Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Redox induced S-S bond cleavage of 2,2′-dithiobisbenzothiazole - leading to a [2Ru-2S] core analogous to [2Fe-2S] cluster

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Experimental

Materials. The precursor complexes *cis*-$Ru(acac)_2(CH_3CN)_2$[1] and $[Ru(Cl)(H)(CO)(PPh_3)_3]$[2] were prepared according to literature procedures. 2,2′-dithiobisbenzothiazole was purchased from Alfa-Aesar. All other chemicals and reagents were of reagent grade and used as received. For spectroscopic and electrochemical studies, HPLC grade solvents were used.

Physical measurements. The electrical conductivity of solutions was checked using an auto-ranging conductivity meter (Toshcon Industries, India). The EPR spectra of isolated complexes and their electrochemically (constant potential coulometry) generated redox species were carried out with a JEOL model FA200 X-band (9.5 GHz) electron spin resonance spectrometer at liquid N_2 temperature using the experimental conditions: frequency, 9.1 GHz; field, 0-5000 G; modulation amplitude, 1 G; modulation frequency, 100 kHz. Cyclic voltammetric and differential pulse voltammetric measurements of the complexes were performed on a PAR model 273A electrochemistry system. Glassy carbon working electrode, platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration cell. The supporting electrolyte was Bu_4NPF_6, and the solute concentration was $\sim 10^{-3}$ M. All electrochemical experiments were carried out under a dinitrogen atmosphere at 298 K with a standard scan rate of 100 mV s^{-1}. The half-wave potential E^0 was set equal to $0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetry peak potentials, respectively. IR spectra of solid samples (in KBr pellets) in the range 400-4000 cm^{-1} was recorded by Bruker Tensor 27 FT-IR spectrophotometer. Absorption spectra were recorded using a Perkin Elmer Lambda 950 spectrophotometer. $^1H/^{13}C/^{31}P$ NMR spectra were recorded on a Bruker Avance III 500 MHz or a Bruker Avance III 400 MHz spectrometer. The elemental analyses were recorded using a Perkin-Elmer 240C elemental analyser. Electrospray mass spectrometry (ESI-MS)

was performed on Bruker's Maxis Impact (282001.0008) spectrometer. GC−MS experiments were performed on an Agilent 5975C spectrometer.

Crystallography. Single crystals were grown by slow evaporation of dichloromenthane/methanol/hexane for **1** and dichloromethane/n-hexane for **2** and **3**. X-ray diffraction data were collected using a Rigaku Saturn-724+ CCD and Bruker D8 quest single crystal diffractometers using Mo-Kα or Cu-Kα radiation at 150(2) K. The data collection was evaluated using the Crystal Clear-SM Expert software. The data were collected by the standard ω-scan technique. The structures were solved by direct methods using SHELXT-2018 and refined by full matrix least-squares with SHELXL-2018, refining on F^2.[3] All data were corrected for Lorentz and polarisation effects and all non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. Hydrogen atoms were included in the refinement process as per the riding model. One toluene molecule and four dichloromethane solvent molecules in the crystals of **1** and **3**, respectively, were masked. The positive residual density around Ru atom in the crystal structure of **1** may be generated due to the poor data of corresponding crystal. CCDC nos. 2082824, 2082825, and 2082826 contain the supplementary crystallographic data for **1**, **2**, and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational studies. Full geometry optimisation as well as the free energy calculation was performed by using the density functional theory method at M06-L level,[4] which was also verified by using (U)B3LYP level of theory.[5] Except ruthenium, all other elements were assigned the 6-31G** basis set. The LANL2DZ basis set with effective core potential was employed for the ruthenium atom.[6] All calculations were performed with Gaussian 09 program package.[7] Calculated structures were visualised with ChemCraft.[8] Calculations of the

fractional contributions of various groups to each molecular orbital were performed by Chemissian 1.7.[9] The zero-point vibrational energies, thermal corrections were obtained from the harmonic frequency calculations.

Preparation of complexes

Synthesis of [Ru(L)(acac)$_2$(MeOH)], 1 and [(acac)$_2$Ru(μ-L)$_2$Ru(acac)$_2$], 2. Complexes **1** and **2** were obtained from the reaction of 1 equivalent of 2,2′-dithiobisbenzothiazole (DTBT) and 2 equivalents of [Ru(acac)$_2$(CH$_3$CN)$_2$] in refluxing tetrahydrofuran (20 cm^3) over a period of 5 h under atmospheric condition. The reaction mixture was then cooled and the solvent was evaporated to dryness under reduced pressure. Purification on a neutral alumina column led to the initial elution of the blue complex (**1**) by 8:2 dichloromethane-pet ether, followed by the yellow complex (**2**) by dichloromethane.

A small quantity of green product corresponding to **1′** was also obtained during column chromatography, which however converted to **2** (blue) in nucleophilic solvents (CH$_3$OH, CH$_3$CN, THF) due to the molecular strain caused by the four-membered chelate. This indeed restricted its further characterisation except via mass spectrometry.

Preformed complex **1** in CH$_2$Cl$_2$ or toluene was also slowly (~48 h) converted to the dinuclear complex **2**.

1. Ru(acac)$_2$(CH$_3$CN)$_2$ (100 mg, 0.26 mmol), DTBT (44 mg, 0.13 mmol), yield 70 mg (58%); ESI-MS (+) in CH$_3$CN: *m*/*Z* {[**1**]–CH$_3$OH +H$^+$} calcd 466.98, found 466.96. ^{1}H NMR (500 MHz, CDCl$_3$) [δ/ppm] = 9.78 (s, 1H), 7.46 (s, 1H), 7.01 (s, 1H), 5.32 (s, 1H), 5.03 (s, 1H), 2.30 (s, 1H), -5.91 (s, 1H), -9.16 (s, 3H), -9.94 (s, 3H), -17.68 (s, 3H), -19.01 (s, 3H). Molar conductivity (CH$_2$Cl$_2$) Λ_M = 8 Ω^{-1} cm^2 M^{-1}. Elemental analysis calcd (%) for C$_{18}$H$_{22}$NO$_5$S$_2$Ru: C, 43.45; H, 4.46; N, 2.82; S, 12.89; found C, 43.64; H, ; N, 3.04; S, 12.72.

2. Ru(acac)$_2$(CH$_3$CN)$_2$ (100 mg, 0.26 mmol), DTBT (44 mg, 0.13 mmol), yield 30 mg (25%); ESI-MS (+) in CH$_3$CN:*m*/*Z* {[**2**]+H$^+$} calcd 932.96, found 932.98.^{1}H NMR (400 MHz,

$CDCl_3$) [δ/ppm]= 8.02 (d, 2H), 7.73 (t, 2H), 7.43 (t, 2H), 7.35 (q, 2H), 5.60 (s, 1H), 5.54 (s, 1H), 4.84 (s, 1H), 4.71 (s, 1H), 2.27 (s, 3H), 2.21 (d, 9H), 1.94 (s, 3H), 1.85 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H). Molar conductivity (CH_2Cl_2) Λ_M = 5 Ω^{-1} cm^2 M^{-1}. Elemental analysis calcd (%) for $C_{34}H_{36}N_2O_8S_4Ru_2$: C, 43.86; H, 3.90; N, 3.01; S, 13.77; found C,43.62; H, 3.74; N, 2.94; S,13.56.

Synthesis of [Ru^{II}(Cl)(L)(CO)(PPh_3)$_2$], 3. The metal precursor Ru(Cl)(H)(CO)(PPh_3)$_3$ (100 mg, 0.137 mmol) and DTBT (23 mg, 0.068 mmol) were taken in a 20 cm^3 of tetrahydrofuran, and the mixture was stirred magnetically at room temperature for 4 h. The solvent was then evaporated under reduced pressure and purification over a neutral alumina column using 3:2 pet ether-dichloromethane as eluent resulted in **3** as a sole product. Yield: 91 mg (78%); ESI-MS (+) in CH_3CN: *m*/*Z* {[**3**–Cl^-]}$^+$ calcd 820.06, found 820.08. ^{1}H NMR (400 MHz, $CDCl_3$) [δ/ppm] = 7.58 (m, 12H), 7.50 (dd, 2H), 7.21–7.08 (m, 19H), 6.87 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) [δ/ppm] = 119.74, 119.80, 122.53, 124.80, 127.76, 129.42, 131.43, 132.12, 132.34, 132.56, 134.19, 149.72, 178.18, 205.66. ^{31}P NMR (202 MHz, $CDCl_3$) [δ/ppm] = 37.93.IR (KBr, cm^{-1}): 1936 [$\nu_{C=O}$]. Molar conductivity (CH_2Cl_2) Λ_M = 7 Ω^{-1} cm^2 M^{-1}. Elemental analysis calcd (%) for $C_{44}H_{34}NOP_2S_2RuCl$: C, 61.79; H, 4.01; N, 1.64; S, 7.50; found C, 61.56; H, 3.88; N, 1.58; S, 7.64.

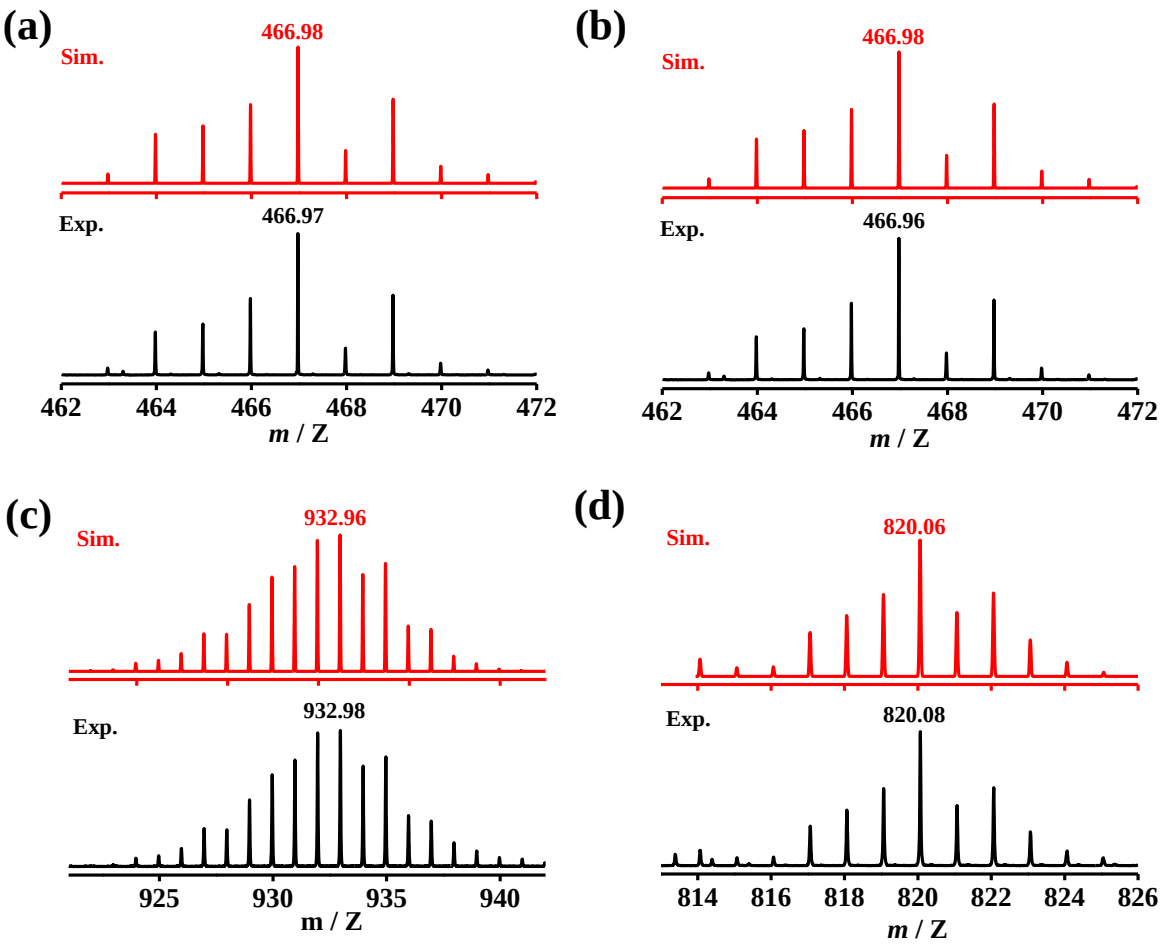


Fig. S1a Experimental and simulated ESI(+) mass spectra of (a) {**1**–CH_3OH+H^+}, (b) {**1′**+ H^+}, (c) {**2**+H^+} and (d) {**3**–Cl^-}$^+$.

