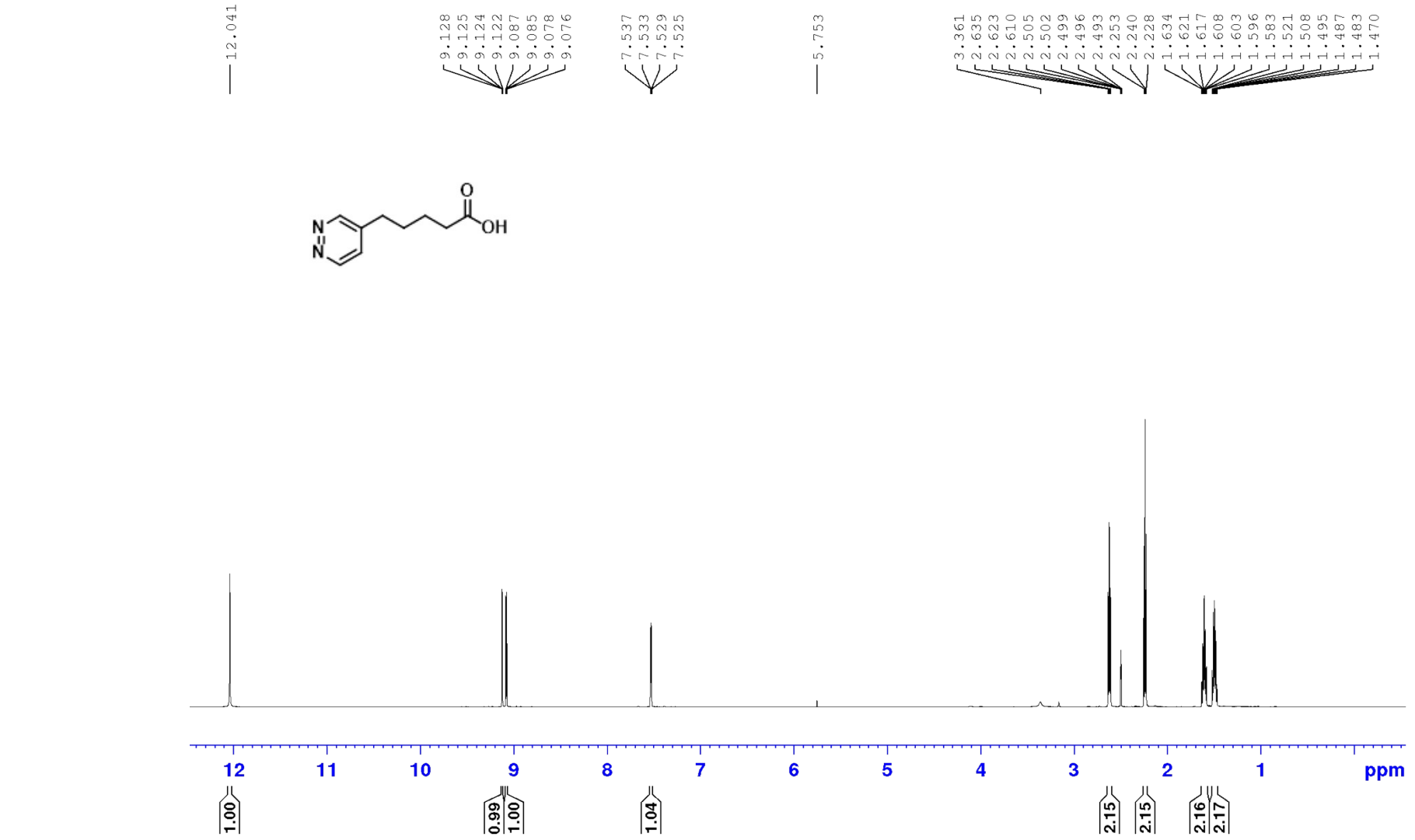

Fig. S6 ^{1}H-NMR spectrum of **7** in DMSO-d_6 (600 MHz)

