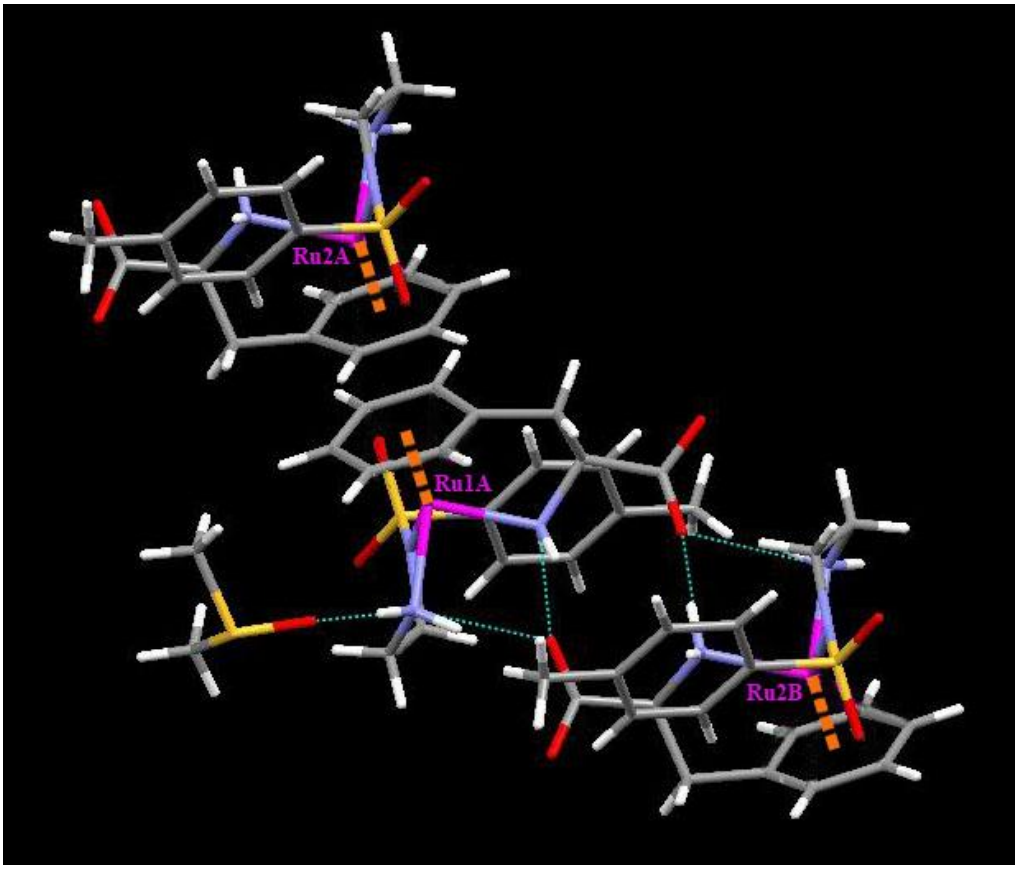
Supplementary table S1. Selected bond lengths (Å) and angles (°) for compound **17**

([(η^6:κ^1-Phe)Ru(enTs)]$_2$·4DMSO)