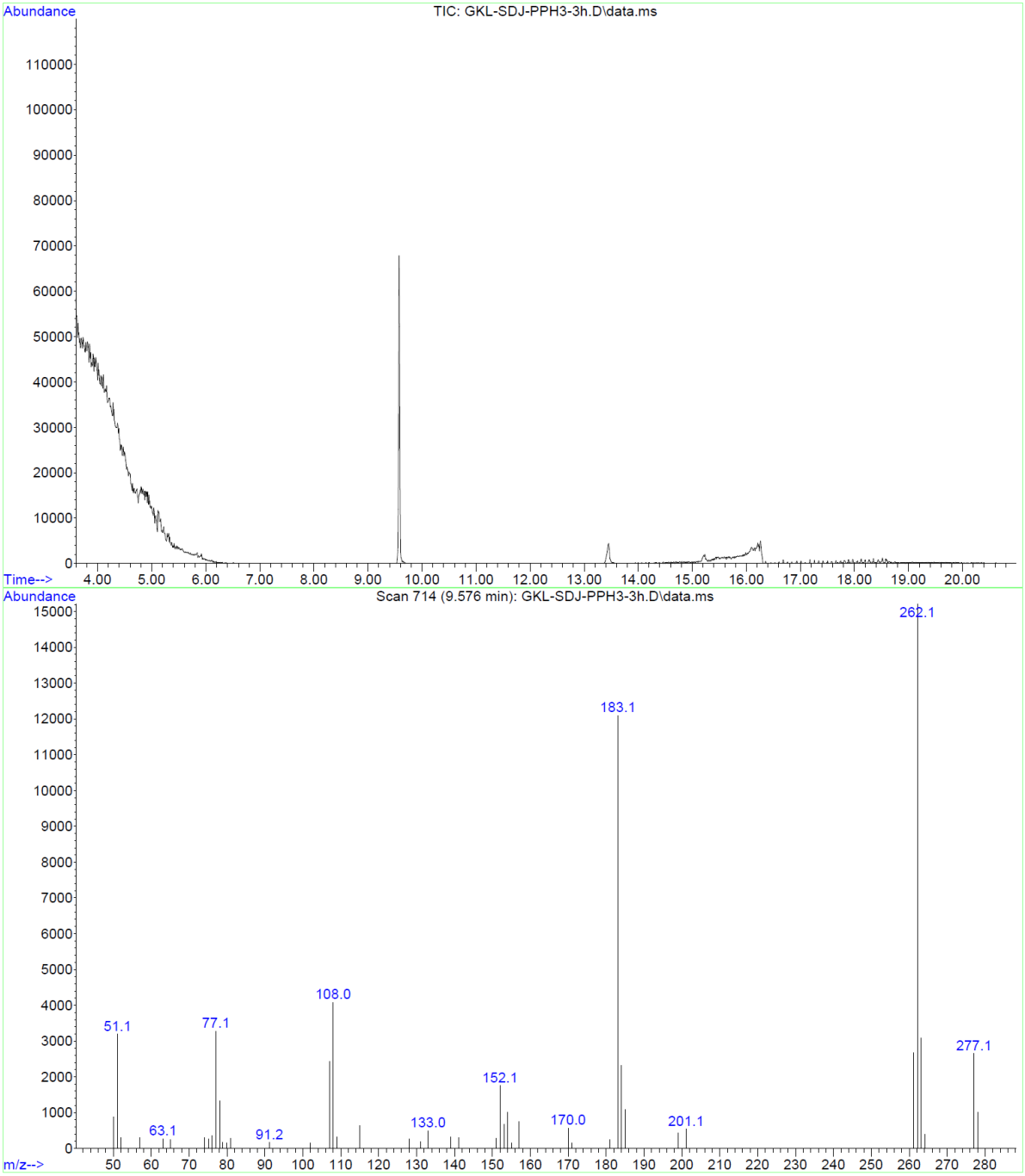


Fig. S1b GC-MS spectrum of the crude reaction mixture of **3**. No trace of benzo[d]thiazole-2-thiol at m/z=167.24.

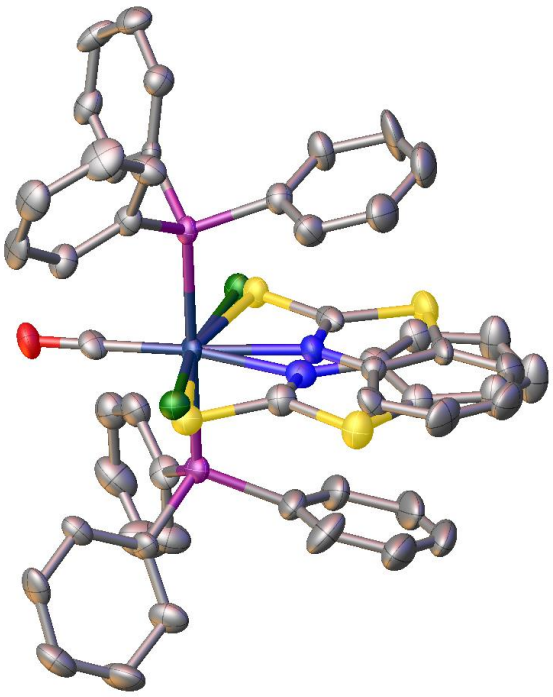


Fig. S2 Perspective view of **3** at 40% probability level. Hydrogen atoms are omitted for clarity. It showed the disorder involved in the crystal structure.

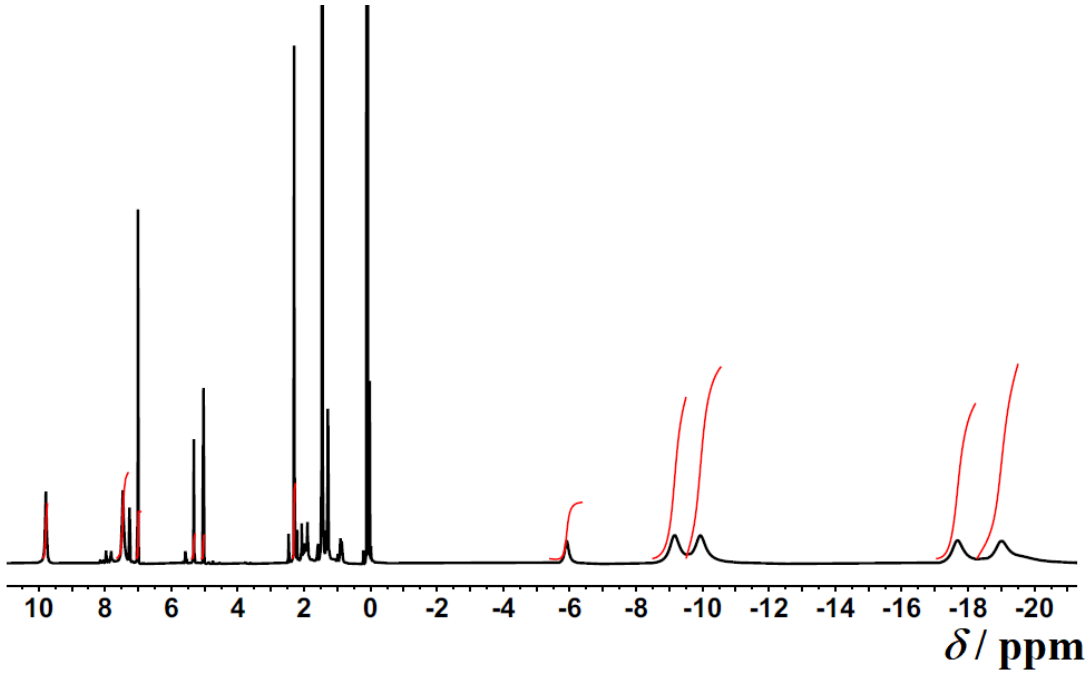


Fig. S3a ^{1}H NMR of **1** in $CDCl_3$ with TMS (δ= 0 ppm) as an internal standard.

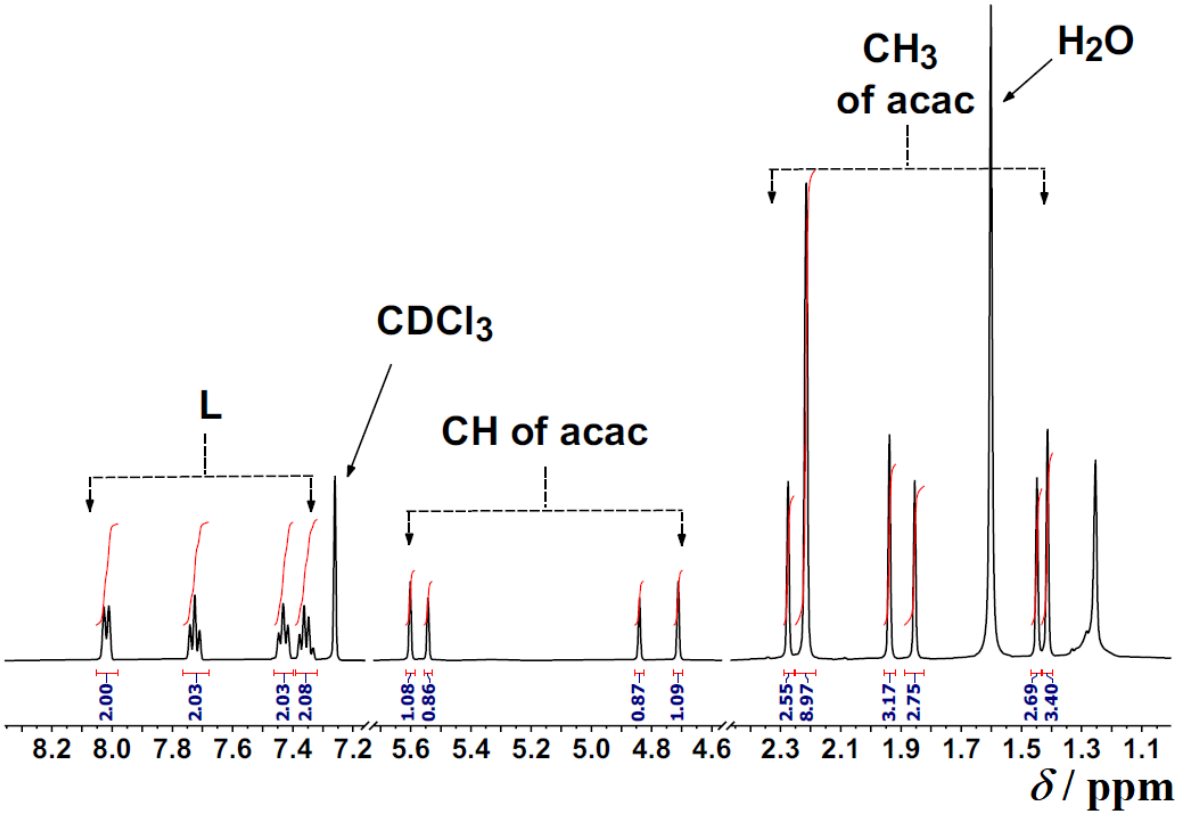


Fig. S3b ^{1}H NMR of **2** in $CDCl_3$ with TMS (δ= 0 ppm) as an internal standard.

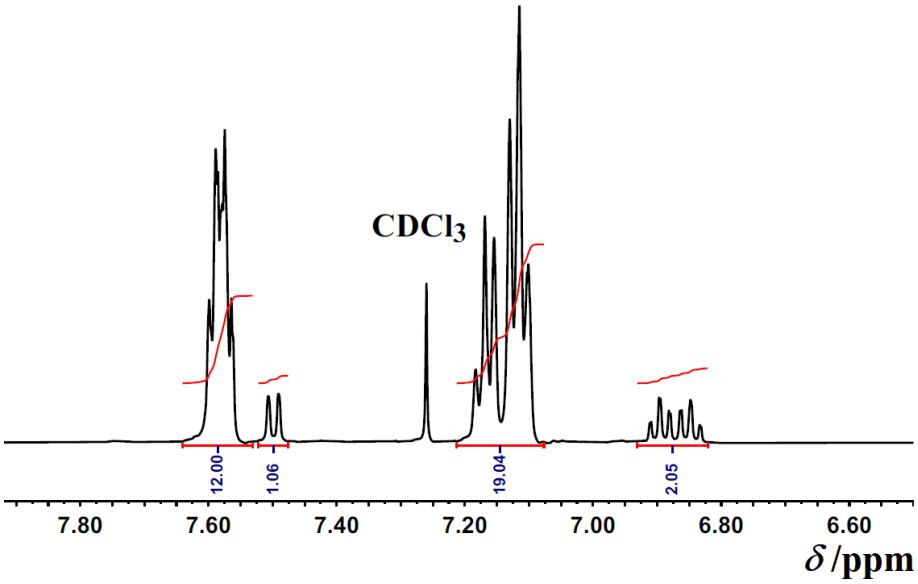


Fig. S3c ^{1}H NMR of **3** in $CDCl_3$ with TMS (δ= 0 ppm) as an internal standard.