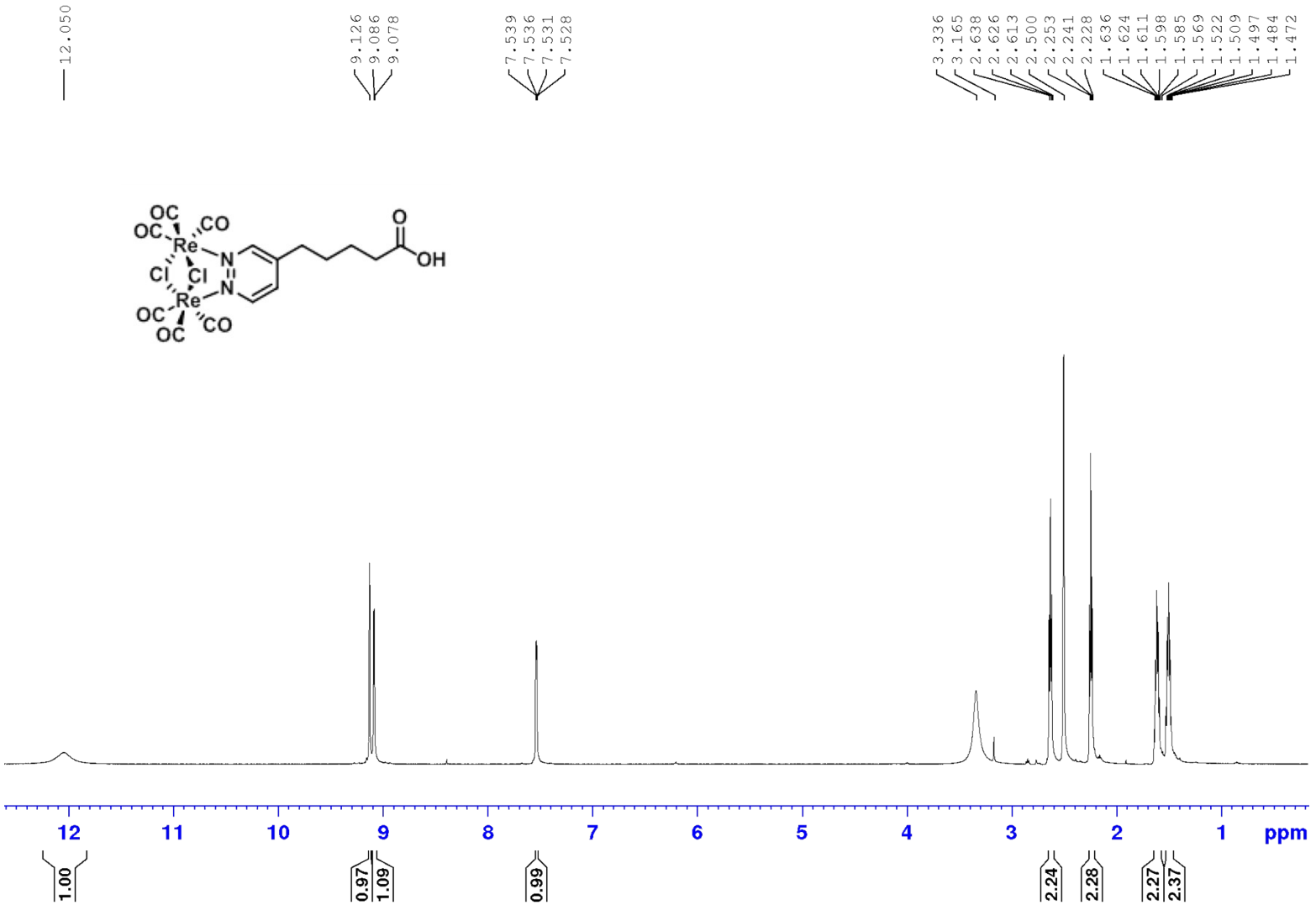

Fig. S7 ^{1}H-NMR spectrum of **8** in DMSO-d_6 (600 MHz)

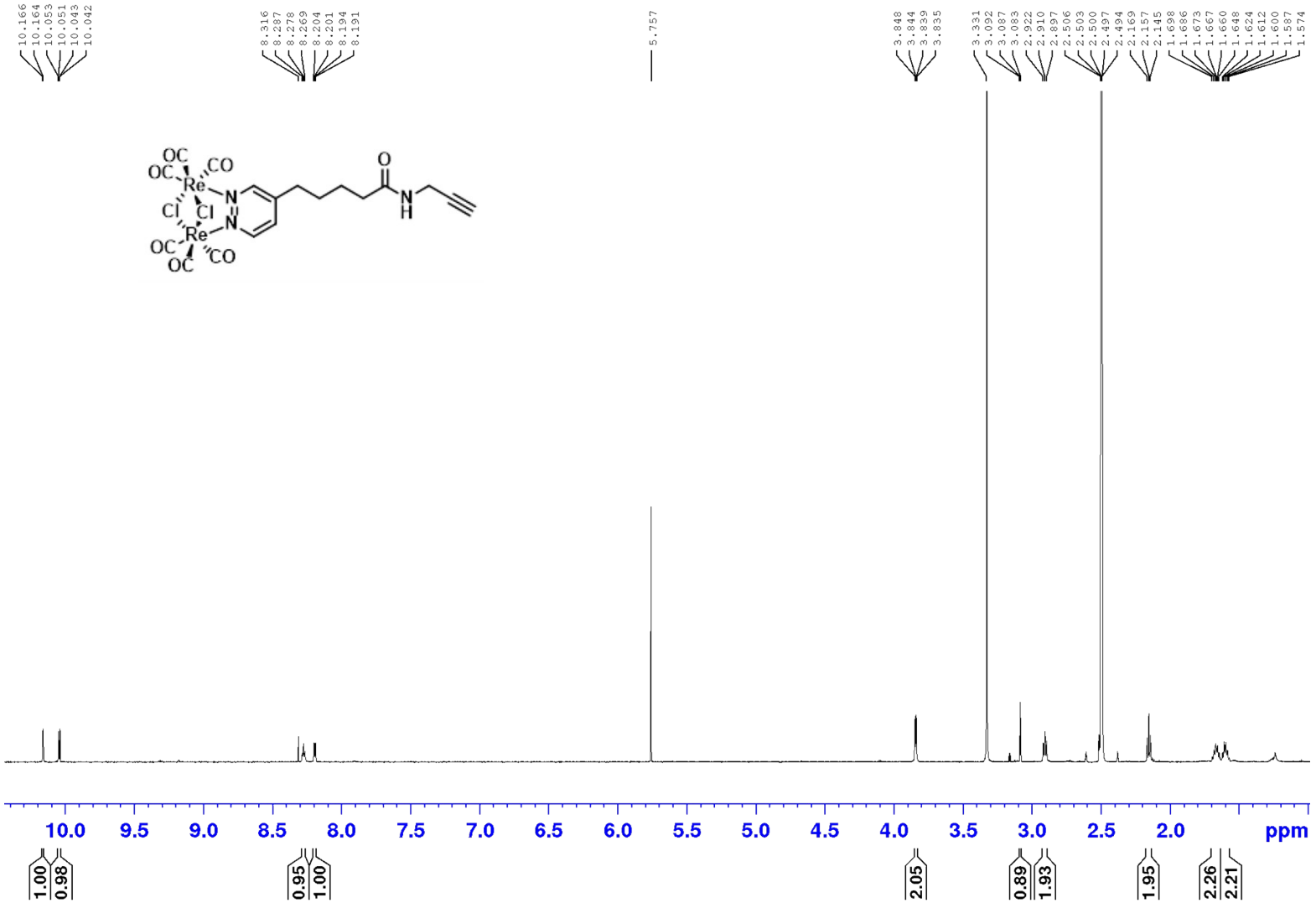

Fig. S8 ^{1}H-NMR spectrum of **9** in DMSO-d_6 (600 MHz)