Ru1-C1	2.094(11)	Ru2-C19	2.126(12)
Ru1-C2	2.173(10)	Ru2-C20	2.151(12)
Ru1-C3	2.175(10)	Ru2-C21	2.172(10)
Ru1-C4	2.167(10)	Ru2-C22	2.240(9)
Ru1-C5	2.167(11)	Ru2-C23	2.195(11)
Ru1-C6	2.191(11)	Ru2-C24	2.158(11)
Ru1-N1	2.153(8)	Ru2-N4	2.148(9)
Ru1-N2	2.103(9)	Ru2-N5	2.137(8)
Ru1-N3	2.079(9)	Ru2-N6	2.130(8)
C8-C9	1.510(11)	C26-C27	1.535(15)
C9-O1	1.205(12)	O5-C27	1.325(16)
C9-O2	1.226(13)	O6-C27	1.211(15)
N3-S1	1.597(9)	N6-S2	1.561(10)
O3-S1	1.431(8)	O7-S2	1.447(8)
O4-S1	1.432(8)	O8-S2	1.444(8)
C6—C1—Ru1	74.9 (6)	C2—C1—Ru1	73.9 (7)
C7—C1—Ru1	115.8 (7)	C3—C2—Ru1	71.2 (6)
C1—C2—Ru1	67.8 (6)	Ru1—C2—H2	134.2
C2—C3—Ru1	71.1 (6)	C4—C3—Ru1	70.5 (6)
Ru1—C3—H3	130.4	C4—C5—Ru1	71.7 (6)
C6—C5—Ru1	72.3 (7)	Ru1—C5—H5	129.0
C1—C6—Ru1	67.3 (6)	C5—C6—Ru1	70.4 (7)
Ru1—C6—H6	135.9	Ru1—N1—H1A	109.5
Ru1—N1—H1B	109.5	C10—N2—Ru1	111.1 (7)
Ru1—N2—H2A	109.4	Ru1—N2—H2B	109.4
C26—N4—Ru2	111.2 (5)	Ru2—N4—H34E	109.4
Ru2—N4—H34F	109.4	C28—N5—Ru2	111.8 (6)
Ru2—N5—H5A	109.3	Ru2—N5—H5B	109.3
N3—Ru1—N2	79.2 (3)	C21—C20—Ru2	72.6 (7)
N3—Ru1—C1	141.2 (4)	C19—C20—Ru2	69.6 (7)
N2—Ru1—C1	135.3 (4)	N3—Ru1—N1	86.8 (3)
N2—Ru1—N1	88.2 (3)	Ru2—C20—H20	131.7
C1—Ru1—N1	78.7 (4)	N3—Ru1—C5	97.1 (4)
C20—C21—Ru2	70.9 (7)	N2—Ru1—C5	139.3 (4)
C22—C21—Ru2	73.7 (6)	C1—Ru1—C5	68.8 (4)
N1—Ru1—C5	132.4 (4)	N3—Ru1—C4	108.6 (4)
Ru2—C21—H21	129.4	N2—Ru1—C4	105.8 (4)
C1—Ru1—C4	81.9 (4)	N1—Ru1—C4	160.6 (3)
C22—C23—Ru2	72.7 (6)	C5—Ru1—C4	36.6 (4)
N3—Ru1—C2	176.9 (4)	N2—Ru1—C2	102.6 (4)
C1—Ru1—C2	38.3 (5)	N1—Ru1—C2	95.8 (4)
C23—C24—Ru2	72.1 (7)	C5—Ru1—C2	79.9 (4)

C19—C24—Ru2	69.4 (6)	C4—Ru1—C2	68.5 (4)
N3—Ru1—C3	140.3 (4)	N2—Ru1—C3	89.5 (4)
Ru2—C24—H24	130.2	C1—Ru1—C3	69.3 (4)
Ru2—C23—H23	131.9	N1—Ru1—C3	131.1 (4)
C5—Ru1—C3	67.6 (4)	C4—Ru1—C3	38.5 (4)
C2—Ru1—C3	37.7 (4)	N3—Ru1—C6	110.8 (4)
N2—Ru1—C6	168.8 (4)	C1—Ru1—C6	37.8 (4)
N1—Ru1—C6	97.2 (4)	C5—Ru1—C6	37.3 (4)
C4—Ru1—C6	66.8 (4)	C2—Ru1—C6	67.2 (4)
C3—Ru1—C6	79.6 (4)	C19—Ru2—N6	134.9 (4)
C19—Ru2—N4	79.8 (4)	N6—Ru2—N4	86.5 (3)
C19—Ru2—N5	142.7 (4)	N6—Ru2—N5	78.7 (4)
N4—Ru2—N5	88.4 (3)	C19—Ru2—C20	38.9 (4)
N6—Ru2—C20	173.4 (5)	N4—Ru2—C20	93.5 (4)
N5—Ru2—C20	107.9 (4)	C19—Ru2—C24	38.8 (4)
N6—Ru2—C24	104.1 (4)	N4—Ru2—C24	100.3 (4)
N5—Ru2—C24	170.9 (4)	C20—Ru2—C24	69.4 (4)
C19—Ru2—C21	68.8 (4)	N6—Ru2—C21	145.7 (4)
N4—Ru2—C21	126.3 (4)	N5—Ru2—C21	91.3 (4)
C20—Ru2—C21	36.6 (4)	C24—Ru2—C21	81.6 (4)
C19—Ru2—C23	69.3 (4)	N6—Ru2—C23	95.4 (4)
N4—Ru2—C23	138.0 (4)	N5—Ru2—C23	133.2 (4)
C20—Ru2—C23	80.3 (4)	C24—Ru2—C23	38.5 (5)
C21—Ru2—C23	67.8 (4)	C19—Ru2—C22	82.4 (4)
N6—Ru2—C22	111.8 (4)	N4—Ru2—C22	160.6 (3)
N5—Ru2—C22	101.1 (3)	C20—Ru2—C22	67.6 (4)
C24—Ru2—C22	69.8 (4)	C21—Ru2—C22	37.7 (4)
C23—Ru2—C22	38.0 (4)		