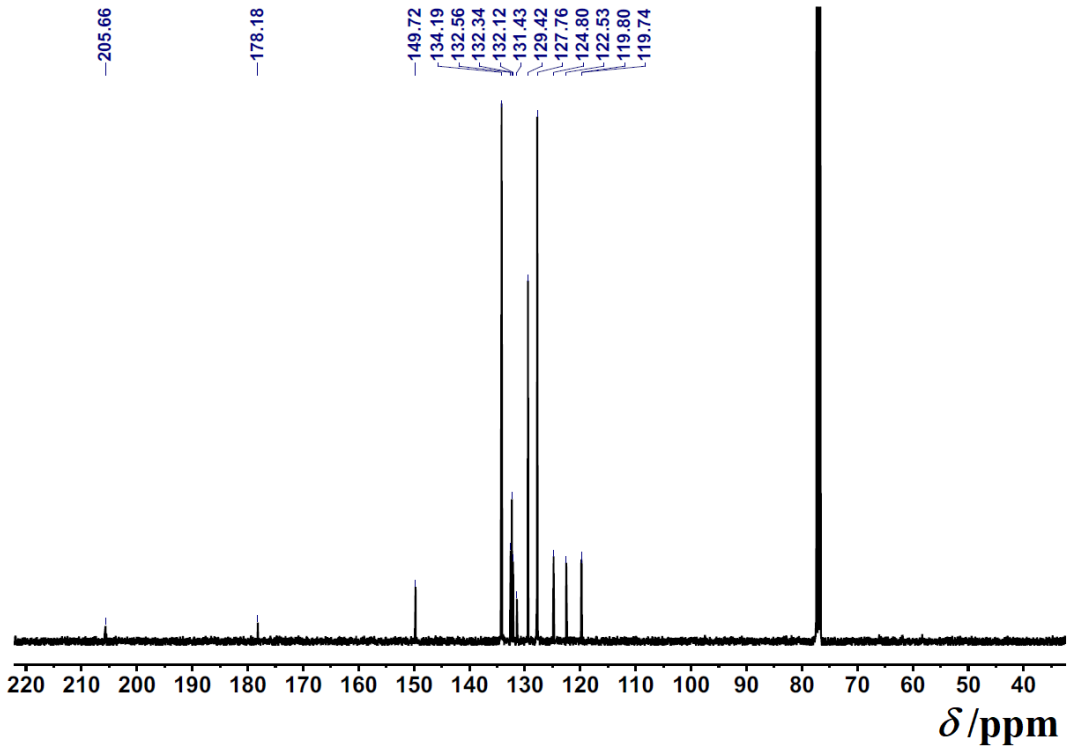


Fig. S3d ^{13}C NMR of **3** in $CDCl_3$ with TMS (δ= 0 ppm) as an internal standard.

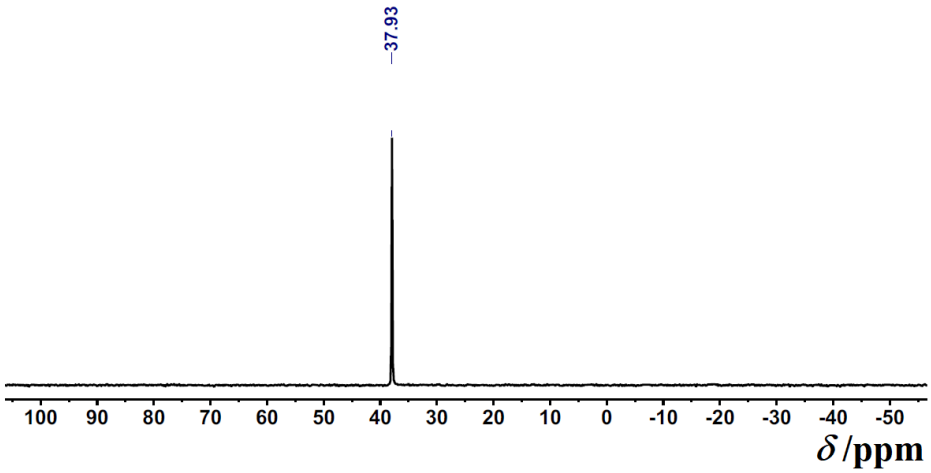


Fig. S3e ^{31}P NMR of **3** in $CDCl_3$.

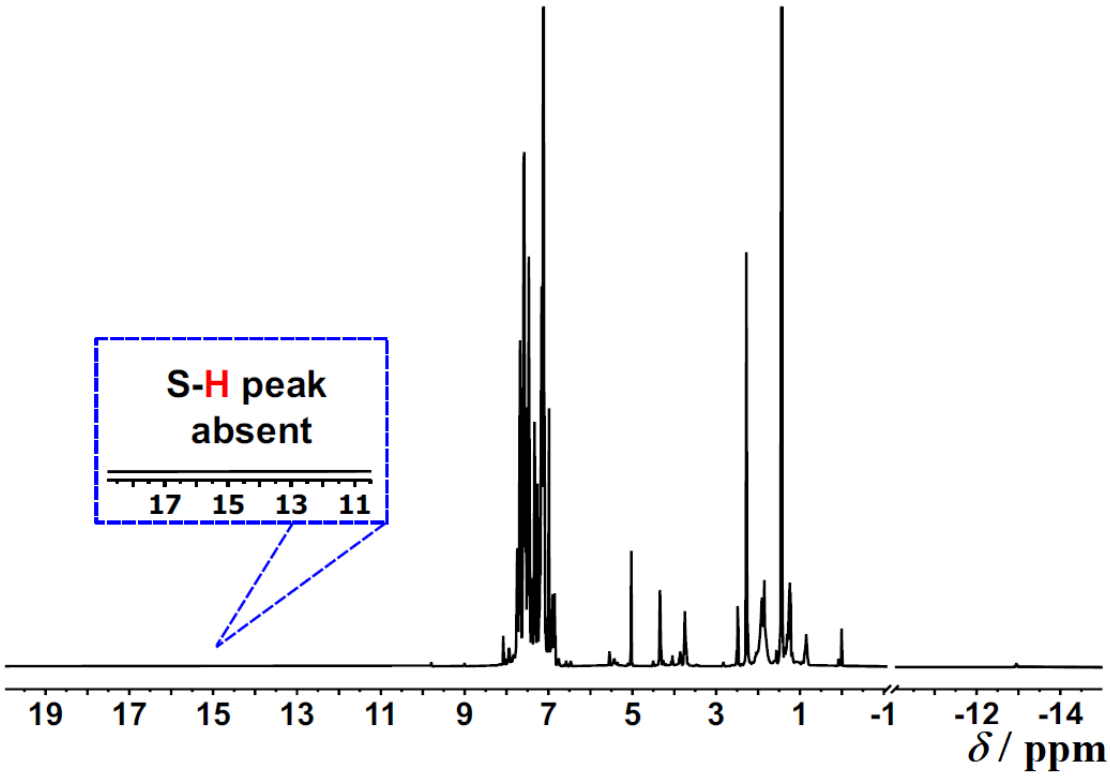


Fig. S3f ^{1}H NMR of crude reaction mixture of **3** in $CDCl_3$. No trace of –SH peak at 13-14 ppm.

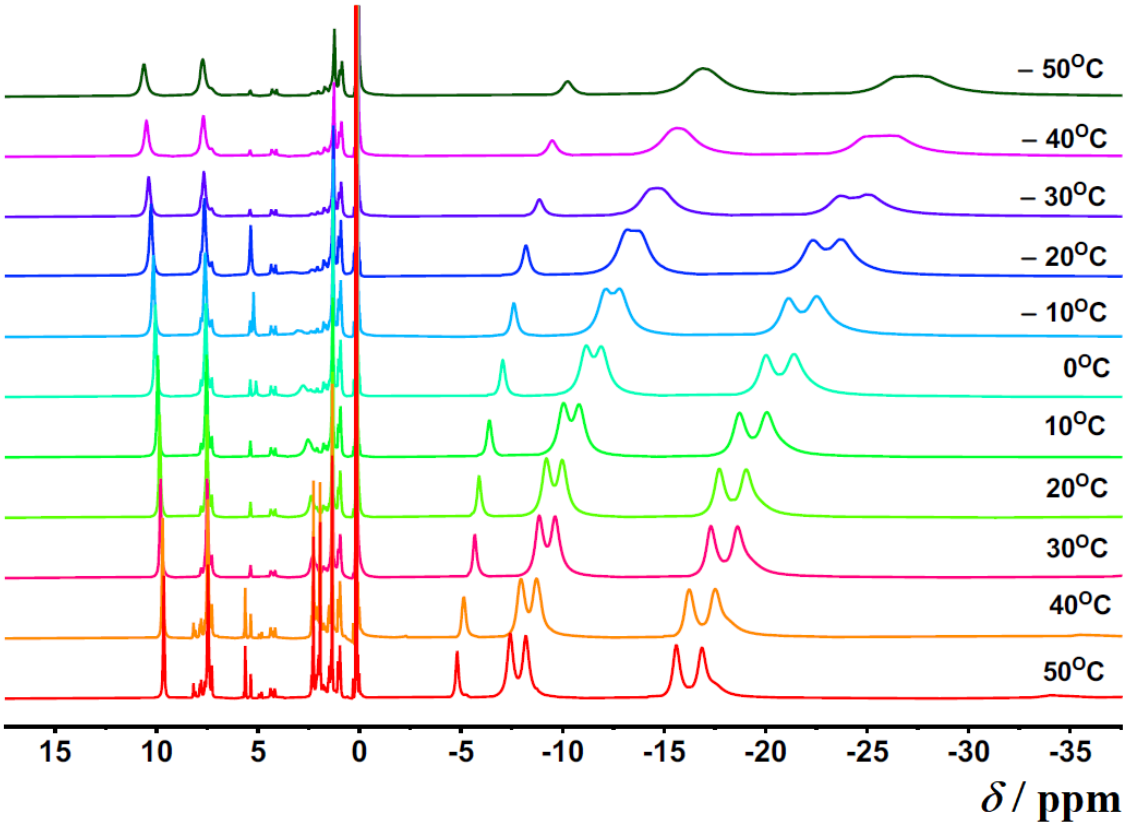


Fig. S3g Variable temperature ^{1}H NMR of **1** in $CDCl_3$ with TMS (δ= 0 ppm) as an internal standard.

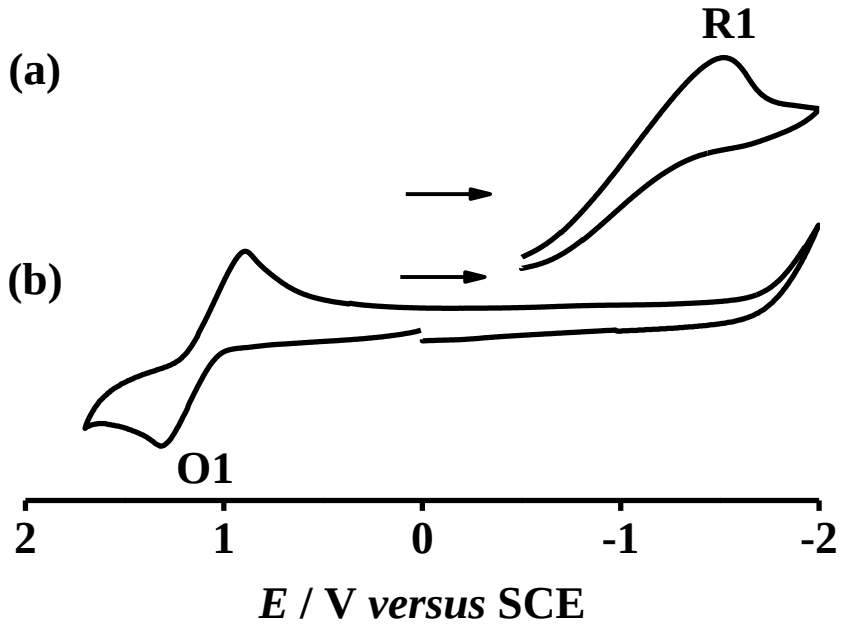


Fig. S4 Cyclic voltammograms of (a) **DTBT** and (b) **3** in CH_2Cl_2/0.1M Bu_4NPF_6.

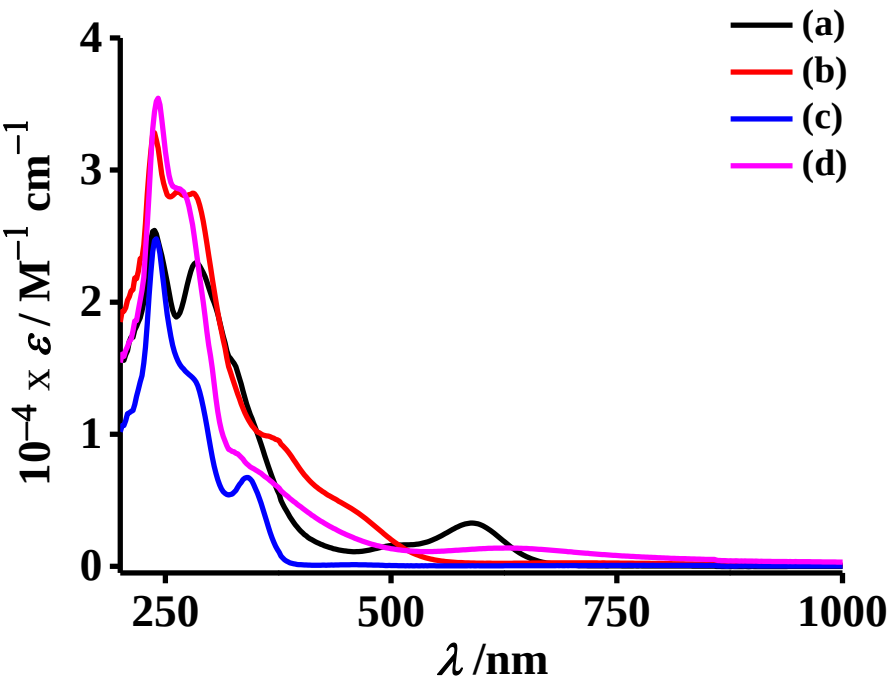


Fig. S5 Electronic spectra of (a) **1**, (b) **2**, (c) **3** and (d) $\mathbf{2}^{-}$ in CH_2Cl_2.