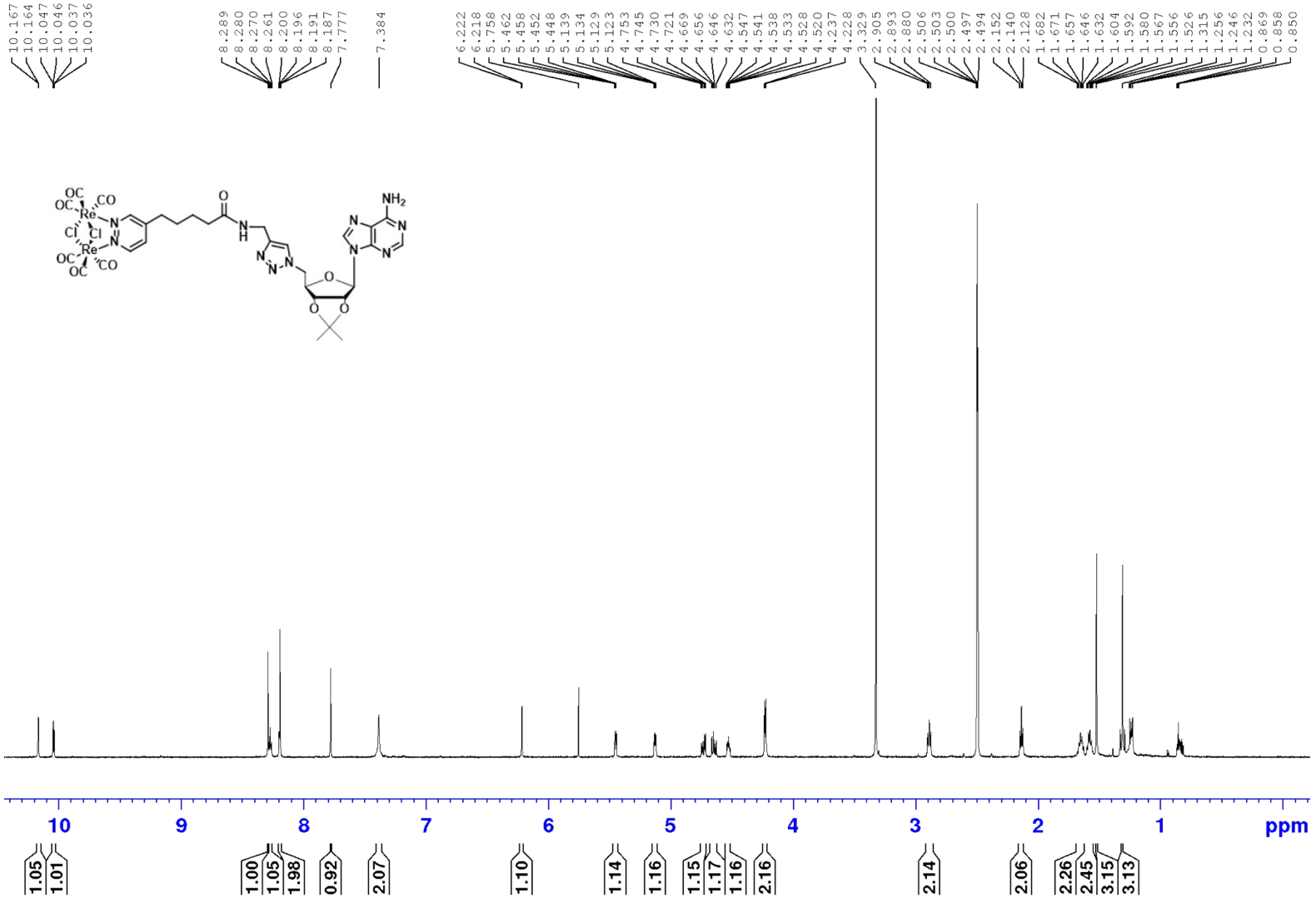

Fig. S9 ^{1}H-NMR spectrum of **10** in DMSO-d_6 (600 MHz)

