Supporting Information

Bidirectional non-innocence of the β-diketonato ligand 9-oxidophenalenone (L¯) in [Ru([9]aneS3)(L)(dmso)]^n, [9]aneS3 = 1,4,7-trithiacyclononane

Hemlata Agarwala,[a] Thomas Michael Scherer,[b] Shaikh M. Mobin,[c] Wolfgang Kaim*[b] and Goutam Kumar Lahiri*[a]

[a]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in*

[b]*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany. E-mail: kaim@iac.uni-stuttgart.de*

[c]*Discipline of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore, Indore-452017, India*

Table S1 Selected experimental and DFT calculated bond distances (Å) and angles (°) of $\mathbf{1}^n$ (n = +3, +2, +1, 0, -1)

	X-ray	DFT				
	$\mathbf{1}^+$ (κ-S)	$\mathbf{1}^+$ (κ-S) (S=0)	$\mathbf{1}^{2+}$ (κ-O) (S=1/2)	$\mathbf{1}^{3+}$ (κ-O) (S=1)	$\mathbf{1}$ (κ-S) (S=1/2)	$\mathbf{1}^-$ (κ-S) (S=1)
bond distances(Å)						
Ru(1)–O(1)	2.063(2)	2.071	2.012	2.024	2.050	2.082
Ru(1)–O(2)	2.061(3)	2.071	2.015	2.013	2.051	2.079
Ru(1)–O(3)	-	-	2.132	2.047	-	-
Ru(1)–S(1)	2.297(10)	2.375	2.392	2.412	2.374	2.322
Ru(1)–S(2)	2.294(10)	2.367	2.393	2.409	2.369	2.322
Ru(1)–S(3)	2.335(10)	2.391	2.363	2.434	2.388	3.153
Ru(1)–S(4)	2.277(9)	2.328	-	-	2.293	2.428
O(1)–C(7)	1.288(4)	1.294	1.306	1.300	1.334	1.315
O(2)–C(17)	1.286(4)	1.294	1.305	1.308	1.334	1.315
S(4)–O(3)	1.483(3)	1.509	1.580	1.614	1.516	1.530
bond angles(°)						
O(1)–Ru(1)–O(2)	89.54(10)	89.145	87.920	88.383	90.887	88.177
O(1)–Ru(1)–O(3)	-	-	92.009	95.099	-	-
O(1)–Ru(1)–S(1)	176.73(8)	176.983	178.168	178.417	175.182	173.160
O(1)–Ru(1)–S(2)	90.88(7)	90.827	91.150	92.116	89.321	91.102
O(1)–Ru(1)–S(3)	88.24(8)	88.871	93.302	91.380	87.054	91.276
O(1)–Ru(1)–S(4)	90.33(8)	91.648	-	-	92.217	92.906
O(2)–Ru(1)–O(3)	-	-	90.919	96.258	-	-
O(2)–Ru(1)–S(1)	91.00(7)	91.830	93.201	92.632	90.999	91.995
O(2)–Ru(1)–S(2)	174.66(8)	176.559	178.062	175.350	174.331	171.315

O(2)–Ru(1)–S(3)	85.71(8)	88.110	93.337	88.396	85.579	90.881
O(2)–Ru(1)–S(4)	92.68(8)	91.742	-	-	92.424	92.900
S(1)–Ru(1)–O(3)	-	-	86.527	86.000	-	-
S(1)–Ru(1)–S(2)	88.28(4)	88.029	87.686	86.774	88.366	87.695
S(1)–Ru(1)–S(3)	88.59(4)	88.308	88.081	87.436	88.671	81.884
S(1)–Ru(1)–S(4)	92.87(3)	91.176	-	-	92.133	93.914
S(2)–Ru(1)–O(3)	-	-	87.414	88.305	-	-
S(2)–Ru(1)–S(3)	88.98(4)	88.449	88.412	86.970	88.775	80.480
S(2)–Ru(1)–S(4)	92.63(4)	91.698	-	-	93.229	95.781
S(3)–Ru(1)–O(3)	-	-	173.309	172.116	-	-
S(3)–Ru(1)–S(4)	177.86(4)	179.458	-	-	177.860	174.447

Table S2 Endocyclic torsion angles of coordinated [9]aneS3 in the crystal of [**1**]ClO_4

	[**1**]ClO_4
S(1)–C(1)–C(2)–S(2)	-43.05
C(1)–C(2)–S(2)–C(3)	131.18
C(2)–S(2)–C(3)–C(4)	-67.63
S(2)–C(3)–C(4)–S(3)	-46.23
C(3)–C(4)–S(3)–C(5)	131.07
C(4)–S(3)–C(5)–C(6)	-66.10
S(3)–C(5)–C(6)–S(1)	-47.07
C(5)–C(6)–S(1)–C(1)	133.98
C(6)–S(1)–C(1)–C(2)	-70.02

Table S3 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (κ-S) (*S*=0)

MO	Energy/eV	Ru	L	[9]aneS3	dmso
HOMO−10	-10.704	0.08	0.73	0.17	0.02
HOMO−9	-10.661	0.07	0.32	0.56	0.04
HOMO−8	-10.409	0.02	0.02	0.02	0.94
HOMO−7	-9.974	0.07	0.69	0.24	0.00
HOMO−6	-9.764	0.11	0.04	0.22	0.63
HOMO−5	-9.550	0.01	0.97	0.01	0.01
HOMO−4	-9.315	0.54	0.26	0.15	0.05
HOMO−3	-9.208	0.59	0.23	0.12	0.06
HOMO−2	-8.630	0.72	0.15	0.11	0.01
HOMO−1	-8.478	0.28	0.65	0.04	0.02
HOMO	-8.128	0.30	0.56	0.07	0.07
LUMO	-4.782	0.03	0.94	0.02	0.02
LUMO+1	-3.693	0.36	0.05	0.33	0.27
LUMO+2	-3.369	0.36	0.16	0.47	0.02
LUMO+3	-2.940	0.59	0.04	0.36	0.02
LUMO+4	-2.795	0.33	0.43	0.22	0.03
LUMO+5	-2.749	0.23	0.03	0.71	0.04
LUMO+6	-2.708	0.10	0.04	0.79	0.07
LUMO+7	-2.382	0.33	0.43	0.19	0.04
LUMO+8	-2.338	0.45	0.08	0.40	0.07
LUMO+9	-2.314	0.47	0.28	0.20	0.06
LUMO+10	-2.244	0.51	0.05	0.42	0.02