Table S1 Selected crystallographic data

	1	**2**	**3**
empirical formula	$C_{25}H_{30}NO_5RuS2$	$C_{17}H_{18}NO_4RuS_2$	$C_{48}H_{38}Cl_9NOP_2RuS_2$
formula weight	589.718	465.51	11195.092
radiation	CuKα	MoKα	MoKα
crystal system	orthorhombic	monoclinic	monoclinic
space group	P 2_1 2_1 2_1	C2/c	P2_1
a (Å)	8.1204(5)	20.7932(7)	11.6447(4)
b (Å)	14.6197(12)	9.0294(2)	16.6071(5)
c (Å)	22.6698(14)	20.3219(5)	11.6908(3)
α (deg)	90	90	90
β (deg)	90	102.513(3)	98.332(3)
γ (deg)	90	90	90
V (Å^3)	2691.3(3)	3724.81(18)	2236.96(12)
Z	4	8	2
μ (mm^{-1})	6.451	1.087	1.096
ρ_{calcd} (g cm^{-3})	1.455	1.660	1.774
Temperature (K)	150(2)	150(2)	150(2)
F (000)	1218.5	1880.0	1209.4
θ range (deg)	3.60 to 64.98	2.006 to 24.996	1.76 to 25
data/restraints/parameters	4578/3/252	3298/0/230	7771/173/569
*R*1, wR_2 [$I > 2\sigma(I)$]	0.0736, 0.1841	0.0440, 0.1022	0.0483, 0.1348
*R*1, wR_2(all data)	0.0972, 0.2075	0.0553, 0.1102	0.0489, 0.1356
GOF on F^2	1.005	1.073	1.039
largest difference in peak and hole (e Å^{-3})	1.03/-1.14	0.92/-0.57	0.90/-0.90

Table S2 Selected experimental bond lengths (Å)

bond	**1**	**2**	bond	**3**
Ru1-O1	1.998(8)	2.043(3)	Ru1-S1	2.426(4)
Ru1-O2	2.030(7)	2.030(3)	Ru1-N1	2.192(6)
Ru1-O3	2.013(7)	2.040(3)	Ru1-C8	1.820(5)
Ru1-O4	2.036(7)	2.049(3)	Ru1-Cl1	2.406(4)
Ru1-O5	2.101(7)	—	Ru1-P1	2.3766(14)
Ru1-S1	2.275(3)	2.2885(13)	Ru1-P2	2.3902(14)
Ru1-S1′	—	2.2951(13)	S1-C1	1.713(8)
S1-C1	1.731(10)	1.772(5)	C1-S2	1.740(6)
C1-S2	1.774(10)	1.734(5)	C1-N1	1.336(10)
C1-N1	1.264(13)	1.295(6)	S2-C2	1.735(8)
S2-C2	1.756(12)	1.736(6)	C2-C3	1.400(10)
C2-C3	1.421(15)	1.399(7)	C3-C4	1.384(13)
C3-C4	1.398(16)	1.402(9)	C4-C5	1.359(13)
C4-C5	1.364(17)	1.392(9)	C5-C6	1.431(10)
C5-C6	1.369(16)	1.373(8)	C6-C7	1.402(11)
C6-C7	1.384(16)	1.405(8)	C7-N1	1.353(9)
C7-N1	1.411(14)	1.386(6)	C8-O1	1.187(7)
05-C18	1.456(14)	—		
Ru1-Ru1′	—	2.7773(8)		

Table S3 Selected experimental bond angles (°)

bond angle	**1**	bond angle	**2**	bond angle	**3**
O1-Ru-S1	94.8(2)	O1-Ru1-S1	96.44(9)	P1-Ru1-Cl1	89.10(8)
O1-Ru-O3	86.8(3)	O1-Ru1-O3	83.04(13)	P1-Ru1-S1	87.66(10)
O1-Ru-O5	89.1(3)	O1-Ru1-O4	175.94(13)	P1-Ru1-P2	178.66(10)
O1-Ru-O4	177.2(3)	O1-Ru1-O2	93.94(13)	Cl1-Ru1-S1	158.55(10)
O1-Ru-O2	93.8(3)	O3-Ru1-S1	87.11(10)	P2-Ru1-Cl1	92.22(8)
O3-Ru-S1	95.2(2)	O3-Ru1-O4	92.93(13)	P2-Ru1-S1	91.03(10)
O3-Ru-O5	87.6(3)	O2-Ru1-O3	83.51(14)	N1-Ru1-P1	88.81(17)
O3-Ru1-O4	92.5(3)	O4-Ru1-S1	83.85(9)	N1-Ru1-Cl1	90.8(2)
O3-Ru1-O2	174.3(3)	O2-Ru1-S1	165.06(10)	N1-Ru1-S1	67.9(2)
O5-Ru1-S1	175.4(3)	O2-Ru1-O4	85.04(13)	N1-Ru1-P2	90.97(17)
O4-Ru1-S1	87.9(2)	S1′-Ru1-Ru1′	52.60(3)	C8-Ru1-P1	91.03(16)
O4-Ru1-O5	88.2(3)	S1-Ru1-Ru1′	52.81(3)	C8-Ru1-Cl1	96.56(19)
O2-Ru1-S1	90.5(2)	Ru1-S1-Ru1′	74.59(4)	C8-Ru1-S1	104.69(19)
O2-Ru1-O5	86.7(3)			C8-Ru1-P2	89.02(16)
O2-Ru1-O4	86.6(3)			C8-Ru1-N1	172.6(3)
				O1-C8-Ru1	179.1(5)

Table S4 EPR data in CH_2Cl_2-toluene (5:1) at 100 K

Complex	g_1	g_2	g_3	$\langle g \rangle^a$	Δg^b
1 (S=1/2)	2.290	2.151	1.880	2.114	0.410
$\mathbf{2}^-$ (S=1/2)	2.399	2.187	1.805	2.144	0.594

$^a\langle g \rangle = \{(1/3)(g_1^2+g_2^2+g_3^2)\}^{1/2}$, $^b\Delta g = g_1-g_3$.

Table S5 Electrochemical data[a]

Complex	E°_{298}/V (ΔE/mV)[b]	
	Ox1	Red1
DTBT	-	−1.50[c]
3	1.11(400)	-

[a]From cyclic voltammetry in CH_2Cl_2/0.1 M Bu_4NPF_6 at 100 mVs^{-1}.

[b]Potentials in V *versus* SCE; peak potential differences ΔE/mV (in parentheses).

[c]Irreversible.

Table S6 Electronic spectral data

Complex	λ / nm (ε / dm^3 mol^{-1} cm^{-1})
1	590(3480), 505(1760), 328(15290), 284(23200), 237(25640)
2	453(4600), 374(9810), 281(28350), 263(28490), 237(33000)
3	340(6980), 282(14330), 239(24920)
2^{-}	642(1340), 357(7020),329(8670), 266(28420), 242(35370)

Table S7 Composition and energies of selected molecular orbitals of **DTBT** (*S*=0)

MO	Energy(ev)	Composition	
		bridge SS	Rings (rest of the ligand)
HOMO–5	-6.953	6	94
HOMO–4	-6.886	40	60
HOMO–3	-6.074	2	98
HOMO–2	-6.057	0	100
HOMO–1	-5.939	15	85
HOMO	-5.363	60	40
LUMO	-2.811	89	11
LUMO+1	-1.738	5	95
LUMO+2	-1.590	11	89
LUMO+3	-0.966	0	100
LUMO+4	-0.964	0	100
LUMO+5	-0.848	7	93

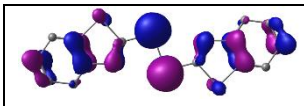
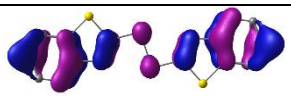
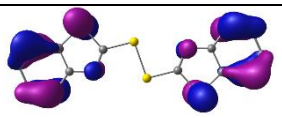
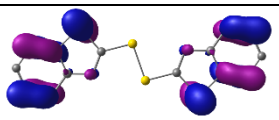
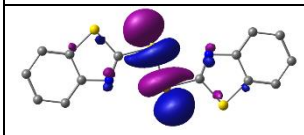
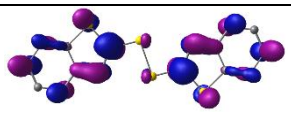
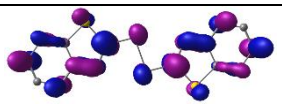
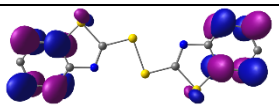
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 Composition and energies of selected molecular orbitals of **1** (*S*=1/2)

MO	Energy(ev)	Composition		
		Ru1	L	acac
		α-spin		
HOMO–5	-5.751	4	3	92
HOMO–4	-5.460	2	95	3
HOMO–3	-5.241	12	46	42
HOMO–2	-5.122	74	12	14
HOMO–1	-4.450	79	1	20
HOMO	-4.369	40	46	15
LUMO	-2.003	50	28	22
LUMO+1	-1.789	7	1	92
LUMO+2	-1.519	6	2	91
LUMO+3	-1.156	55	1	44
LUMO+4	-0.969	3	96	2
LUMO+5	-0.423	1	98	1
		β-spin		
HOMO–5	-5.483	11	22	68
HOMO–4	-5.652	4	5	91
HOMO–3	-5.417	1	98	1
HOMO–2	-5.034	9	68	23
HOMO–1	-4.803	74	12	14
HOMO	-4.131	80	1	19
LUMO	-3.509	61	25	13
LUMO+1	-1.772	4	1	95
LUMO+2	-1.588	50	27	23
LUMO+3	-1.488	8	3	89
LUMO+4	-0.933	3	94	2
LUMO+5	-0.670	59	1	40

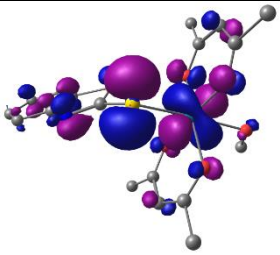
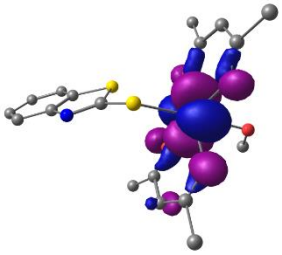
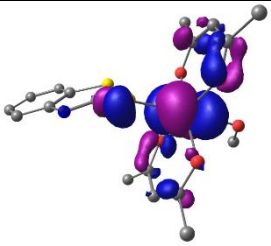
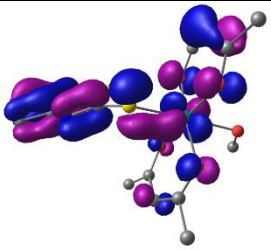
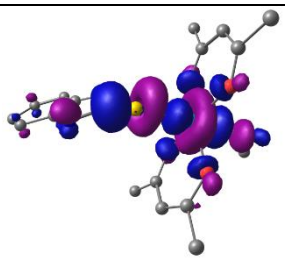
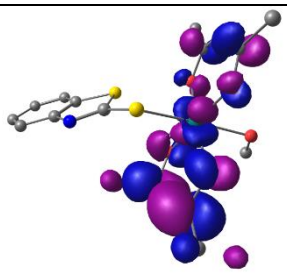
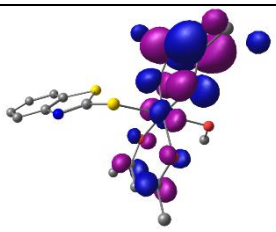
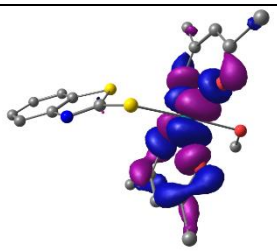
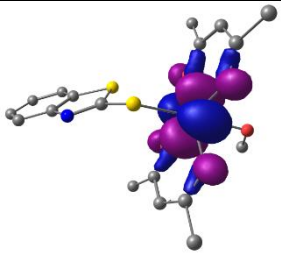
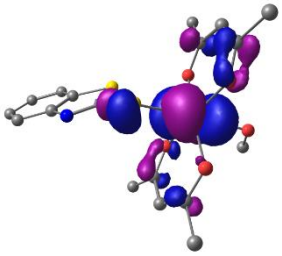
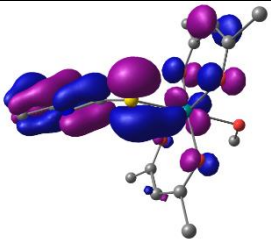
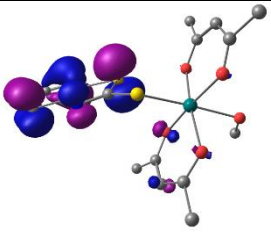
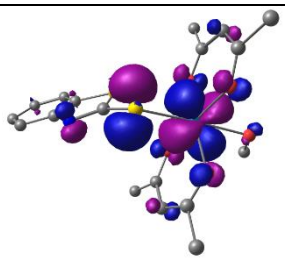
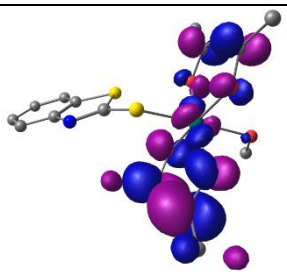
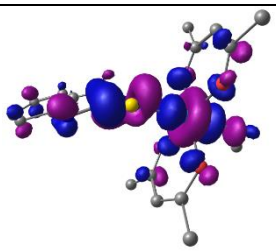
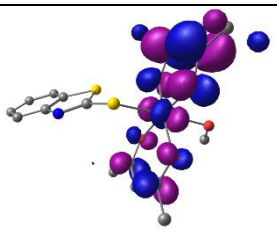
α-spin			
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (S=1)