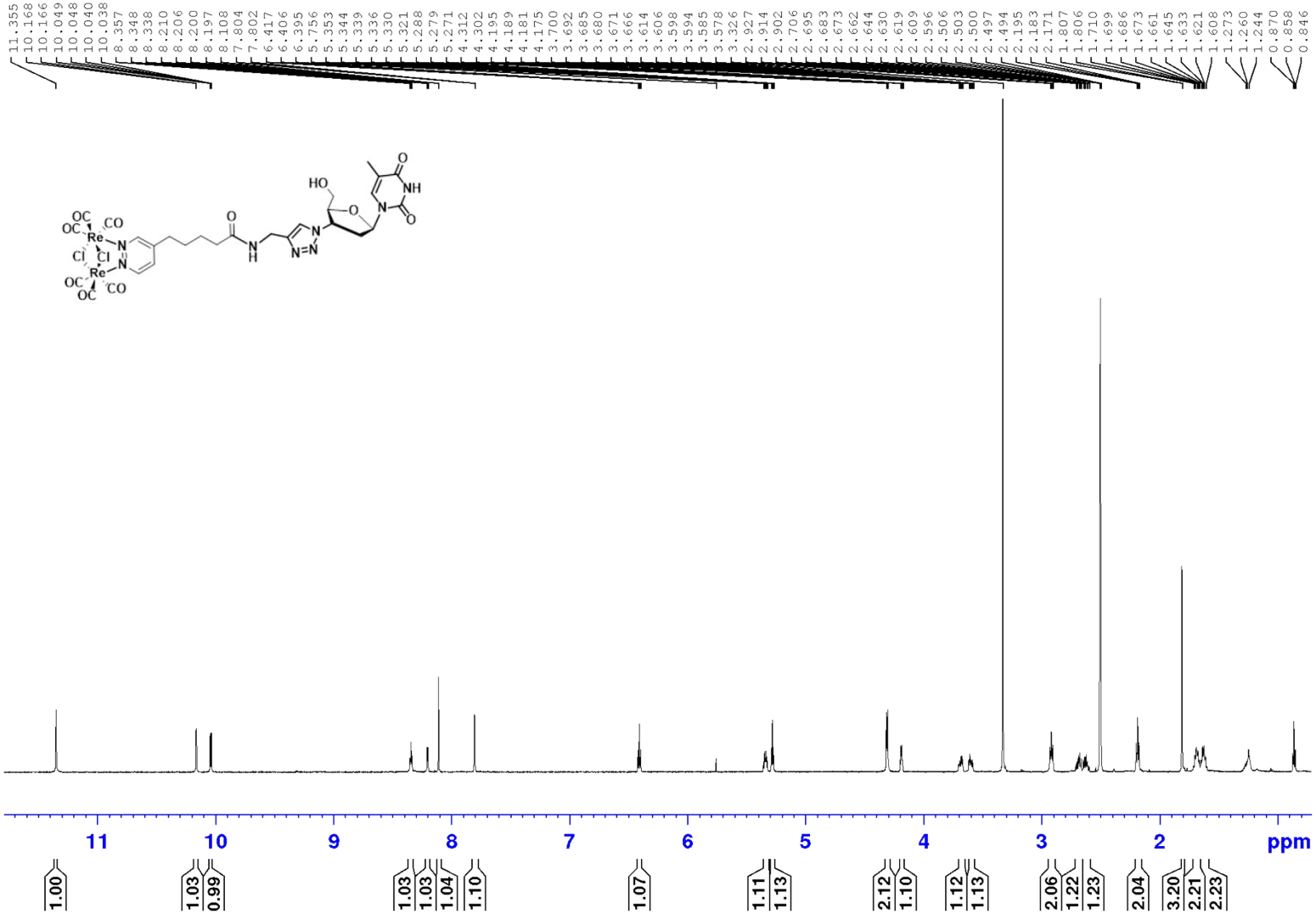

Fig. S10 ^{1}H-NMR spectrum of **11** in DMSO-d_6 (600 MHz)

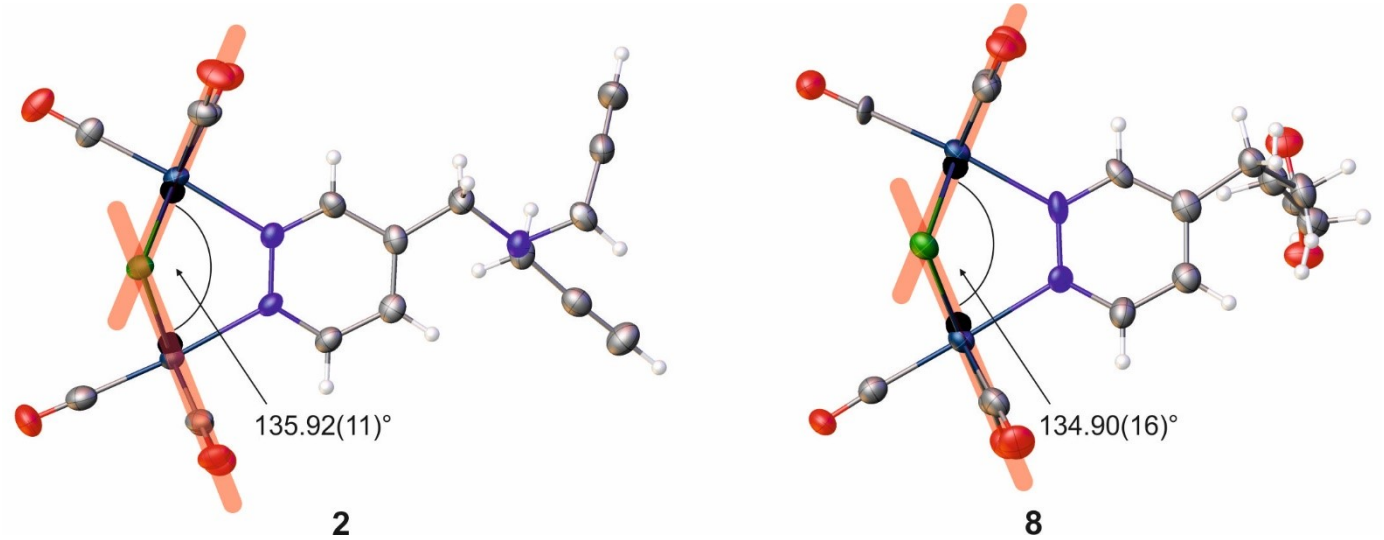

Fig. S21 inclination of the planes defined by the equatorial C-atoms and bridging Cl atoms within the coordination spheres of Re1 and Re2 in **2** and **8**