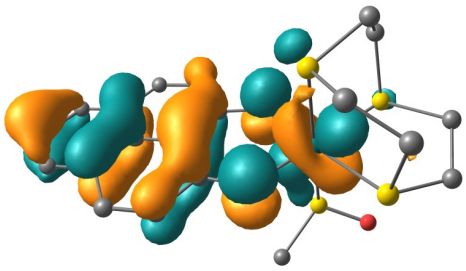
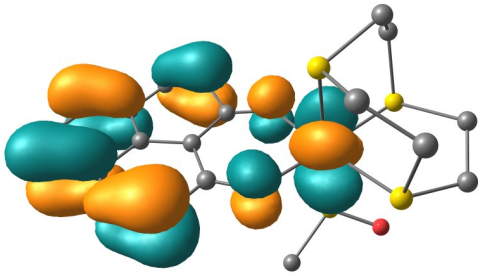
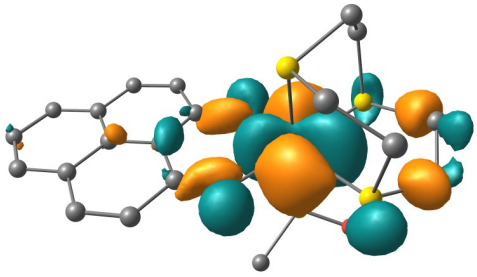
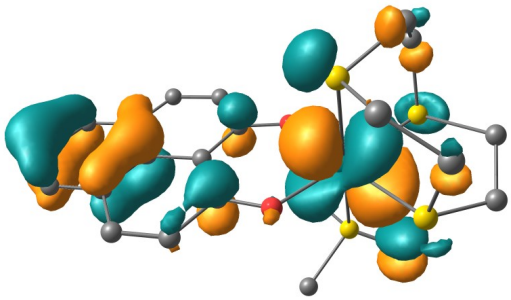
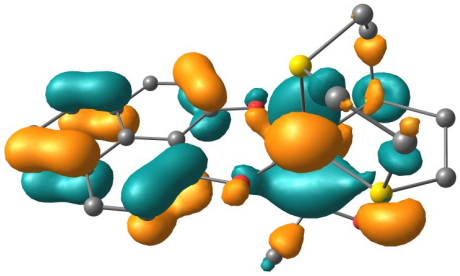
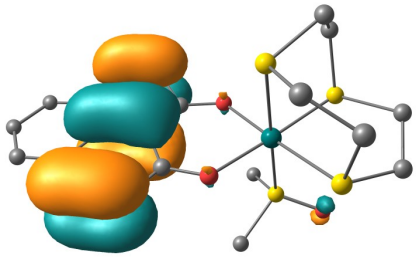
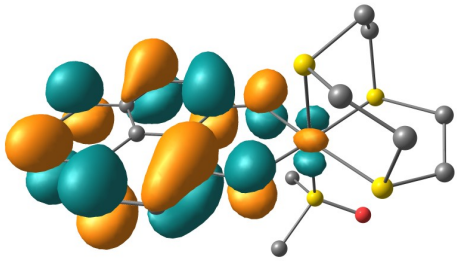
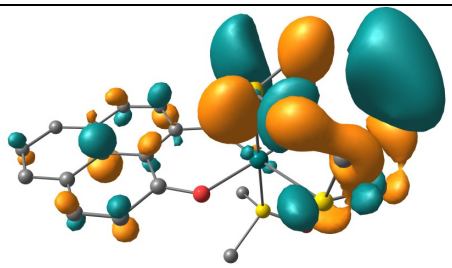
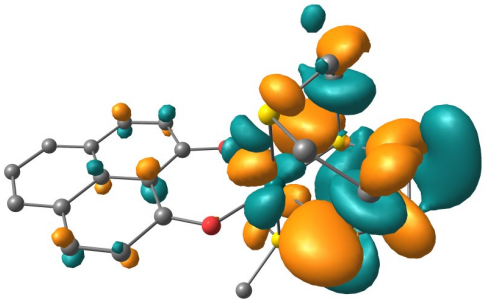
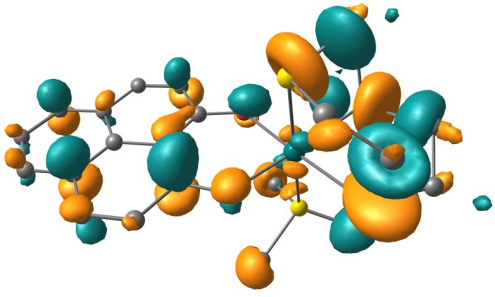
	
HOMO	HOMO-1
	
HOMO-2	HOMO-3
	
HOMO-4	HOMO-5
	
LUMO	LUMO+3
	
LUMO+6	LUMO+8

Table S4 Composition and energies of selected molecular orbitals of $\mathbf{1}^{2+}$ (κ-O) (*S*=1/2)

MO	Energy/eV	Composition			
		Ru	L	[9]aneS3	dmso
		α-spin			
HOMO−10	-13.954	0.04	0.15	0.39	0.42
HOMO−9	-13.907	0.08	0.36	0.50	0.06
HOMO−8	-13.833	0.10	0.45	0.43	0.02
HOMO−7	-13.255	0.05	0.62	0.32	0.01
HOMO−6	-13.154	0.05	0.03	0.16	0.77
HOMO−5	-12.668	0.54	0.23	0.18	0.05
HOMO−4	-12.541	0.06	0.92	0.02	0.00
HOMO−3	-12.417	0.56	0.17	0.10	0.17
HOMO−2	-12.390	0.70	0.18	0.09	0.02
HOMO−1	-11.573	0.21	0.74	0.03	0.03
SOMO	-11.455	0.15	0.79	0.04	0.01
LUMO	-7.934	0.06	0.90	0.04	0.01
LUMO+1	-7.310	0.41	0.06	0.38	0.15
LUMO+2	-6.887	0.40	0.20	0.40	0.00
LUMO+3	-5.880	0.07	0.11	0.80	0.03
LUMO+4	-5.798	0.08	0.28	0.54	0.09
LUMO+5	-5.750	0.07	0.17	0.61	0.14
LUMO+6	-5.632	0.17	0.01	0.80	0.02
LUMO+7	-5.412	0.23	0.07	0.54	0.16
LUMO+8	-5.344	0.13	0.69	0.14	0.04
LUMO+9	-5.254	0.18	0.50	0.18	0.14
LUMO+10	-5.149	0.14	0.02	0.57	0.28
		β-spin			
HOMO−10	-14.148	0.06	0.58	0.30	0.05
HOMO−9	-13.897	0.03	0.14	0.41	0.42
HOMO−8	-13.801	0.07	0.22	0.64	0.07