MO	Energy(ev)	Composition		
		Ru1	L	acac
		α-spin		
HOMO–5	-9.620	35	56	9
HOMO–4	-9.433	41	51	8
HOMO–3	-9.097	39	3	58
HOMO–2	-8.844	25	29	46
HOMO–1	-8.552	2	94	4
SOMO1	-8.049	19	71	10
LUMO	-6.045	50	28	22
LUMO+1	-5.890	46	0	53
LUMO+2	-5.232	9	1	90
LUMO+3	-5.139	13	1	86
LUMO+4	-4.321	1	97	2
LUMO+5	-3.450	0	1	99
		β-spin		
HOMO–5	-9.499	4	85	11
HOMO–4	-9.479	9	42	49
HOMO–3	-9.335	10	7	83
HOMO–2	-8.929	74	12	14
HOMO–1	-8.554	6	88	5
HOMO	-8.375	20	59	22
LUMO	-7.882	72	1	27
LUMO+1	-7.436	40	46	14
LUMO+2	-5.509	18	1	81
LUMO+3	-5.414	51	27	22
LUMO+4	-5.160	7	2	92
LUMO+5	-4.780	47	1	53

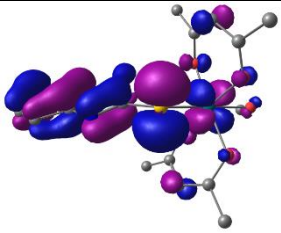
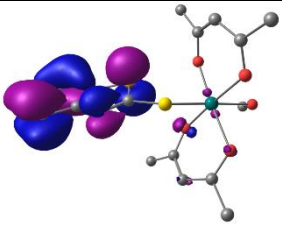
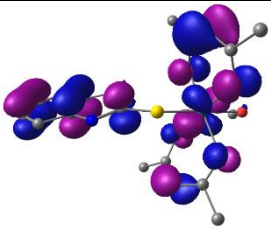
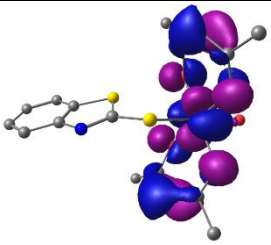
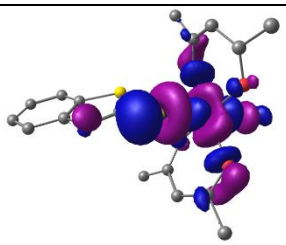
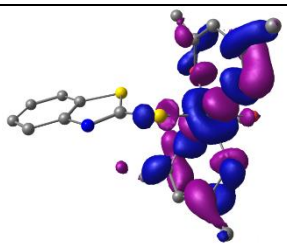
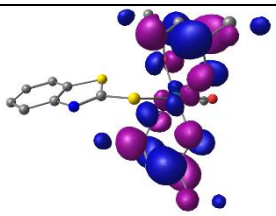
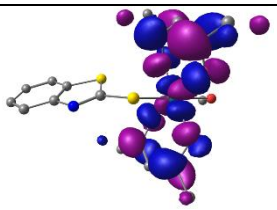
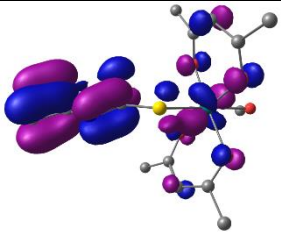
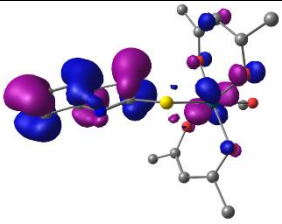
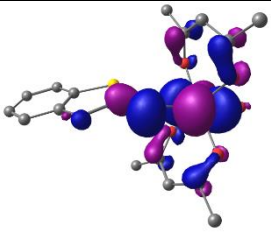
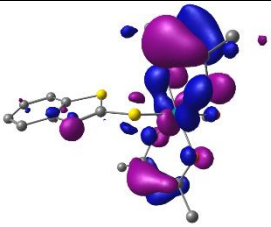
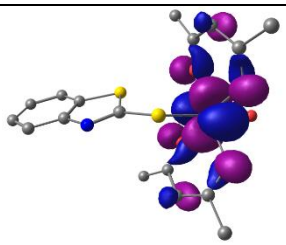
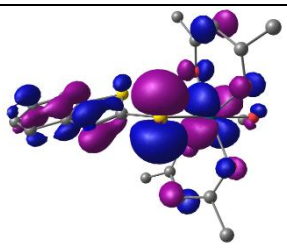
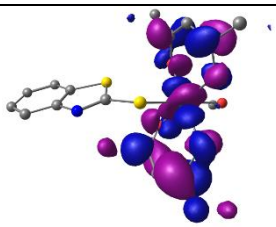
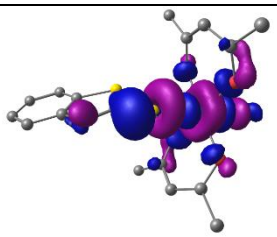
α-spin			
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 Composition and energies of selected molecular orbitals of $\mathbf{1}^{-}$ (*S*=0)

MO	Energy(ev)	Composition		
		Ru1	L	acac
HOMO–5	-2.255	4	74	22
HOMO–4	-2.128	4	7	89
HOMO–3	-1.441	7	72	21
HOMO–2	-0.555	71	12	18
HOMO–1	0.239	83	1	16
HOMO	0.438	66	22	13
LUMO	1.736	1	1	98
LUMO+1	2.099	12	3	85
LUMO+2	2.299	5	92	2
LUMO+3	2.610	17	76	8
LUMO+4	2.696	40	40	20
LUMO+5	3.213	72	6	21

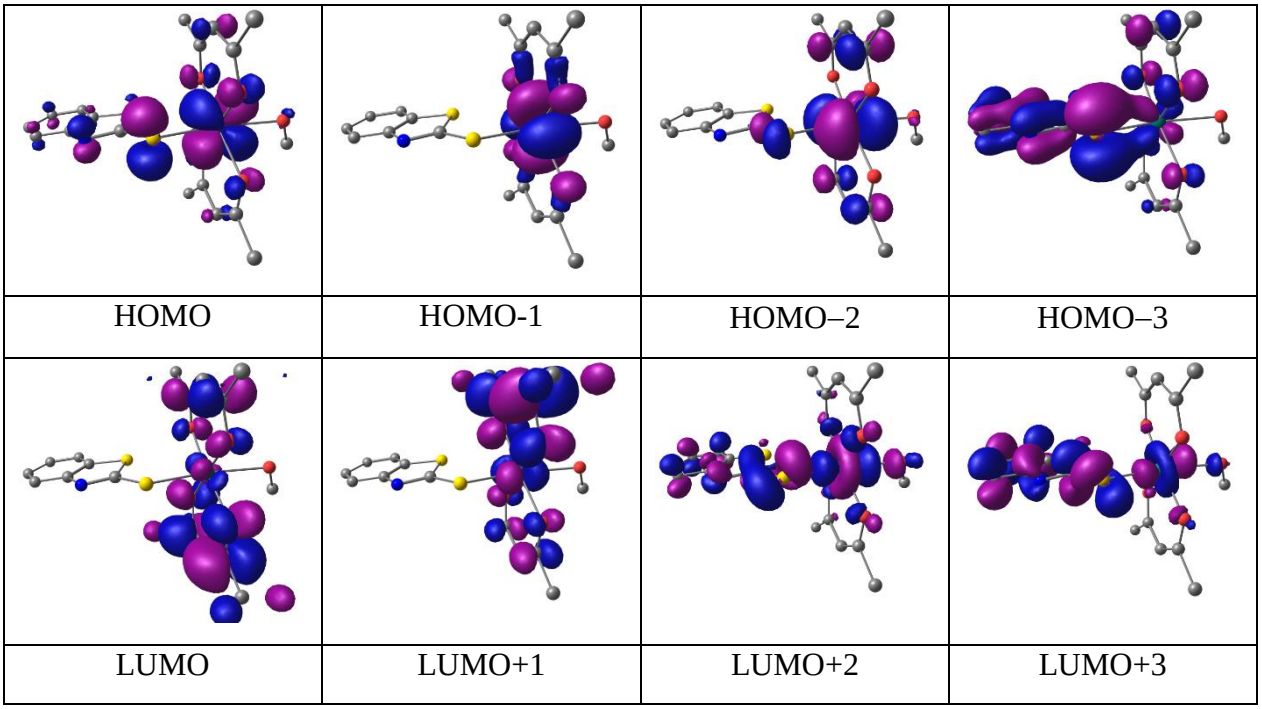


Table S11 Composition and energies of selected molecular orbitals of **2** (*S*=0)

MO	Energy(ev)	Composition			
		Ru1	Ru2	L	acac
HOMO–5	-5.392	5	5	23	67
HOMO–4	-5.361	7	7	19	67
HOMO–3	-4.983	27	27	11	36
HOMO–2	-4.734	37	37	2	24
HOMO–1	-4.550	31	31	14	23
HOMO	-4.306	40	40	1	19
LUMO	-3.515	31	31	30	9
LUMO+1	-2.502	26	26	25	22
LUMO+2	-1.782	20	20	42	18
LUMO+3	-1.509	3	3	7	87
LUMO+4	-1.508	7	7	10	76
LUMO+5	-1.464	13	13	24	50

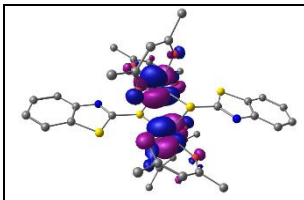
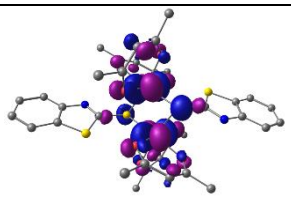
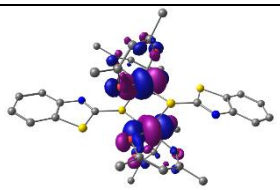
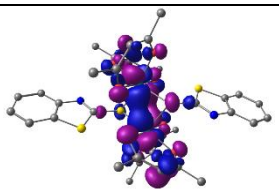
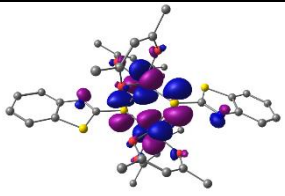
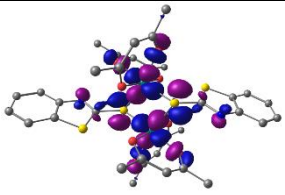
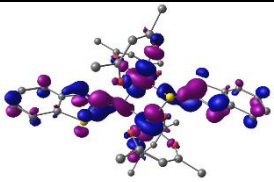
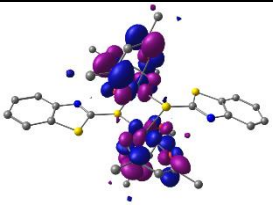
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Composition and energies of selected molecular orbitals of $\mathbf{2}^{+}$ (S=1/2)

MO	Energy(ev)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO–5	-8.098	1	26	54	19
HOMO–4	-8.057	1	2	94	3
HOMO–3	-8.016	0	7	70	22
HOMO–2	-7.979	2	31	15	52
HOMO–1	-7.658	51	7	10	32
SOMO1	-7.566	58	15	3	24
LUMO	-6.085	38	19	31	11
LUMO+1	-5.709	9	40	28	23
LUMO+2	-4.988	5	47	12	36
LUMO+3	-4.638	18	4	14	63
LUMO+4	-4.491	28	6	26	41
LUMO+5	-4.457	1	15	6	79
			β-spin		
HOMO–5	-8.112	10	7	53	30
HOMO–4	-8.055	1	2	93	4
HOMO–3	-8.032	3	8	74	15
HOMO–2	-7.948	8	32	22	37
HOMO–1	-7.637	52	10	6	32
HOMO	-7.484	48	28	2	22
LUMO	-7.248	10	47	11	32
LUMO+1	-6.638	31	30	28	11
LUMO+2	-5.449	15	36	26	22
LUMO+3	-4.703	7	32	11	49
LUMO+4	-4.598	11	5	11	73
LUMO+5	-4.426	27	9	31	33