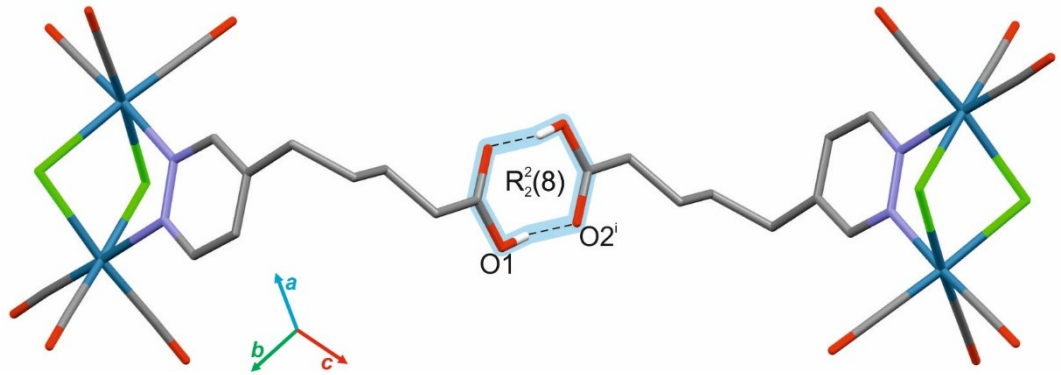

Fig. S22 Individual molecules of **8** held together by the O−H···O hydrogen bonds arranged in R22(8) motif

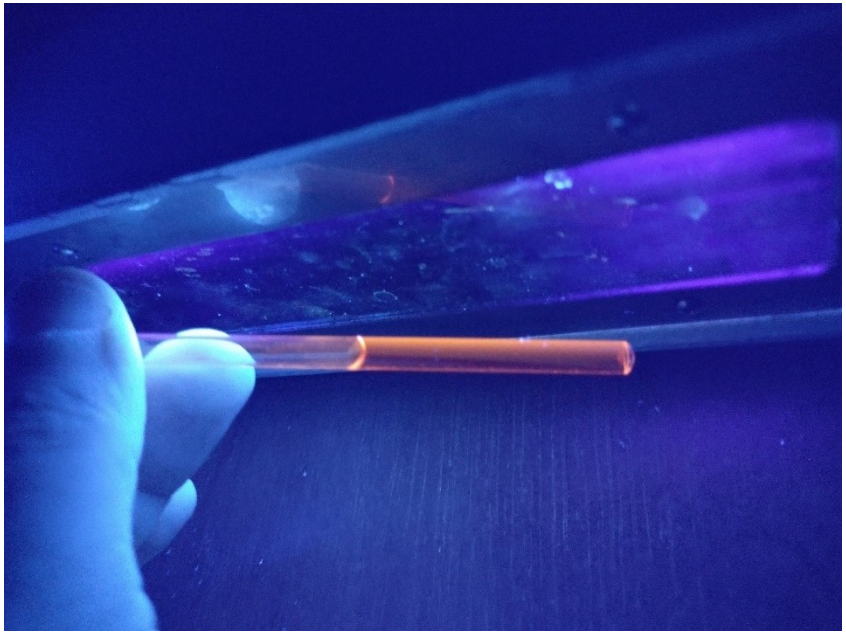

Fig. S13 Luminescence of **5** in air-equilibrated DMSO solution at ambient temperature