HOMO−7	-13.606	0.08	0.78	0.10	0.03
HOMO−6	-13.155	0.05	0.18	0.19	0.59
HOMO−5	-13.144	0.04	0.49	0.28	0.20
HOMO−4	-12.488	0.01	0.98	0.01	0.00
HOMO−3	-12.224	0.54	0.22	0.10	0.14
HOMO−2	-12.145	0.71	0.14	0.10	0.04
HOMO−1	-11.639	0.29	0.65	0.05	0.01
HOMO	-11.392	0.27	0.66	0.04	0.03
LUMO	-9.667	0.57	0.29	0.12	0.02
LUMO+1	-7.880	0.06	0.90	0.03	0.01
LUMO+2	-7.095	0.40	0.05	0.39	0.16
LUMO+3	-6.682	0.39	0.19	0.42	0.00
LUMO+4	-5.844	0.07	0.08	0.82	0.03
LUMO+5	-5.751	0.09	0.20	0.60	0.11
LUMO+6	-5.699	0.09	0.26	0.54	0.12
LUMO+7	-5.614	0.18	0.02	0.79	0.01
LUMO+8	-5.371	0.21	0.07	0.50	0.22
LUMO+9	-5.296	0.13	0.68	0.13	0.06
LUMO+10	-5.156	0.08	0.38	0.15	0.39

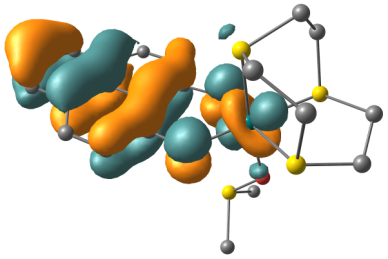
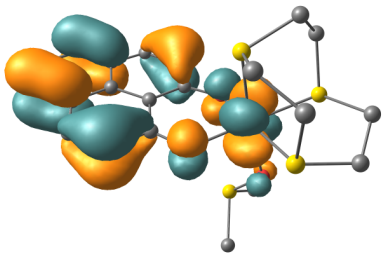
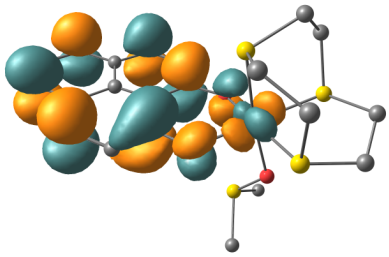
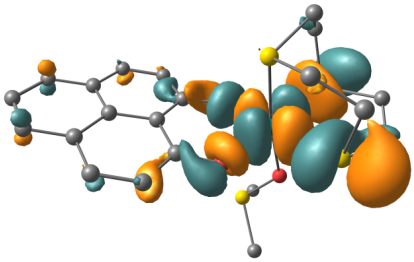
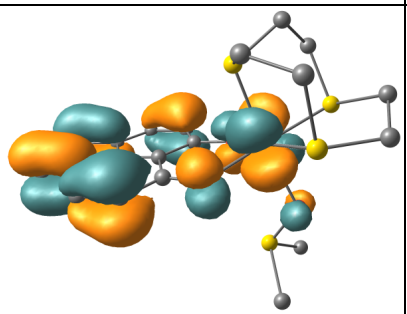
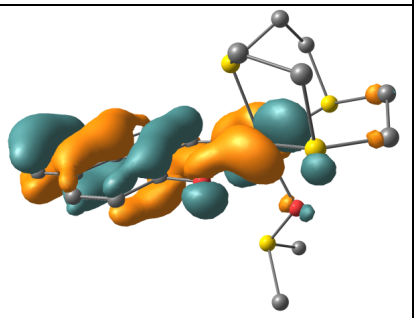
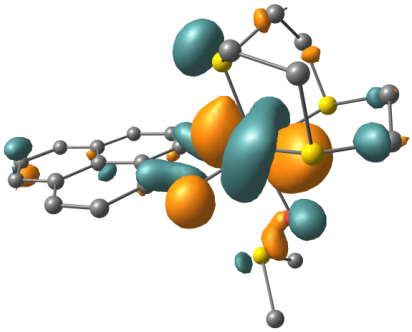
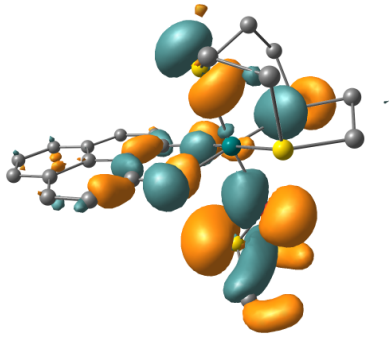
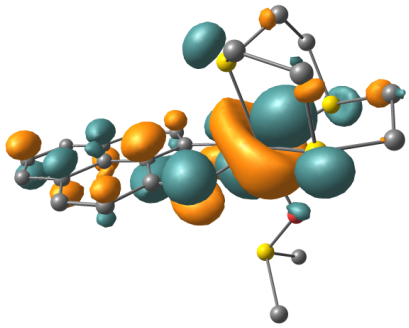
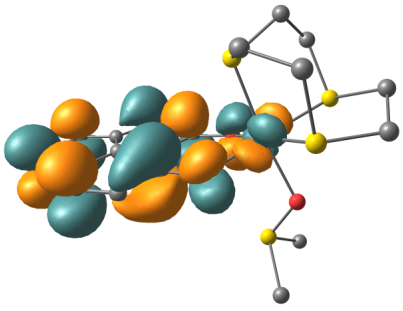
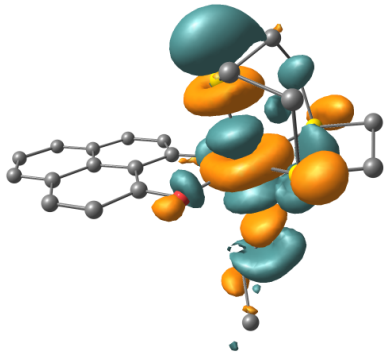
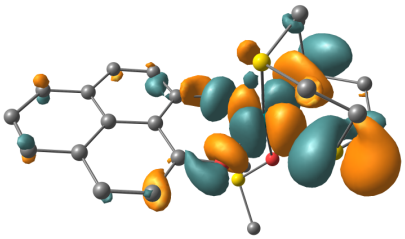
		
SOMO(α)	HOMO-1(α)	LUMO(α)
		
LUMO+2(α)	HOMO(β)	HOMO-1(β)
		
HOMO-2(β)	HOMO-6(β)	LUMO(β)
		
LUMO+1(β)	LUMO+2(β)	LUMO+3(β)

Table S5 Composition and energies of selected molecular orbitals of $\mathbf{1}^{3+}$ (κ-O) (*S*=1)