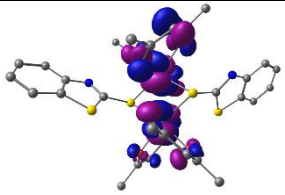
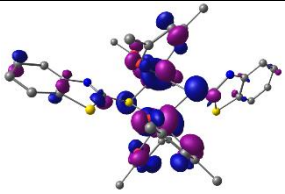
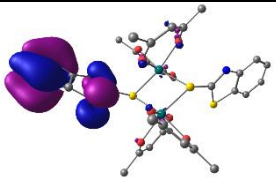
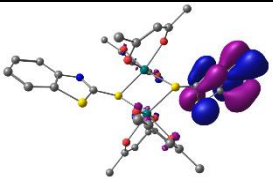
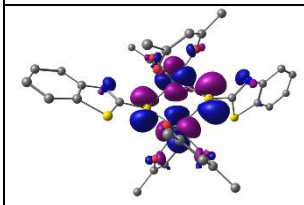
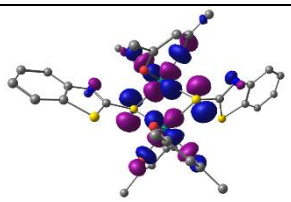
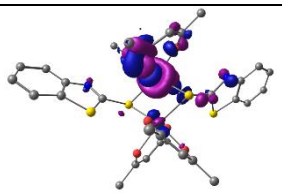
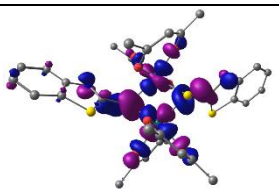
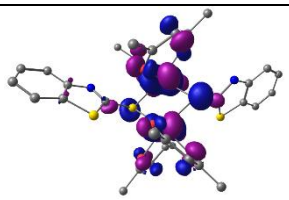
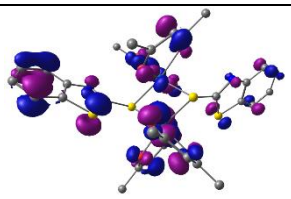
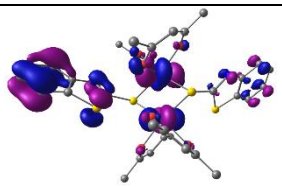
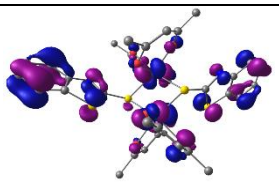
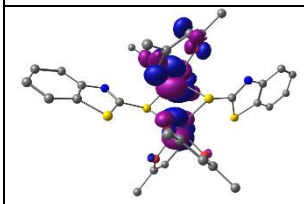
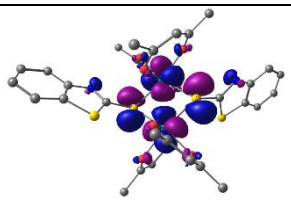
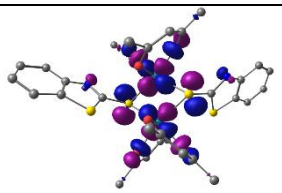
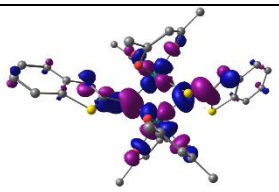
α-spin			
			
SOMO1	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Composition and energies of selected molecular orbitals of $\mathbf{2}^{-}$ (S=1/2)

MO	Energy(ev)	Composition			
		Ru1	Ru2	L	acac
			α-spin		
HOMO–5	-2.119	28	28	20	24
HOMO–4	-1.625	33	33	12	21
HOMO–3	-1.580	40	40	2	19
HOMO–2	-1.369	35	35	12	18
HOMO–1	-1.327	40	40	1	18
HOMO	-1.060	35	35	17	13
LUMO	0.574	21	21	41	16
LUMO+1	0.954	14	14	60	11
LUMO+2	1.293	1	1	94	3
LUMO+3	1.321	3	3	2	93
LUMO+4	1.343	5	5	19	71
LUMO+5	1.415	5	5	3	88
			β-spin		
HOMO–5	-2.574	2	2	27	69
HOMO–4	-1.787	33	33	19	16
HOMO–3	-1.438	34	34	13	20
HOMO–2	-1.356	40	40	2	18
HOMO–1	-1.102	41	41	2	17
HOMO	-0.995	36	36	11	16
LUMO	-0.386	36	36	17	11
LUMO+1	0.731	19	19	48	14
LUMO+2	1.047	11	11	67	11
LUMO+3	1.302	2	2	3	93
LUMO+4	1.341	3	3	2	93
LUMO+5	1.370	3	3	8	86

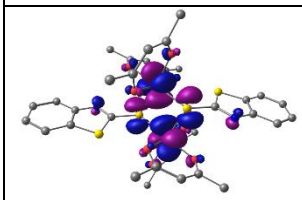
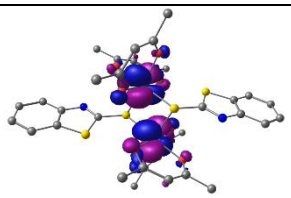
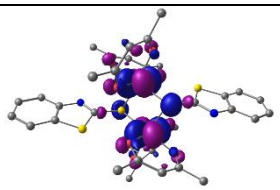
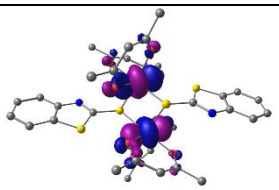
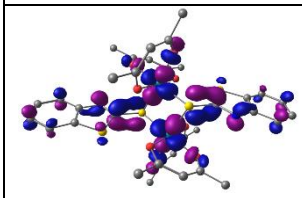
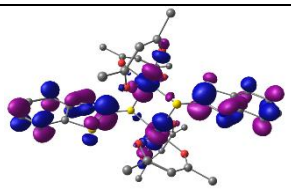
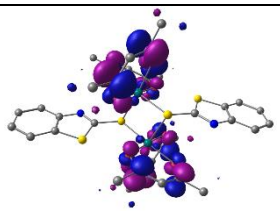
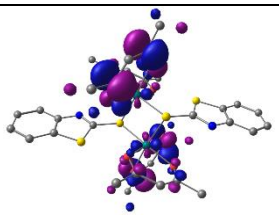
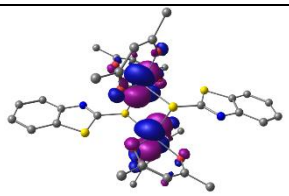
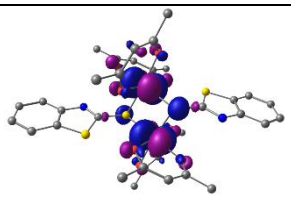
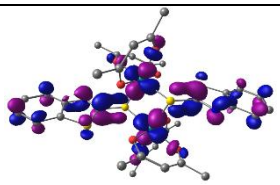
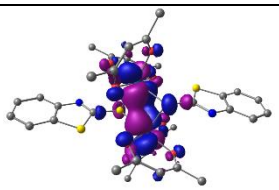
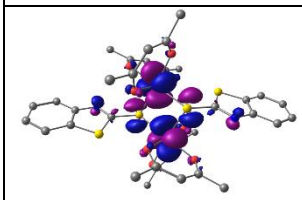
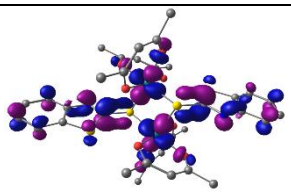
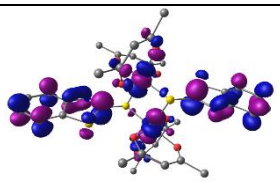
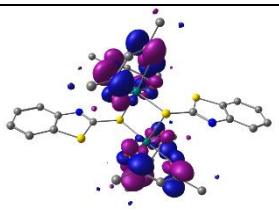
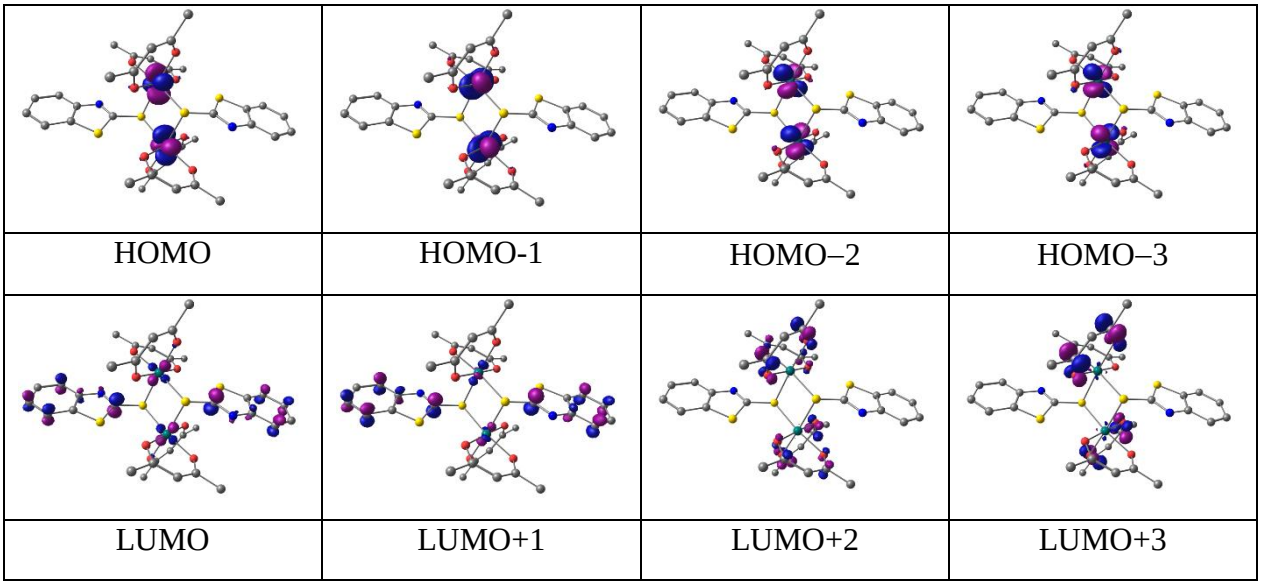
α-spin			
			
HOMO	HOMO-1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Composition and energies of selected molecular orbitals of $\mathbf{2^{2-}}$ (*S*=0)

MO	Energy(ev)	Composition			
		Ru1	Ru2	L	acac
HOMO–5	1.563	34	34	18	15
HOMO–4	1.704	41	41	2	17
HOMO–3	1.882	34	34	16	16
HOMO–2	1.915	41	41	1	17
HOMO–1	2.106	42	42	3	14
HOMO	2.189	38	38	12	13
LUMO	3.489	8	8	78	6
LUMO+1	3.562	7	7	82	4
LUMO+2	4.041	2	2	52	44
LUMO+3	4.057	1	1	95	3
LUMO+4	4.070	2	2	42	54
LUMO+5	4.087	3	3	2	93



A. *Optimised Cartesian coordinates using M06-L density functional for free energy calculation.*

DTBT (*S*=0)

Zero-point correction= 0.188107 (Hartree/Particle)
Thermal correction to Energy= 0.204758
Thermal correction to Enthalpy= 0.205702
Thermal correction to Gibbs Free Energy= 0.140998
Sum of electronic and zero-point Energies= -2240.262623
Sum of electronic and thermal Energies= -2240.245972
Sum of electronic and thermal Enthalpies= -2240.245028
Sum of electronic and thermal Free Energies= -2240.309732

Cartesian Coordinates

S	7.073196000	10.289940000	4.390957000
N	7.793829000	11.333219000	6.688775000
C	8.218650000	12.206070000	5.705823000
C	8.291303000	12.602565000	3.289350000
H	8.059102000	12.298931000	2.273661000
C	8.901675000	13.403964000	5.935235000
H	9.128448000	13.697222000	6.955021000
C	7.195484000	10.314372000	6.157960000
C	7.920781000	11.818963000	4.378587000
C	8.970188000	13.789302000	3.541217000
H	9.269142000	14.416181000	2.706670000
C	9.271886000	14.184474000	4.849947000
H	9.802572000	15.116894000	5.017543000
S	6.475675000	8.404092000	11.607997000
N	5.754922000	7.360866000	9.310194000
C	5.330042000	6.488052000	10.293155000
C	5.257394000	6.091569000	12.709630000
H	5.489638000	6.395185000	13.725314000
C	4.646911000	5.290216000	10.063757000
H	4.420095000	4.996977000	9.043975000
C	6.353369000	8.379660000	9.840995000
C	5.627962000	6.875140000	11.620386000
C	4.578405000	4.904888000	12.457776000
H	4.279413000	4.278036000	13.292329000
C	4.276651000	4.509740000	11.149052000
H	3.745883000	3.577366000	10.981467000
S	7.039019000	9.718693000	8.950114000
S	6.509907000	8.975295000	7.048833000

L• (*S*=1/2)

Zero-point correction= 0.092367 (Hartree/Particle)
Thermal correction to Energy= 0.100007
Thermal correction to Enthalpy= 0.100952
Thermal correction to Gibbs Free Energy= 0.058576
Sum of electronic and zero-point Energies= -1120.104554
Sum of electronic and thermal Energies= -1120.096913
Sum of electronic and thermal Enthalpies= -1120.095969
Sum of electronic and thermal Free Energies= -1120.138345

Cartesian Coordinates

S	7.119744000	10.419045000	4.055759000
N	7.792602000	11.361367000	6.429134000
C	8.226183000	12.244992000	5.507163000
C	8.369932000	12.767700000	3.106314000
H	8.169936000	12.524909000	2.068139000
C	8.913964000	13.439734000	5.816020000
H	9.110484000	13.673211000	6.856922000
C	7.181919000	10.320344000	5.864994000
C	7.958873000	11.919306000	4.134160000
C	9.043532000	13.932143000	3.445369000
H	9.371901000	14.602478000	2.656338000
C	9.313836000	14.265831000	4.790101000
H	9.844471000	15.186459000	5.011806000
S	6.521972000	9.009375000	6.663966000

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1 (*S*=1/2)

Zero-point correction= 0.376492 (Hartree/Particle)
Thermal correction to Energy= 0.407028
Thermal correction to Enthalpy= 0.407972
Thermal correction to Gibbs Free Energy= 0.313204
Sum of electronic and zero-point Energies= -2019.920154
Sum of electronic and thermal Energies= -2019.889618
Sum of electronic and thermal Enthalpies= -2019.888674
Sum of electronic and thermal Free Energies= -2019.983442