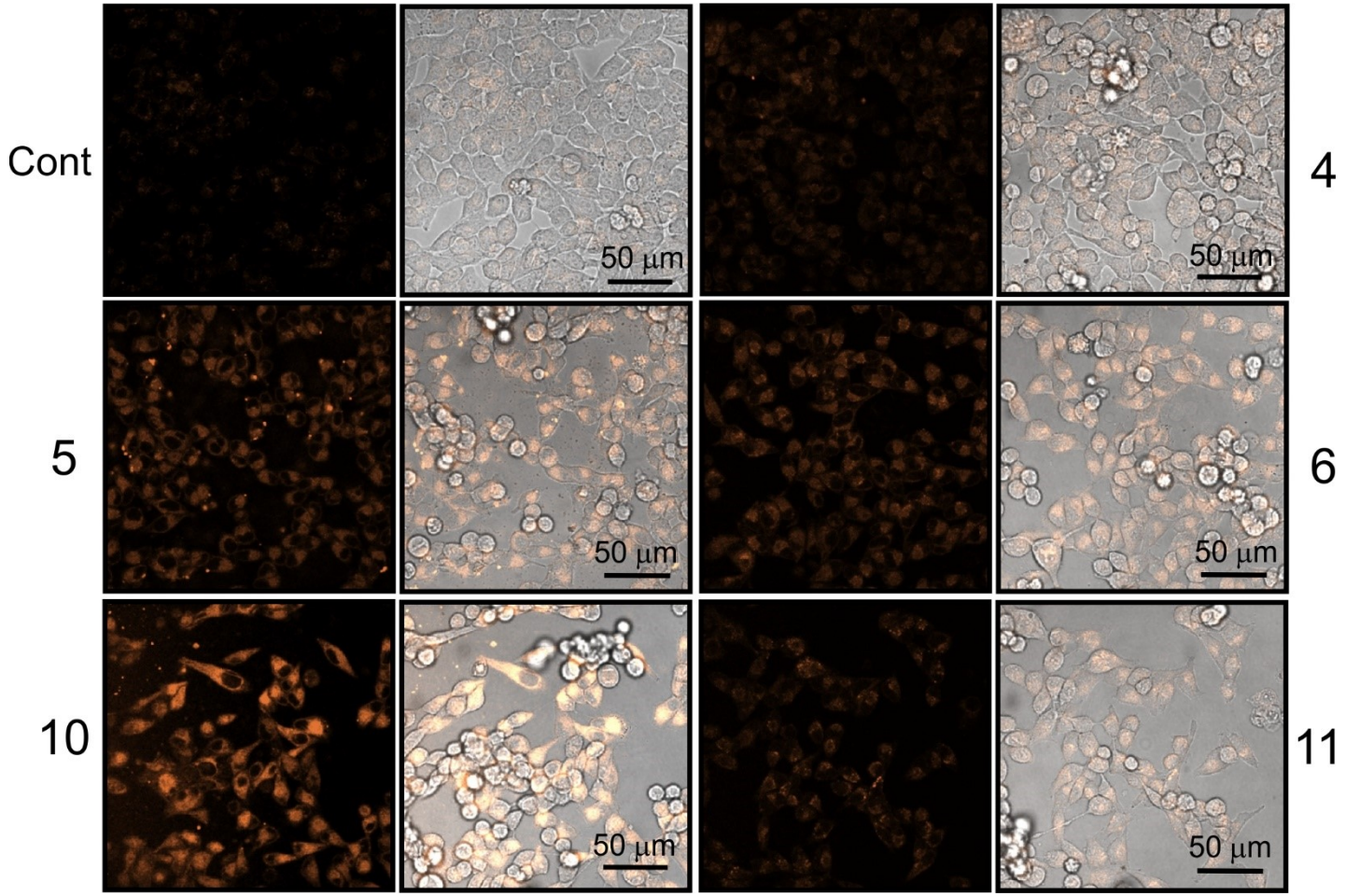

Fig. 14 Comparison of luminescence of HeLa cells after 30 min incubation with dinucleosides (**4, 5**, **6**) and nucleosides (**10**, **11**) given at a concentration of 10 μM with control cells (Cont.). Left column – luminescence images, right column - merged images of luminescence and transmitted light. Excitation/emission - 405/500 – 700 nm. Bars = 50 μm.

Table S1. Crystal data and structure refinement for **2** and **8**

Identification code	**2**	**8**
Empirical formula	$C_{17}H_{11}Cl_2N_3O_6Re_2$	$C_{15}H_{12}Cl_2N_2O_8Re_2$
Formula weight	796.59	791.57
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	19.1476(4)	9.8252(4)
b/Å	6.13921(8)	21.1777(7)
c/Å	20.3399(4)	10.3389(4)
α/°	90	90
β/°	115.439(2)	107.937(5)
γ/°	90	90
Volume/Å^3	2159.15(8)	2046.70(15)
Z	4	4
ρ_{calc}g/cm^3	2.451	2.569
μ/mm^{-1}	24.224	25.605
F(000)	1464.0	1456.0
Crystal size/mm^3	0.24 × 0.05 × 0.03	0.16 × 0.11 × 0.06
Radiation	Cu$K\alpha$ (λ = 1.54184)	Cu$K\alpha$ (λ = 1.54184)
2Θ range for data collection/°	8.394 to 134.158	8.35 to 134.142
Index ranges	$-21 \le h \le 22$, $-7 \le k \le 7$, $-24 \le l \le 23$	$-11 \le h \le 11$, $-17 \le k \le 25$, $-12 \le l \le 12$
Reflections collected	17830	7816
Independent reflections	3855 [R_{int} = 0.0411, R_{sigma} = 0.0322]	3647 [R_{int} = 0.0338, R_{sigma} = 0.0382]
Data/restraints/parameters	3855/0/271	3647/1/265
Goodness-of-fit on F^2	1.064	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0270, wR_2 = 0.0643	R_1 = 0.0389, wR_2 = 0.1028
Final R indexes [all data]	R_1 = 0.0305, wR_2 = 0.0663	R_1 = 0.0439, wR_2 = 0.1063
Largest diff. peak/hole / e Å^{-3}	1.35/-0.89	2.62/-1.43

Table S2. Bond lengths for **2** [Å].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.408(8)	C13	Re1	1.942(7)
C1	N2	1.328(7)	C14	O3	1.153(7)
C2	C3	1.351(8)	C14	Re1	1.899(6)
C2	C5	1.508(8)	C15	O4	1.142(8)
C3	C4	1.396(9)	C15	Re2	1.905(6)
C4	N1	1.335(7)	C16	O5	1.152(7)
C5	N3	1.455(7)	C16	Re2	1.914(6)
C6	C7	1.478(9)	C17	O6	1.157(7)
C6	N3	1.453(7)	C17	Re2	1.907(6)
C7	C8	1.196(10)	Cl1	Re1	2.4830(12)
C9	C10	1.493(9)	Cl1	Re2	2.4925(13)
C9	N3	1.478(7)	Cl2	Re1	2.4978(12)
C10	C11	1.180(10)	Cl2	Re2	2.5034(12)
C12	O1	1.140(7)	N1	N2	1.354(6)
C12	Re1	1.918(6)	N1	Re1	2.204(5)
C13	O2	1.130(8)	N2	Re2	2.204(4)

Table S3. Values of valence angles for **2** [°].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	C1	C2	124.0(5)	C12	Re1	Cl1	95.76(17)
C1	C2	C5	120.1(5)	C12	Re1	Cl2	175.34(17)
C3	C2	C1	116.5(5)	C12	Re1	N1	92.3(2)

C3	C2	C5	123.3(5)	C13	Re1	Cl1	93.08(19)
C2	C3	C4	118.8(5)	C13	Re1	Cl2	93.72(19)
N1	C4	C3	122.3(5)	C13	Re1	N1	174.8(2)
N3	C5	C2	110.7(5)	C14	Re1	C12	89.3(2)
N3	C6	C7	111.4(5)	C14	Re1	C13	90.2(3)
C8	C7	C6	176.8(7)	C14	Re1	Cl1	173.99(18)
N3	C9	C10	113.0(5)	C14	Re1	Cl2	93.34(16)
C11	C10	C9	175.2(7)	C14	Re1	N1	94.4(2)
O1	C12	Re1	178.6(5)	Cl1	Re1	Cl2	81.41(4)
O2	C13	Re1	177.9(6)	N1	Re1	Cl1	82.15(11)
O3	C14	Re1	177.9(5)	N1	Re1	Cl2	83.63(12)
O4	C15	Re2	177.6(6)	C15	Re2	C16	87.8(3)
O5	C16	Re2	178.9(6)	C15	Re2	C17	89.2(2)
O6	C17	Re2	178.5(5)	C15	Re2	Cl1	175.57(18)
Re1	Cl1	Re2	90.91(4)	C15	Re2	Cl2	94.46(17)
Re1	Cl2	Re2	90.31(4)	C15	Re2	N2	96.1(2)
C4	N1	N2	119.9(5)	C16	Re2	Cl1	92.81(19)
C4	N1	Re1	120.1(4)	C16	Re2	Cl2	95.49(17)
N2	N1	Re1	120.1(3)	C16	Re2	N2	175.8(2)
C1	N2	N1	118.4(4)	C17	Re2	C16	88.2(2)
C1	N2	Re2	122.0(4)	C17	Re2	Cl1	95.18(17)
N1	N2	Re2	119.5(3)	C17	Re2	Cl2	174.85(16)
C5	N3	C9	111.6(5)	C17	Re2	N2	93.3(2)
C6	N3	C5	110.8(5)	Cl1	Re2	Cl2	81.12(4)
C6	N3	C9	111.2(5)	N2	Re2	Cl1	83.15(12)
C12	Re1	C13	90.1(2)	N2	Re2	Cl2	82.75(12)