MO	Energy/eV	Composition			
		Ru	L	9S3	dmso
		α-spin			
HOMO−10	-17.331	0.05	0.55	0.39	0.01
HOMO−9	-17.257	0.04	0.37	0.50	0.08
HOMO−8	-17.046	0.11	0.17	0.54	0.17
HOMO−7	-16.786	0.23	0.31	0.25	0.20
HOMO−6	-16.526	0.05	0.05	0.31	0.59
HOMO−5	-16.205	0.44	0.19	0.23	0.15
HOMO−4	-16.15	0.43	0.20	0.23	0.13
HOMO−3	-16.035	0.05	0.93	0.01	0.01
HOMO−2	-16.028	0.59	0.18	0.22	0.01
SOMO2	-15.214	0.10	0.87	0.02	0.01
SOMO1	-15.011	0.14	0.80	0.05	0.01
LUMO	-11.409	0.03	0.96	0.01	0.00
LUMO+1	-11.033	0.43	0.06	0.35	0.16
LUMO+2	-10.604	0.44	0.20	0.36	0.00
LUMO+3	-9.304	0.02	0.93	0.04	0.01
LUMO+4	-9.103	0.08	0.07	0.31	0.54
LUMO+5	-8.899	0.05	0.82	0.09	0.04
LUMO+6	-8.869	0.04	0.05	0.89	0.02
LUMO+7	-8.796	0.08	0.67	0.09	0.16
LUMO+8	-8.565	0.09	0.02	0.80	0.09
LUMO+9	-8.432	0.08	0.01	0.83	0.08
LUMO+10	-8.171	0.14	0.01	0.79	0.06
		β-spin			
HOMO−10	-17.545	0.24	0.05	0.56	0.14
HOMO−9	-17.402	0.06	0.60	0.11	0.23
HOMO−8	-17.111	0.04	0.30	0.43	0.23

HOMO−7	-16.968	0.10	0.18	0.59	0.13
HOMO−6	-16.892	0.09	0.51	0.29	0.11
HOMO−5	-16.501	0.05	0.35	0.46	0.13
HOMO−4	-16.459	0.04	0.14	0.34	0.49
HOMO−3	-15.85	0.03	0.97	0.01	0.00
HOMO−2	-15.715	0.71	0.18	0.08	0.04
HOMO−1	-15.248	0.50	0.34	0.13	0.04
HOMO	-15.068	0.14	0.76	0.04	0.06
LUMO	-13.475	0.36	0.52	0.08	0.04
LUMO+1	-13.264	0.57	0.26	0.09	0.08
LUMO+2	-11.102	0.08	0.88	0.03	0.01
LUMO+3	-10.706	0.43	0.06	0.34	0.17
LUMO+4	-10.181	0.44	0.20	0.36	0.00
LUMO+5	-9.084	0.03	0.83	0.06	0.08
LUMO+6	-9.038	0.10	0.05	0.32	0.53
LUMO+7	-8.774	0.05	0.04	0.89	0.01
LUMO+8	-8.637	0.06	0.86	0.07	0.01
LUMO+9	-8.561	0.13	0.36	0.32	0.19
LUMO+10	-8.529	0.06	0.16	0.75	0.03

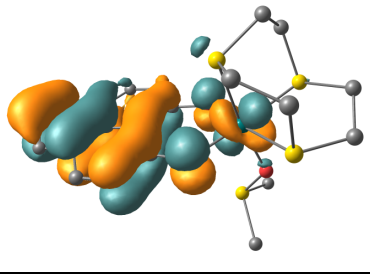
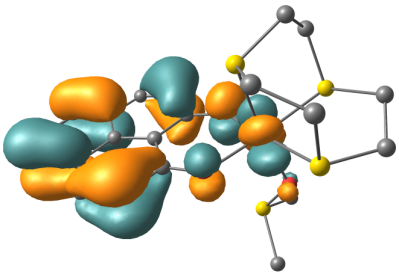
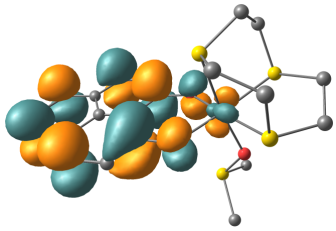
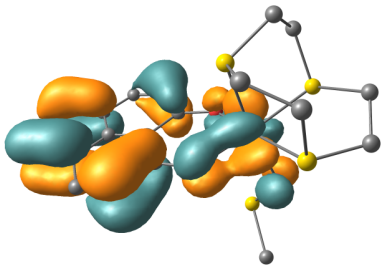
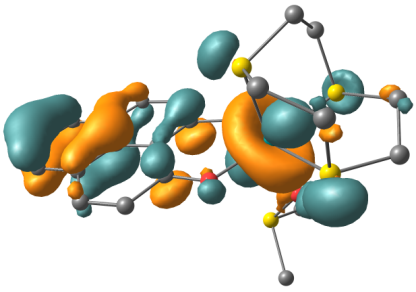
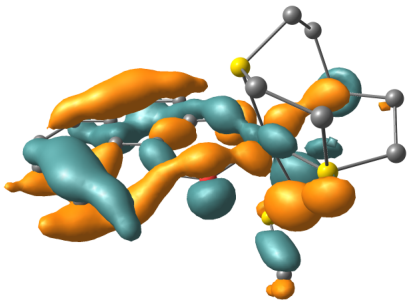
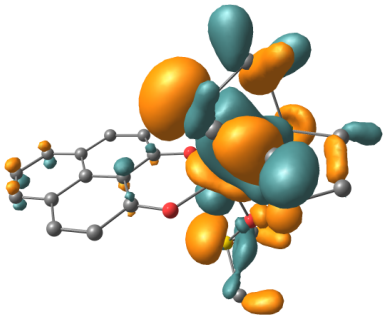
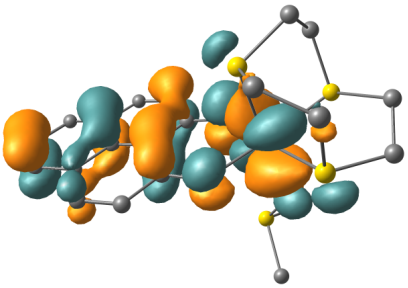
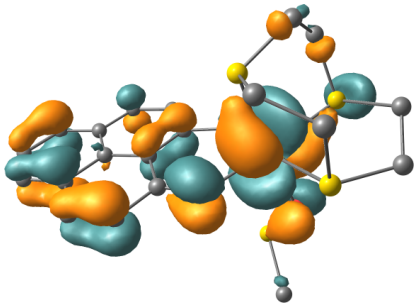
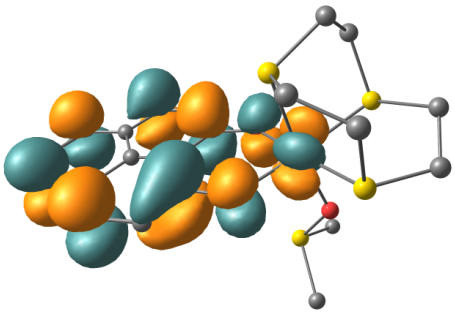
		