Cartesian Coordinates

Ru	4.541520000	8.131244000	16.506028000
S	3.538242000	6.153511000	17.012627000
S	2.273769000	6.261261000	14.166959000
O	2.960513000	8.930669000	15.470990000

O	5.219033000	7.385169000	14.698923000
O	5.671043000	10.064096000	16.187050000
H	6.367124000	10.021177000	16.855166000
O	6.288559000	7.553350000	17.469551000
O	3.959860000	8.974983000	18.299693000
N	3.003318000	4.079969000	15.429484000
C	2.449172000	3.683681000	14.236975000
C	1.423644000	4.460077000	12.152054000
H	1.075025000	5.264104000	11.510691000
C	1.987811000	4.730491000	13.398948000
C	2.029250000	9.596936000	16.047331000
C	1.314788000	3.134401000	11.751092000
H	0.873520000	2.905333000	10.785111000
C	2.985095000	5.378217000	15.546836000
C	6.163935000	6.528580000	14.626657000
C	2.609064000	10.140972000	19.811943000
H	2.500698000	9.291923000	20.492922000
H	1.710534000	10.757060000	19.870271000
H	3.464791000	10.720395000	20.168838000
C	8.199490000	6.263798000	17.878840000
H	8.703907000	7.136833000	18.301762000
H	8.935004000	5.627375000	17.384319000
H	7.768401000	5.714916000	18.721475000
C	2.876729000	9.638485000	18.421836000
C	0.929729000	10.034841000	15.123966000
H	1.354551000	10.506406000	14.234042000
H	0.230441000	10.723640000	15.600500000
H	0.374834000	9.156610000	14.778560000
C	1.764483000	2.091017000	12.573271000
H	1.667274000	1.063618000	12.233987000
C	7.096814000	6.700138000	16.958290000
C	6.256303000	10.262259000	14.897883000
H	7.019348000	9.508006000	14.678284000
H	6.687523000	11.265600000	14.828381000
H	5.445949000	10.157734000	14.176918000
C	6.308705000	5.871627000	13.285464000
H	5.524733000	5.113163000	13.178715000
H	7.275839000	5.382870000	13.155718000
H	6.151256000	6.601505000	12.488409000
C	1.951414000	9.931085000	17.405262000
H	1.081089000	10.506042000	17.704035000
C	2.331135000	2.354153000	13.809737000
H	2.684856000	1.558693000	14.458402000
C	7.040999000	6.166716000	15.663397000
H	7.799728000	5.431942000	15.414206000

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2 (*S*=0)

Zero-point correction= 0.646962 (Hartree/Particle)
Thermal correction to Energy= 0.700770
Thermal correction to Enthalpy= 0.701715
Thermal correction to Gibbs Free Energy= 0.555634
Sum of electronic and zero-point Energies= -3808.554288
Sum of electronic and thermal Energies= -3808.500479
Sum of electronic and thermal Enthalpies= -3808.499535
Sum of electronic and thermal Free Energies= -3808.645616

Cartesian Coordinates

Ru	9.425470000	5.166071000	9.714899000
S	9.101053000	2.955566000	10.495842000
S	8.780075000	3.472808000	13.583168000
O	9.258954000	6.019217000	11.604137000
O	9.721819000	4.311161000	7.838775000
O	10.243424000	6.864537000	8.858217000
O	11.386927000	4.884960000	10.301417000
N	10.893055000	2.497825000	12.382148000
C	10.848580000	3.830865000	7.498342000
C	9.740506000	7.166289000	11.857671000
C	11.192782000	2.551670000	13.721927000
C	10.890337000	3.298379000	6.093072000
H	10.091231000	2.565384000	5.953377000
H	11.847835000	2.836998000	5.846111000
H	10.697770000	4.113051000	5.388594000
C	9.690974000	2.947178000	12.164495000
C	10.154258000	3.041526000	14.552288000
C	12.014987000	3.750886000	8.282666000
H	12.863423000	3.257048000	7.820769000
C	10.519915000	7.895830000	9.568822000
C	10.304431000	8.073334000	10.938445000
H	10.630964000	9.022848000	11.349594000
C	9.696850000	7.540785000	13.312576000
H	8.732893000	7.253375000	13.738923000
H	9.876016000	8.603870000	13.482324000
H	10.459692000	6.968396000	13.851405000
C	12.226186000	4.250161000	9.571960000
C	11.534222000	2.736460000	16.478798000
H	11.682448000	2.801138000	17.552982000
C	11.154432000	9.009016000	8.784285000
H	12.087914000	8.656178000	8.336723000
H	11.363169000	9.886637000	9.397866000
H	10.499453000	9.297121000	7.957375000
C	12.569288000	2.250564000	15.665223000

H	13.506726000	1.944171000	16.120308000
C	12.409269000	2.153992000	14.293230000
H	13.198439000	1.773550000	13.651427000
C	10.320893000	3.135285000	15.935023000
H	9.523621000	3.508420000	16.570976000
C	13.555556000	4.036414000	10.234254000
H	13.933234000	4.982010000	10.631181000
H	14.295426000	3.602901000	9.559592000
H	13.411693000	3.365847000	11.087785000
Ru	6.964699000	3.863433000	10.124355000
S	7.289120000	6.073917000	9.343374000
S	7.610154000	5.556121000	6.256175000
O	7.131189000	3.010310000	8.235106000
O	6.668358000	4.718360000	12.000472000
O	6.146741000	2.164967000	10.981031000
O	5.003238000	4.144553000	9.537847000
N	5.497240000	6.531597000	7.456920000
C	5.541603000	5.198674000	12.340906000
C	6.649618000	1.863249000	7.981564000
C	5.197586000	6.477581000	6.117131000
C	5.499856000	5.731182000	13.746167000
H	6.298983000	6.464157000	13.885853000
H	4.542371000	6.192592000	13.993117000
H	5.692397000	4.916516000	14.450660000
C	6.699272000	6.082175000	7.674700000
C	6.236098000	5.987467000	5.286905000
C	4.375196000	5.278658000	11.556585000
H	3.526767000	5.772510000	12.018480000
C	5.870231000	1.133687000	10.270416000
C	6.085694000	0.956199000	8.900787000
H	5.759142000	0.006694000	8.489631000
C	6.693243000	1.488779000	6.526652000
H	7.657198000	1.776180000	6.100294000
H	6.514053000	0.425700000	6.356885000
H	5.930405000	2.061195000	5.987847000
C	4.163988000	4.779368000	10.267298000
C	4.856292000	6.292425000	3.360265000
H	4.708121000	6.227603000	2.286083000
C	5.235712000	0.020496000	11.054946000
H	4.302239000	0.373337000	11.502524000
H	5.026958000	-0.857114000	10.441355000
H	5.890698000	-0.267627000	11.881844000
C	3.821237000	6.778573000	4.173705000
H	2.883867000	7.085019000	3.718518000
C	3.981185000	6.875328000	5.545694000
H	3.192025000	7.255968000	6.187391000
C	6.069535000	5.893523000	3.904174000
H	6.866795000	5.520182000	3.268327000
C	2.834615000	4.993114000	9.605010000
H	2.456931000	4.047516000	9.208096000

H	2.094751000	5.426639000	10.279671000
H	2.978479000	5.663671000	8.751471000

CH_3OH (*S*=0)

Zero-point correction= 0.051606 (Hartree/Particle)
Thermal correction to Energy= 0.054900
Thermal correction to Enthalpy= 0.055844
Thermal correction to Gibbs Free Energy= 0.028897
Sum of electronic and zero-point Energies= -115.652007
Sum of electronic and thermal Energies= -115.648712
Sum of electronic and thermal Enthalpies= -115.647768
Sum of electronic and thermal Free Energies= -115.674715

Cartesian Coordinates

O	5.588578000	9.871936000	16.179855000
H	6.410919000	9.375261000	16.193031000
C	5.565805000	10.614162000	14.984199000
H	5.590385000	9.984378000	14.081729000
H	6.386693000	11.344052000	14.910763000
H	4.626768000	11.171753000	14.971859000

B. *Optimized Cartesian coordinates using (U)B3LYP density functional for the free energy calculation.*

DTBT (*S*=0)

Zero-point correction= 0.187545 (Hartree/Particle)
Thermal correction to Energy= 0.204348
Thermal correction to Enthalpy= 0.205292
Thermal correction to Gibbs Free Energy= 0.139422
Sum of electronic and zero-point Energies= -2240.397788
Sum of electronic and thermal Energies= -2240.380986
Sum of electronic and thermal Enthalpies= -2240.380042
Sum of electronic and thermal Free Energies= -2240.445912

Cartesian Coordinates

S	7.077469000	10.304257000	4.354979000
N	7.800589000	11.344377000	6.657338000
C	8.230948000	12.226989000	5.674130000
C	8.305912000	12.632272000	3.256930000
H	8.075404000	12.332915000	2.239872000

C	8.914588000	13.426034000	5.911851000
H	9.139789000	13.715569000	6.932565000
C	7.201431000	10.327235000	6.135051000
C	7.933771000	11.843086000	4.345221000
C	8.985576000	13.821647000	3.513761000
H	9.285585000	14.452228000	2.682585000
C	9.286382000	14.213574000	4.827850000
H	9.816734000	15.145091000	4.999324000
S	6.469305000	8.390904000	11.644214000
N	5.748301000	7.349737000	9.341695000
C	5.317972000	6.467045000	10.324855000
C	5.241973000	6.062207000	12.742101000
H	5.471729000	6.361928000	13.759222000
C	4.635285000	5.267479000	10.087012000
H	4.410854000	4.977569000	9.066235000
C	6.346470000	8.367385000	9.864125000
C	5.614144000	6.851433000	11.653847000
C	4.563266000	4.872313000	12.485145000
H	4.263240000	4.241695000	13.316287000
C	4.263440000	4.479911000	11.170973000
H	3.733819000	3.547995000	10.999406000
S	7.040574000	9.716791000	8.965332000
S	6.506994000	8.978208000	7.033814000

L• (*S*=1/2)

Zero-point correction= 0.092216 (Hartree/Particle)
Thermal correction to Energy= 0.099852
Thermal correction to Enthalpy= 0.100796
Thermal correction to Gibbs Free Energy= 0.058407
Sum of electronic and zero-point Energies= -1120.175938
Sum of electronic and thermal Energies= -1120.168302
Sum of electronic and thermal Enthalpies= -1120.167358
Sum of electronic and thermal Free Energies= -1120.209747

Cartesian Coordinates

S	7.118050000	10.406238000	4.056506000
N	7.793849000	11.351471000	6.427065000
C	8.231798000	12.243050000	5.503469000
C	8.372970000	12.770627000	3.101285000
H	8.172679000	12.529271000	2.062931000
C	8.917956000	13.440496000	5.817120000
H	9.113200000	13.673124000	6.858074000
C	7.181139000	10.314483000	5.866602000
C	7.964259000	11.918471000	4.131710000
C	9.044669000	13.938983000	3.441881000
H	9.369436000	14.612301000	2.654450000

C	9.315559000	14.272109000	4.790042000
H	9.842657000	15.194298000	5.012349000
S	6.501129000	9.001972000	6.682701000

A (*S*=0)

Zero-point correction= 0.645176 (Hartree/Particle)
Thermal correction to Energy= 0.699906
Thermal correction to Enthalpy= 0.700851
Thermal correction to Gibbs Free Energy= 0.551901
Sum of electronic and zero-point Energies= -3808.693371
Sum of electronic and thermal Energies= -3808.638640
Sum of electronic and thermal Enthalpies= -3808.637696
Sum of electronic and thermal Free Energies= -3808.786646

Cartesian Coordinates

Ru	5.974642000	7.030006000	6.906916000
S	7.580066000	10.240213000	4.549131000
O	4.311920000	8.269089000	6.768131000
O	4.641739000	5.441948000	6.805881000
O	6.086870000	6.823639000	4.860895000
O	7.592342000	5.694860000	7.026663000
N	7.663066000	11.444134000	6.869743000
C	7.767970000	12.451737000	5.901456000
C	4.995297000	4.253358000	6.494562000
C	7.496126000	4.465387000	6.719637000
C	3.713381000	8.518489000	5.673757000
C	4.103346000	8.096300000	4.385422000
H	3.472764000	8.409775000	3.562198000
C	7.882342000	12.848389000	3.479795000
H	7.884623000	12.469804000	2.462799000
C	7.858202000	13.830030000	6.141866000
H	7.831500000	14.206979000	7.153483000
C	5.214698000	7.304700000	4.057555000
C	5.461321000	6.948887000	2.604505000
H	6.460921000	7.285256000	2.310205000
H	4.721646000	7.389998000	1.933615000
H	5.444697000	5.859876000	2.490927000
C	7.547735000	10.260339000	6.297308000
C	7.767336000	11.980966000	4.569009000
C	7.983914000	14.210860000	3.738268000
H	8.070949000	14.907626000	2.910130000
C	3.838714000	3.318882000	6.198784000
H	3.268229000	3.710048000	5.349942000
H	3.159018000	3.296041000	7.056897000
H	4.166828000	2.302491000	5.971679000
C	2.458046000	9.354486000	5.823297000