Table S4. Values of torsion angles for **2** [°].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-1.6(8)	C4	N1	N2	Re2	175.8(4)
C1	C2	C5	N3	-167.5(5)	C5	C2	C3	C4	176.7(5)
C2	C1	N2	N1	-0.3(8)	C7	C6	N3	C5	-175.2(5)
C2	C1	N2	Re2	-177.5(4)	C7	C6	N3	C9	60.1(7)
C2	C3	C4	N1	-0.1(8)	C10	C9	N3	C5	-63.3(7)
C2	C5	N3	C6	76.3(6)	C10	C9	N3	C6	61.0(7)
C2	C5	N3	C9	-159.1(5)	N2	C1	C2	C3	1.9(8)
C3	C2	C5	N3	14.1(8)	N2	C1	C2	C5	-176.6(5)
C3	C4	N1	N2	1.7(8)	Re1	N1	N2	C1	178.2(4)
C3	C4	N1	Re1	-178.0(4)	Re1	N1	N2	Re2	-4.4(5)
C4	N1	N2	C1	-1.5(7)					

Table S5. Bond lengths for **8** [Å].

Atom	Atom	Length/Å	Atom	Atom	Length/Å

C1	C2	1.412(13)	C12	O5	1.173(11)
C1	N2	1.337(11)	C12	Re1	1.892(10)
C2	C3	1.362(14)	C13	O6	1.176(11)
C2	C5	1.500(13)	C13	Re2	1.889(10)
C3	C4	1.384(13)	C14	O7	1.140(10)
C4	N1	1.341(11)	C14	Re2	1.922(7)
C5	C6	1.554(13)	C15	O8	1.170(11)
C6	C7	1.533(13)	C15	Re2	1.897(9)
C7	C8	1.508(13)	Cl1	Re1	2.5033(19)
C8	C9	1.489(13)	Cl1	Re2	2.4921(19)
C9	O1	1.306(11)	Cl2	Re1	2.503(2)
C9	O2	1.227(11)	Cl2	Re2	2.4883(19)
C10	O3	1.148(11)	N1	N2	1.356(10)
C10	Re1	1.905(9)	N1	Re1	2.204(7)
C11	O4	1.130(11)	N2	Re2	2.182(7)
C11	Re1	1.935(9)			

Table S6. Values of valence angles for **8** [°].

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N2	C1	C2	124.9(9)	C10	Re1	Cl2	174.3(3)
C1	C2	C5	120.2(9)	C10	Re1	N1	95.1(3)
C3	C2	C1	116.3(9)	C11	Re1	Cl1	95.9(3)
C3	C2	C5	123.6(9)	C11	Re1	Cl2	96.0(3)
C2	C3	C4	118.3(9)	C11	Re1	N1	178.2(3)
N1	C4	C3	123.1(9)	C12	Re1	C10	89.8(4)
C2	C5	C6	111.4(8)	C12	Re1	C11	89.2(4)
C7	C6	C5	110.9(8)	C12	Re1	Cl1	173.8(3)
C8	C7	C6	110.7(8)	C12	Re1	Cl2	95.4(3)
C9	C8	C7	114.2(8)	C12	Re1	N1	92.0(3)

O1	C9	C8	114.5(8)	Cl1	Re1	Cl2	80.61(6)
O2	C9	C8	122.6(8)	N1	Re1	Cl1	82.90(18)
O2	C9	O1	122.9(8)	N1	Re1	Cl2	82.46(19)
O3	C10	Re1	177.0(7)	C13	Re2	C14	89.6(4)
O4	C11	Re1	176.8(8)	C13	Re2	C15	87.5(4)
O5	C12	Re1	178.6(9)	C13	Re2	Cl1	174.0(3)
O6	C13	Re2	178.7(8)	C13	Re2	Cl2	93.7(3)
O7	C14	Re2	179.0(9)	C13	Re2	N2	94.4(3)
O8	C15	Re2	176.9(8)	C14	Re2	Cl1	93.7(3)
Re2	Cl1	Re1	90.78(6)	C14	Re2	Cl2	93.6(3)
Re2	Cl2	Re1	90.87(6)	C14	Re2	N2	175.4(3)
C4	N1	N2	120.4(7)	C15	Re2	C14	89.7(4)
C4	N1	Re1	120.2(6)	C15	Re2	Cl1	97.4(3)
N2	N1	Re1	119.4(5)	C15	Re2	Cl2	176.4(3)
C1	N2	N1	117.1(7)	C15	Re2	N2	92.8(3)
C1	N2	Re2	122.2(6)	Cl2	Re2	Cl1	81.12(7)
N1	N2	Re2	120.7(5)	N2	Re2	Cl1	82.1(2)
C10	Re1	C11	86.4(4)	N2	Re2	Cl2	83.78(19)
C10	Re1	Cl1	94.0(2)				

Table S7. Values of torsion angles for **8** [°].