Supplementary figure S2. Representation of hydrogen bonding network and pi stacking in the crystal of **17** ([(η^6:κ^1-Phe)Ru(enTs)]$_2$·4DMSO). The pi-stacking interaction occurs between Phenyl rings within the same unit cell, the hydrogen bonding connects two complexes of mirrored stereochemistry.

Supplementary table S3. Summery of distances and angles of hydrogen bonds.

Nr	Donor --- H....Acceptor	[ARU]	d [pm]: D–H, H...A, D...A	angle [°]: D - H...A
1	1 N(1) --H(1A) ..O(6)	[x,-1+y,z]	0.92, 1.99, 2.859(15)	157
2	1 N(2) --H(2A) ..O(6)	[x,-1+y,z]	0.92, 1.92, 2.820(14)	165
3	1 N(2) --H(2B) ..O(9)	[ ]	0.92, 1.95, 2.875(15)	179
4	2 N(5) --H(5A) ..O(12)	[1+x,y,1+z]	0.92, 2.01, 2.926(15)	174
5	2 N(5) --H(5B) ..O(1)	[x,1+y,z]	0.92, 2.02, 2.916(15)	165
6	2 N(4) --H(34F) ..O(1)	[x,1+y,z]	0.92, 1.99, 2.844(15)	155

Supplementary table S4. Analysis of short ring-interactions with Cg-Cg Distances < 6.0 Angstrom and Beta < 60.0 Deg.

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Cg(I) Res(I) Cg(J) [ARU(J)]	Cg(1) [1] -> Cg(3) [X,Y,Z]
Cg-Cg	3.508(8)
Transformed J-plane P, Q, R, S:	-0.4578 0.7562 0.4674 6.3724
Alpha Beta Gamma:	2.83 22.94 25.47
CgI_Perp CgJ_Perp:	3.167 3.231

Cg(1)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Cg(3)	C(19)	C(20)	C(21)	C(22)	C(23)	C(24)

- Cg(I) = Plane number I (= ring number in () above)
- Cg-Cg = Distance between ring Centroids (Ang.)
- Alpha = Dihedral Angle between Planes I and J (Deg)
- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)

Supplementary table S5. Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 30.0 Deg)

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X--H(I) Res(I) Cg(J) [ARU(J)]	C(18) -H(18B) [1] -> Cg(4) [1+X,-1+Y,Z]
H..Cg transformed	2.73
J-Plane P, Q, R, S	0.5543 0.8031 0.2186 0.5587
H-Perp Gamma	2.680 10.50
X-H..Cg X..Cg X-H,Pi	149 3.599(18) 65

6-Membered Ring (4) C(30) --> C(31) --> C(32) --> C(33) --> C(34) --> C(35)