SOMO1(α)	SOMO2(α)	LUMO(α)
		
HOMO(β)	HOMO-1(β)	HOMO-9(β)
		
HOMO-10(β)	LUMO(β)	LUMO+1(β)
		
LUMO+2(β)		

Table S6 Composition and energies of selected molecular orbitals of **1** (κ-S) (*S*=1/2)

MO	Energy/eV	Composition			
		Ru	L	[9]aneS3	dmso
		α-spin			
HOMO−10	-7.389	0.16	0.55	0.29	0.00
HOMO−9	-7.231	0.16	0.52	0.11	0.21
HOMO−8	-6.872	0.11	0.11	0.21	0.56
HOMO−7	-6.501	0.17	0.67	0.16	0.00
HOMO−6	-6.066	0.51	0.28	0.14	0.06
HOMO−5	-5.984	0.58	0.26	0.11	0.06
HOMO−4	-5.733	0.05	0.92	0.01	0.01
HOMO−3	-5.354	0.70	0.18	0.12	0.01
HOMO−2	-5.009	0.17	0.78	0.03	0.03
HOMO−1	-4.691	0.24	0.62	0.06	0.08
SOMO	-2.414	0.03	0.91	0.03	0.03
LUMO	-0.618	0.36	0.04	0.37	0.23
LUMO+1	-0.577	0.81	0.00	0.16	0.03
LUMO+2	-0.267	0.25	0.09	0.62	0.04
LUMO+3	0.008	0.18	0.02	0.76	0.04
LUMO+4	0.126	0.22	0.06	0.68	0.04
LUMO+5	0.289	0.61	0.01	0.35	0.03
LUMO+6	0.456	0.35	0.01	0.60	0.04
LUMO+7	0.529	0.57	0.02	0.38	0.03
LUMO+8	0.647	0.44	0.05	0.44	0.07
LUMO+9	0.821	0.18	0.43	0.36	0.03
LUMO+10	0.938	0.58	0.03	0.34	0.06
		β-spin			
HOMO−10	-7.342	0.12	0.61	0.19	0.08
HOMO−9	-7.329	0.13	0.60	0.22	0.05

HOMO−8	-7.095	0.17	0.27	0.15	0.42
HOMO−7	-6.789	0.15	0.24	0.19	0.42
HOMO−6	-6.437	0.14	0.69	0.16	0.00
HOMO−5	-5.93	0.55	0.25	0.13	0.06
HOMO−4	-5.867	0.57	0.26	0.11	0.07
HOMO−3	-5.596	0.02	0.97	0.00	0.00
HOMO−2	-5.334	0.70	0.18	0.11	0.01
HOMO−1	-4.638	0.13	0.82	0.02	0.03
HOMO	-4.505	0.22	0.64	0.06	0.08
LUMO	-0.785	0.12	0.73	0.11	0.04
LUMO+1	-0.609	0.37	0.04	0.37	0.22
LUMO+2	-0.571	0.81	0.01	0.15	0.03
LUMO+3	-0.248	0.24	0.09	0.64	0.04
LUMO+4	0.011	0.17	0.02	0.76	0.04
LUMO+5	0.152	0.22	0.06	0.68	0.04
LUMO+6	0.294	0.61	0.01	0.35	0.03
LUMO+7	0.461	0.34	0.01	0.61	0.04
LUMO+8	0.531	0.58	0.02	0.38	0.03
LUMO+9	0.672	0.46	0.02	0.45	0.07
LUMO+10	0.943	0.58	0.03	0.34	0.05

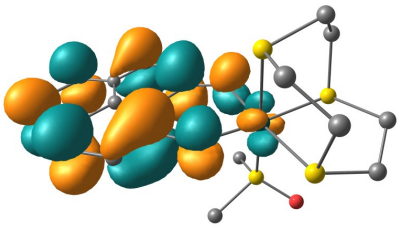
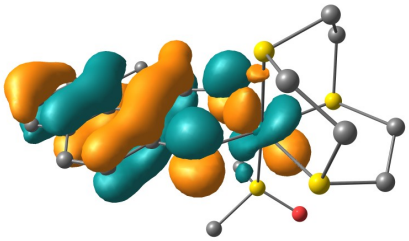
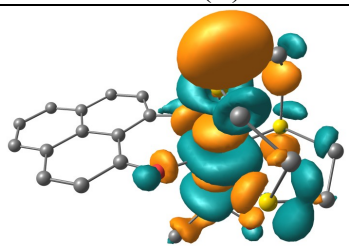
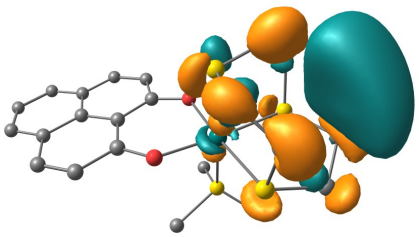
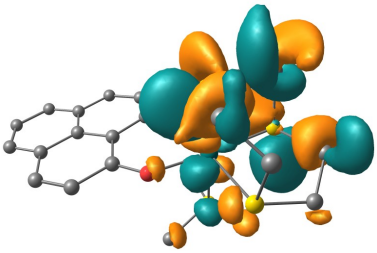
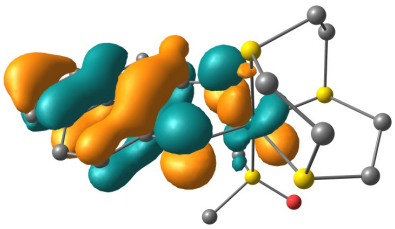
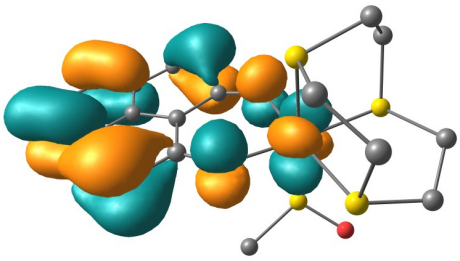
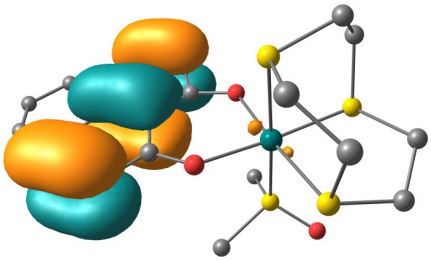
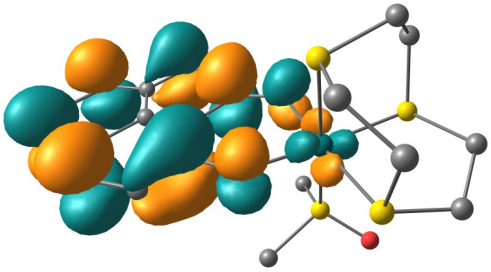
	