H	1.733480000	8.806518000	6.435010000
H	1.999880000	9.600669000	4.863340000
H	2.697622000	10.278489000	6.358854000
C	7.965570000	14.692454000	5.058032000
H	8.034609000	15.761070000	5.237437000
C	8.816214000	3.719322000	6.686321000
H	9.496509000	4.223108000	5.992454000
H	8.703238000	2.675579000	6.386229000
H	9.281140000	3.757532000	7.677215000
C	6.307355000	3.754231000	6.438017000
H	6.419221000	2.709409000	6.174215000
S	5.963428000	8.455176000	11.452286000
N	5.880585000	7.251372000	9.131631000
C	5.775828000	6.243724000	10.099845000
C	5.661543000	5.846929000	12.521504000
H	5.659186000	6.225468000	13.538517000
C	5.685838000	4.865419000	9.859381000
H	5.712653000	4.488481000	8.847772000
C	5.995799000	8.435191000	9.704119000
C	5.776405000	6.714414000	11.432327000
C	5.560179000	4.484453000	12.262967000
H	5.473239000	3.787635000	13.091073000
C	5.578613000	4.002930000	10.943179000
H	5.509768000	2.934312000	10.763715000
Ru	7.569090000	11.665468000	9.094365000
O	9.231704000	10.426171000	9.233067000
O	8.902152000	13.253398000	9.195332000
O	7.457102000	11.871840000	11.140406000
O	5.951544000	13.000752000	8.974644000
C	8.548707000	14.441986000	9.506774000
C	6.047872000	14.230235000	9.281616000
C	9.830148000	10.176471000	10.327415000
C	9.440212000	10.598518000	11.615810000
H	10.070654000	10.284717000	12.439019000
C	8.329062000	11.390381000	11.943729000
C	8.082446000	11.746031000	13.396824000
H	7.082684000	11.410012000	13.690965000
H	8.821885000	11.304505000	14.067701000
H	8.099500000	12.835016000	13.510610000
C	9.705367000	15.376283000	9.802814000
H	10.275559000	14.985047000	10.651823000
H	10.385299000	15.398988000	8.944885000
H	9.377358000	16.392732000	10.029810000
C	11.085362000	9.340300000	10.177791000
H	11.810224000	9.888464000	9.566598000
H	11.543204000	9.093523000	11.137751000
H	10.845764000	8.416639000	9.641659000
C	4.727798000	14.976307000	9.315265000
H	4.048883000	14.474472000	10.011926000
H	4.841220000	16.020892000	9.612233000

H	4.260963000	14.935128000	8.325411000
C	7.236701000	14.941275000	9.563231000
H	7.124944000	15.986104000	9.827059000
S	6.097016000	9.934003000	8.769385000
S	7.446281000	8.761553000	7.232143000

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1 (*S*=1/2)

Zero-point correction= 0.375332 (Hartree/Particle)
Thermal correction to Energy= 0.406413
Thermal correction to Enthalpy= 0.407357
Thermal correction to Gibbs Free Energy= 0.309553
Sum of electronic and zero-point Energies= -2020.038389
Sum of electronic and thermal Energies= -2020.007308
Sum of electronic and thermal Enthalpies= -2020.006364
Sum of electronic and thermal Free Energies= -2020.104167

Cartesian Coordinates

Ru	4.709230000	8.053584000	16.458891000
S	3.729641000	6.035721000	16.904672000
S	2.738480000	6.106229000	13.907342000
O	3.147096000	8.822628000	15.379727000
O	5.560549000	7.436202000	14.686136000
O	5.741755000	10.039124000	16.242590000
H	6.516193000	9.996940000	16.821248000
O	6.407764000	7.509687000	17.508270000
O	3.963931000	8.810250000	18.219114000
N	2.536066000	4.077686000	15.562421000
C	1.959417000	3.675573000	14.374640000
C	1.420339000	4.361261000	12.081526000
H	1.429180000	5.102748000	11.288420000
C	1.969028000	4.641098000	13.336277000
C	2.122756000	9.385189000	15.909307000
C	0.857910000	3.104123000	11.871880000
H	0.425314000	2.867848000	10.904008000
C	2.984060000	5.296793000	15.491183000
C	6.625119000	6.730353000	14.610682000
C	2.456835000	9.782286000	19.735036000
H	2.408412000	8.889622000	20.367287000
H	1.501451000	10.307799000	19.784717000
H	3.244202000	10.423604000	20.143424000
C	8.407983000	6.383948000	18.018943000
H	8.758182000	7.264574000	18.566184000
H	9.258368000	5.884367000	17.551257000
H	7.958124000	5.708189000	18.754374000
C	2.822315000	9.372070000	18.324486000
C	1.063809000	9.803455000	14.912911000

H	1.521392000	10.411336000	14.126141000
H	0.251080000	10.364901000	15.377307000
H	0.652841000	8.910229000	14.430444000
C	0.842621000	2.139003000	12.894821000
H	0.397774000	1.166577000	12.704798000
C	7.349822000	6.793500000	17.017352000
C	6.100625000	10.542865000	14.944669000
H	6.883995000	9.936287000	14.481532000
H	6.424988000	11.584962000	15.028587000
H	5.197219000	10.481850000	14.339142000
C	6.962298000	6.259718000	13.212573000
H	6.169525000	5.589745000	12.863260000
H	7.919890000	5.738031000	13.164229000
H	6.979726000	7.115936000	12.530960000
C	1.920934000	9.636029000	17.274987000
H	0.990426000	10.119981000	17.545811000
C	1.388163000	2.413737000	14.142662000
H	1.384182000	1.680421000	14.942409000
C	7.474115000	6.384211000	15.678340000
H	8.335718000	5.774400000	15.434824000

1′ (*S*=1/2)

Zero-point correction= 0.321968 (Hartree/Particle)
Thermal correction to Energy= 0.348483
Thermal correction to Enthalpy= 0.349427
Thermal correction to Gibbs Free Energy= 0.263130
Sum of electronic and zero-point Energies= -1904.366553
Sum of electronic and thermal Energies= -1904.340038
Sum of electronic and thermal Enthalpies= -1904.339093
Sum of electronic and thermal Free Energies= -1904.425391

Cartesian Coordinates

Ru	10.298171000	4.579099000	6.177399000
S	10.190625000	6.611401000	4.739583000
O	10.762849000	2.857641000	7.219001000
O	9.783851000	3.451555000	4.552251000
C	8.905829000	1.654253000	3.323255000
H	8.012150000	2.226972000	3.056105000
H	8.648207000	0.596645000	3.404209000
H	9.627534000	1.787770000	2.510878000
O	10.821440000	5.672345000	7.810370000
C	10.335432000	1.694540000	6.900474000
O	8.377484000	4.389722000	6.872316000
C	8.814759000	5.264782000	9.054805000
H	8.353695000	5.437810000	10.019440000
C	10.625078000	0.618656000	7.925248000

H	11.708046000	0.520749000	8.055745000
H	10.213022000	-0.350766000	7.639126000
H	10.210883000	0.917603000	8.893247000
C	6.570905000	4.330771000	8.373967000
H	5.916136000	4.945143000	7.746678000
H	6.318831000	4.500945000	9.422301000
H	6.374841000	3.285337000	8.117048000
C	10.804383000	6.477467000	10.015504000
H	11.761624000	5.992546000	10.231460000
H	10.197291000	6.500097000	10.922376000
H	11.025817000	7.504161000	9.706021000
C	8.014257000	4.664405000	8.064947000
C	10.119892000	5.750106000	8.880080000
C	9.486076000	2.208707000	4.605011000
C	11.852405000	6.174727000	4.675755000
C	9.684415000	1.354107000	5.703507000
H	9.392907000	0.318409000	5.579349000
S	13.235461000	6.939787000	3.889384000
N	12.165315000	5.080630000	5.352575000
C	13.513422000	4.773226000	5.331930000
C	15.654733000	5.516366000	4.415661000
H	16.240142000	6.211218000	3.821956000
C	14.277470000	5.679628000	4.560722000
C	16.263296000	4.437739000	5.057703000
H	17.335021000	4.295081000	4.958883000
C	15.509509000	3.540317000	5.830595000
H	16.008088000	2.711768000	6.324634000
C	14.134315000	3.696239000	5.975623000
H	13.536293000	3.018086000	6.574838000

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2 (*S*=0)

Zero-point correction= 0.645403 (Hartree/Particle)
Thermal correction to Energy= 0.698124
Thermal correction to Enthalpy= 0.699068
Thermal correction to Gibbs Free Energy= 0.554635
Sum of electronic and zero-point Energies= -3808.722135
Sum of electronic and thermal Energies= -3808.669414
Sum of electronic and thermal Enthalpies= -3808.668470
Sum of electronic and thermal Free Energies= -3808.812903

Cartesian Coordinates

Ru	9.441846000	5.191830000	9.688982000
S	9.125390000	2.991729000	10.538086000
S	8.774213000	3.493512000	13.654398000
O	9.302436000	6.143847000	11.534158000
O	9.719176000	4.275588000	7.841176000

O	10.200850000	6.867697000	8.769506000
O	11.417593000	4.951005000	10.204702000
N	10.812952000	2.349418000	12.473278000
C	10.848938000	3.839482000	7.449464000
C	9.702968000	7.333760000	11.724793000
C	11.086763000	2.330741000	13.827181000
C	10.846965000	3.266177000	6.046592000
H	10.062447000	2.508219000	5.964716000
H	11.807209000	2.824329000	5.774364000
H	10.605572000	4.061286000	5.333392000
C	9.670055000	2.918995000	12.232444000
C	10.082180000	2.898360000	14.649676000
C	12.058501000	3.841900000	8.175225000
H	12.914546000	3.394522000	7.685296000
C	10.437377000	7.961985000	9.397868000
C	10.212408000	8.224775000	10.753038000
H	10.481670000	9.213754000	11.103358000
C	9.629548000	7.797221000	13.165477000
H	8.689123000	7.459995000	13.607992000
H	9.717338000	8.881449000	13.260540000
H	10.442117000	7.328731000	13.732389000
C	12.278489000	4.371124000	9.453037000
C	11.378600000	2.395349000	16.599646000
H	11.507094000	2.412342000	17.678003000
C	11.026261000	9.045584000	8.519074000
H	11.968004000	8.689909000	8.088467000
H	11.208622000	9.972182000	9.066333000
H	10.345613000	9.246241000	7.685592000
C	12.382743000	1.830553000	15.790292000
H	13.273521000	1.418641000	16.255069000
C	12.246288000	1.792826000	14.409500000
H	13.008365000	1.357782000	13.771158000
C	10.222395000	2.931921000	16.041574000
H	9.452187000	3.364870000	16.672333000
C	13.653397000	4.267647000	10.075937000
H	13.984620000	5.259365000	10.399078000
H	14.390087000	3.842766000	9.391595000
H	13.584655000	3.638451000	10.969421000
Ru	6.948393000	3.837575000	10.150208000
S	7.264849000	6.037677000	9.301105000
S	7.616007000	5.535870000	6.184795000
O	7.087804000	2.885559000	8.305032000
O	6.671063000	4.753815000	11.998015000
O	6.189388000	2.161707000	11.069682000
O	4.972646000	4.078400000	9.634488000
N	5.577272000	6.679970000	7.365917000
C	5.541300000	5.189920000	12.389728000
C	6.687272000	1.695646000	8.114395000
C	5.303458000	6.698645000	6.012015000
C	5.543274000	5.763222000	13.792600000

H	6.327792000	6.521182000	13.874477000
H	4.583030000	6.205070000	14.064830000
H	5.784668000	4.968113000	14.505798000
C	6.720179000	6.110411000	7.606749000
C	6.308045000	6.131035000	5.189517000
C	4.331737000	5.187501000	11.663966000
H	3.475691000	5.634878000	12.153896000
C	5.952862000	1.067419000	10.441319000
C	6.177832000	0.804631000	9.086150000
H	5.908572000	-0.184348000	8.735828000
C	6.760693000	1.232186000	6.673711000
H	7.701118000	1.569413000	6.231196000
H	6.672904000	0.147958000	6.578648000
H	5.948125000	1.700676000	6.106799000
C	4.111749000	4.658279000	10.386154000
C	5.011623000	6.634049000	3.239549000
H	4.883129000	6.617058000	2.161192000
C	5.363979000	-0.016180000	11.320112000
H	4.422235000	0.339494000	11.750720000
H	5.181618000	-0.942778000	10.772852000
H	6.044626000	-0.216838000	12.153594000
C	4.007477000	7.198836000	4.048905000
H	3.116697000	7.610746000	3.584129000
C	4.143931000	7.236557000	5.429697000
H	3.381852000	7.671596000	6.068041000
C	6.167830000	6.097479000	3.797619000
H	6.938038000	5.664531000	3.166859000
C	2.736841000	4.761755000	9.763254000
H	2.405618000	3.770037000	9.440113000
H	2.000151000	5.186636000	10.447596000
H	2.805583000	5.390953000	8.869771000

CH_3OH (*S*=0)

Zero-point correction= 0.051405 (Hartree/Particle)
Thermal correction to Energy= 0.054706
Thermal correction to Enthalpy= 0.055651
Thermal correction to Gibbs Free Energy= 0.028678
Sum of electronic and zero-point Energies= -115.672558
Sum of electronic and thermal Energies= -115.669256
Sum of electronic and thermal Enthalpies= -115.668312
Sum of electronic and thermal Free Energies= -115.695285

Cartesian Coordinates

O	5.588798000	9.867991000	16.181447000
H	6.415664000	9.370349000	16.200712000
C	5.563968000	10.618419000	14.978379000

H	5.589157000	9.984539000	14.079112000
H	6.387961000	11.344849000	14.911202000
H	4.623602000	11.175394000	14.970583000

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