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	2.0(13)	C4	N1	N2	Re2	-176.9(6)
C1	C2	C5	C6	-130.9(9)	C5	C2	C3	C4	-178.6(9)
C2	C1	N2	N1	0.4(12)	C5	C6	C7	C8	-165.9(8)

C2	C1	N2	Re2	178.0(7)	C6	C7	C8	C9	-167.2(8)
C2	C3	C4	N1	-1.1(14)	C7	C8	C9	O1	-149.8(9)
C2	C5	C6	C7	68.6(10)	C7	C8	C9	O2	33.1(13)
C3	C2	C5	C6	49.7(12)	N2	C1	C2	C3	-1.8(13)
C3	C4	N1	N2	-0.4(13)	N2	C1	C2	C5	178.8(8)
C3	C4	N1	Re1	178.0(7)	Re1	N1	N2	C1	-177.7(6)
C4	N1	N2	C1	0.7(11)	Re1	N1	N2	Re2	4.7(8)

Table S8. DFT optimized ground state (S_0) and T_1 state geometry of **2** in cartesian (XYZ) coordinates.

	State S_0				State T_1		
C	-1.851985000	0.753659000	-0.326587000	C	-1.950525000	0.546544000	-0.498222000
H	-2.021113000	1.837778000	-0.255729000	H	-2.226433000	1.611903000	-0.433304000
C	-2.915810000	-0.119419000	-0.526258000	C	-2.916988000	-0.393837000	-0.767818000
C	-2.585245000	-1.459326000	-0.585469000	C	-2.472674000	-1.739599000	-0.813909000
H	-3.352431000	-2.230261000	-0.732269000	H	-3.162321000	-2.572687000	-0.985824000
C	-1.254192000	-1.797610000	-0.450363000	C	-1.128705000	-1.944848000	-0.606517000
H	-0.929001000	-2.845679000	-0.491260000	H	-0.720870000	-2.968220000	-0.637122000
C	-4.308443000	0.381724000	-0.700011000	C	-4.330696000	-0.026474000	-1.039882000
H	-4.436144000	1.335764000	-0.128703000	H	-4.504172000	1.048515000	-0.771386000
H	-4.420003000	0.677121000	-1.765031000	H	-4.517269000	-0.084219000	-2.136698000
C	-6.530833000	-0.432431000	-1.080054000	C	-6.570028000	-0.875597000	-0.966066000
H	-7.170539000	-1.316875000	-0.883637000	H	-7.176853000	-1.683326000	-0.507220000
H	-6.345744000	-0.448042000	-2.172760000	H	-6.513431000	-1.128341000	-2.045172000
C	-7.253023000	0.781341000	-0.719098000	C	-7.255073000	0.400325000	-0.800711000
C	-7.795805000	1.807309000	-0.373101000	C	-7.757068000	1.487951000	-0.628622000

H	-8.300705000	2.715363000	-0.081440000	H	-8.233992000	2.443639000	-0.488030000
C	-5.421861000	-0.813546000	1.021264000	C	-5.220194000	-0.827608000	1.018006000
H	-5.912374000	0.058487000	1.527089000	H	-5.642657000	0.144637000	1.387915000
H	-4.408664000	-0.867436000	1.473012000	H	-4.157943000	-0.823118000	1.341534000
C	-6.141651000	-2.024844000	1.351282000	C	-5.903072000	-1.919068000	1.677617000
C	-6.753153000	-3.028170000	1.639201000	C	-6.485385000	-2.813500000	2.245147000
H	-7.293124000	-3.925904000	1.897192000	H	-6.993821000	-3.614889000	2.754164000
C	1.338475000	-3.011211000	1.139886000	C	1.576317000	-2.932940000	1.184041000
C	3.676464000	-2.038690000	0.133972000	C	3.833078000	-1.793332000	0.214709000
C	1.672027000	-2.797640000	-1.548590000	C	2.039631000	-2.624814000	-1.632785000
C	0.298430000	3.043554000	-1.256252000	C	0.106363000	3.026566000	-1.265259000
C	2.470892000	3.094947000	0.390901000	C	2.168153000	3.201798000	0.505782000
C	-0.033979000	2.831083000	1.432557000	C	-0.350189000	2.723707000	1.426415000
Cl	2.257994000	0.428654000	-1.531566000	Cl	2.285243000	0.542550000	-1.437979000
Cl	1.846557000	0.167622000	1.767373000	Cl	1.748833000	0.186101000	1.757201000
N	-0.287364000	-0.910495000	-0.268062000	N	-0.238665000	-0.999731000	-0.367068000
N	-0.593380000	0.370414000	-0.206016000	N	-0.659649000	0.293731000	-0.302321000
N	-5.280039000	-0.612949000	-0.396898000	N	-5.247493000	-0.927672000	-0.414215000
O	1.043418000	-3.841801000	1.868105000	O	1.355750000	-3.767735000	1.920011000
O	4.787179000	-2.258255000	0.253508000	O	4.941952000	-1.970304000	0.376834000
O	1.578921000	-3.498188000	-2.447305000	O	2.090131000	-3.280286000	-2.557696000
O	-0.117927000	3.711541000	-2.085480000	O	-0.304991000	3.677721000	-2.106470000
O	3.371846000	3.770702000	0.556646000	O	2.994416000	3.950183000	0.730036000
O	-0.651064000	3.370177000	2.229926000	O	-1.037289000	3.191452000	2.207437000
Re	1.799521000	-1.603575000	-0.064310000	Re	1.938007000	-1.477301000	-0.061542000
Re	0.976174000	1.895393000	0.110160000	Re	0.777642000	1.894565000	0.122967000