SOMO(α)	HOMO-1(α)
	
LUMO(α)	LUMO+1(α)
	
LUMO+3(α)	HOMO(β)
	
HOMO-1(β)	HOMO-3(β)
	
LUMO(β)	

Table S7 Composition and energies of selected molecular orbitals of $\mathbf{1}^{-}$ (κ-S) (*S*=1)

MO	Energy/eV	Composition			
		Ru	L	[9]aneS3	dmso
		α-spin			
HOMO−10	-3.984	0.13	0.45	0.29	0.13
HOMO−9	-3.578	0.10	0.02	0.40	0.48
HOMO−8	-3.077	0.09	0.76	0.15	0.00
HOMO−7	-2.898	0.01	0.99	0.00	0.00
HOMO−6	-2.549	0.17	0.75	0.06	0.02
HOMO−5	-2.363	0.37	0.53	0.07	0.03
HOMO−4	-1.659	0.68	0.15	0.16	0.01
HOMO−3	-1.611	0.56	0.23	0.14	0.07
HOMO−2	-1.322	0.50	0.29	0.14	0.08
SOMO2	-0.063	0.50	0.05	0.15	0.31
SOMO1	0.588	0.05	0.89	0.04	0.03
LUMO	2.211	0.91	0.00	0.08	0.02
LUMO+1	2.965	0.39	0.03	0.54	0.03
LUMO+2	3.099	0.66	0.02	0.28	0.04
LUMO+3	3.204	0.64	0.03	0.30	0.04
LUMO+4	3.397	0.41	0.07	0.51	0.01
LUMO+5	3.537	0.40	0.12	0.45	0.03
LUMO+6	3.665	0.34	0.27	0.35	0.04
LUMO+7	3.747	0.36	0.04	0.55	0.04
LUMO+8	3.825	0.40	0.04	0.51	0.06
LUMO+9	3.953	0.30	0.19	0.48	0.03
LUMO+10	4.065	0.09	0.64	0.22	0.05
LUMO+11	4.092	0.35	0.09	0.54	0.02
		β-spin			
HOMO−10	-4.011	0.11	0.78	0.06	0.05
HOMO−9	-3.966	0.09	0.62	0.29	0.01

HOMO−8	-3.809	0.09	0.10	0.60	0.21
HOMO−7	-3.448	0.11	0.04	0.27	0.58
HOMO−6	-2.978	0.07	0.78	0.15	0.00
HOMO−5	-2.76	0.01	0.99	0.00	0.00
HOMO−4	-2.139	0.21	0.69	0.06	0.03
HOMO−3	-2.057	0.33	0.57	0.06	0.04
HOMO−2	-1.297	0.66	0.14	0.19	0.01
HOMO−1	-1.143	0.51	0.25	0.16	0.08
HOMO	-0.998	0.50	0.26	0.15	0.09
LUMO	2.115	0.26	0.62	0.09	0.03
LUMO+1	2.204	0.90	0.01	0.08	0.01
LUMO+2	2.818	0.64	0.02	0.27	0.07
LUMO+3	3.083	0.70	0.02	0.24	0.04
LUMO+4	3.215	0.42	0.02	0.48	0.08
LUMO+5	3.262	0.60	0.03	0.31	0.07
LUMO+6	3.480	0.37	0.05	0.56	0.02
LUMO+7	3.602	0.45	0.03	0.49	0.03
LUMO+8	3.799	0.22	0.53	0.22	0.03
LUMO+9	3.819	0.44	0.04	0.46	0.06
LUMO+10	3.984	0.30	0.04	0.64	0.02

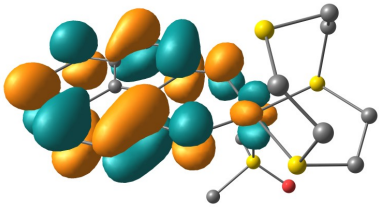
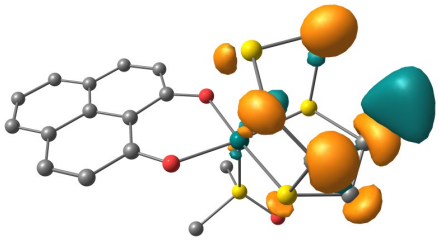
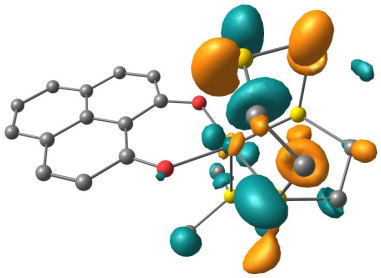
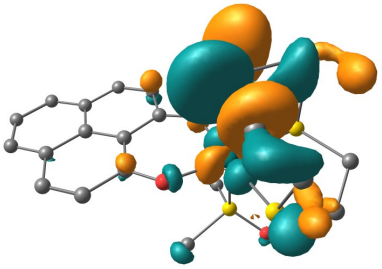
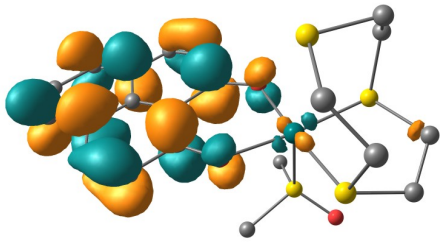
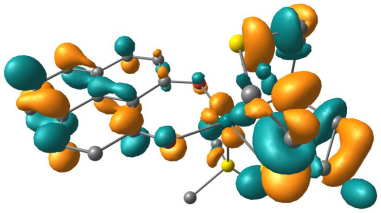
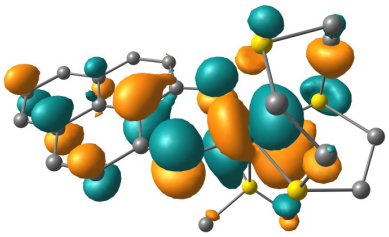
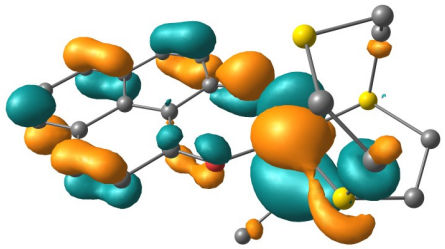
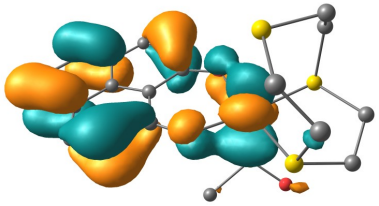
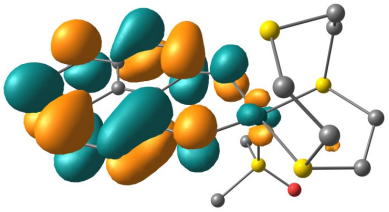
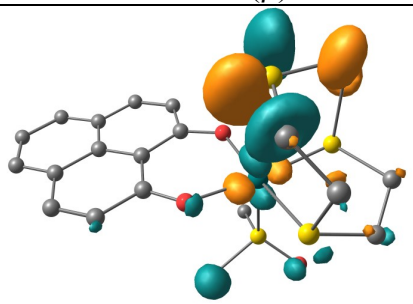
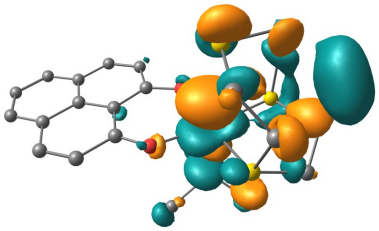
		
SOMO1(α)	LUMO(α)	LUMO+2(α)
		
LUMO+7(α)	LUMO+10(α)	LUMO+11(α)
		
HOMO(β)	HOMO-1(β)	HOMO-4(β)
		
LUMO(β)	LUMO+3(β)	LUMO+5(β)

Table S8a Energies of DFT optimised structures of $\mathbf{1}^{3+}$ and $\mathbf{1}^{-}$

Compound	$E_{(S=0)}$ (Hartrees)	$E_{(S=1)}$ (Hartrees)	$\Delta E_{(S=0-S=1)}$
$\mathbf{1}^{3+}$ (κ-O)	-2727.7473029	-2727.7558077	0.0085048 Hartrees 0.231427 eV 22.32935 kJ mol^{-1} 5.33684 kcal mol^{-1} 1866.5878 cm^{-1}
$\mathbf{1}^{-}$ (κ-S)	-2728.6598475	-2728.6695774	0.0097299 Hartrees 0.2647641911 eV 25.5458544 kJ mol^{-1} 6.105605735 kcal mol^{-1} 2135.466202 cm^{-1}

Table S8b Energies of DFT optimised structures of $\mathbf{1}^{3+}$ and $\mathbf{1}^{2+}$ (both S- and O-bonded dmso)

Compound	$E_{(\kappa\text{-S})}$ (Hartrees)	$E_{(\kappa\text{-O})}$ (Hartrees)	$\Delta E_{(\kappa\text{-S}-\kappa\text{-O})}$
$\mathbf{1}^{3+}$ (S=1)	-2727.7180134	-2727.7558077	0.03779 Hartrees 1.02831877 eV 99.2176526 kJ mol^{-1} 23.7135881 kcal mol^{-1} 8293.94627 cm^{-1}
$\mathbf{1}^{2+}$ (S=1/2)	–2728.1973832	–2728.2146933	0.01731 Hartrees 0.471029317 eV 45.4474085 kJ mol^{-1} 10.8621913 kcal mol^{-1} 3799.10585 cm^{-1}

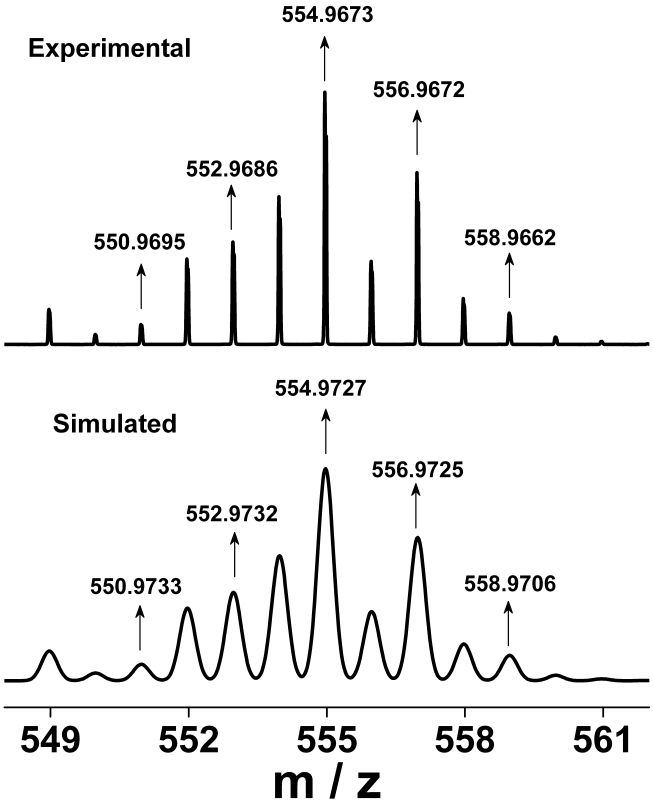


Fig. S1 ESI-MS(+) of [**1**]ClO_4 in CH_2Cl_2 {experimental (top), simulated (bottom)}.

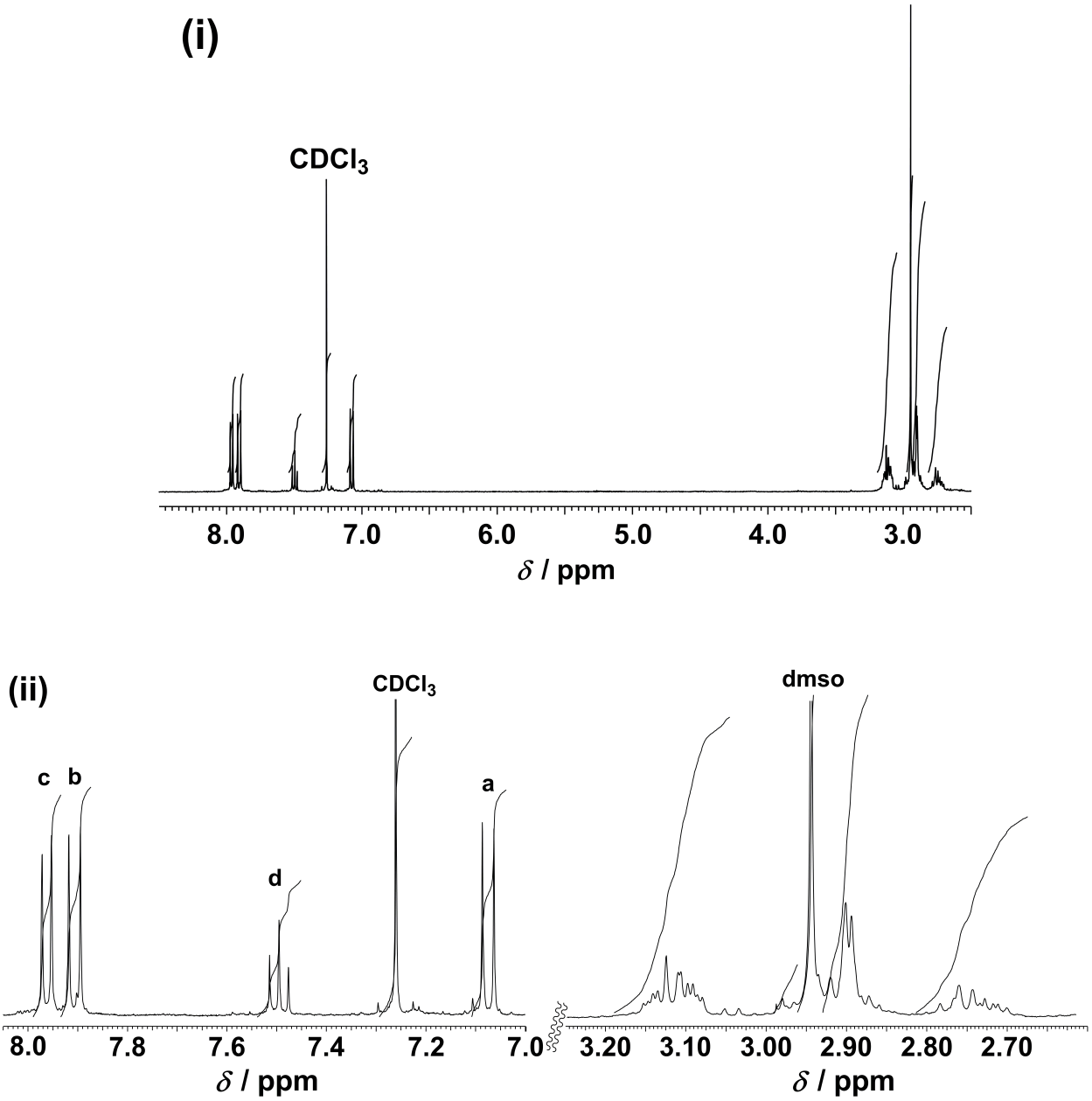


Fig. S2(a) ^{1}H NMR spectrum of [**1**]ClO_4 in $CDCl_3$: (i) full, (ii) expanded.

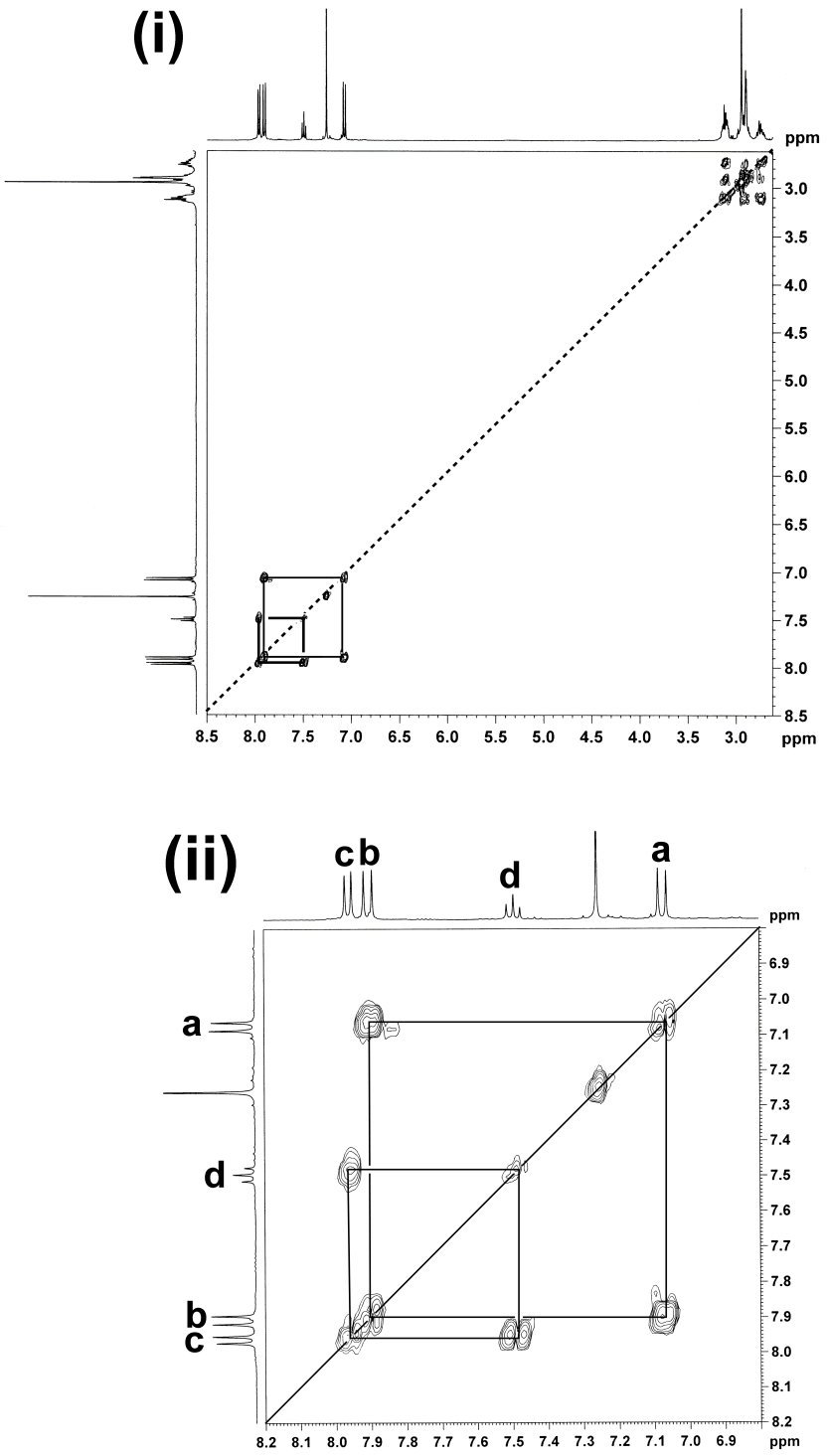


Fig. S2(b) ^{1}H-^{1}H COSY NMR spectrum of [**1**]ClO_4 in $CDCl_3$: (i) full, (ii) expanded aromatic region.

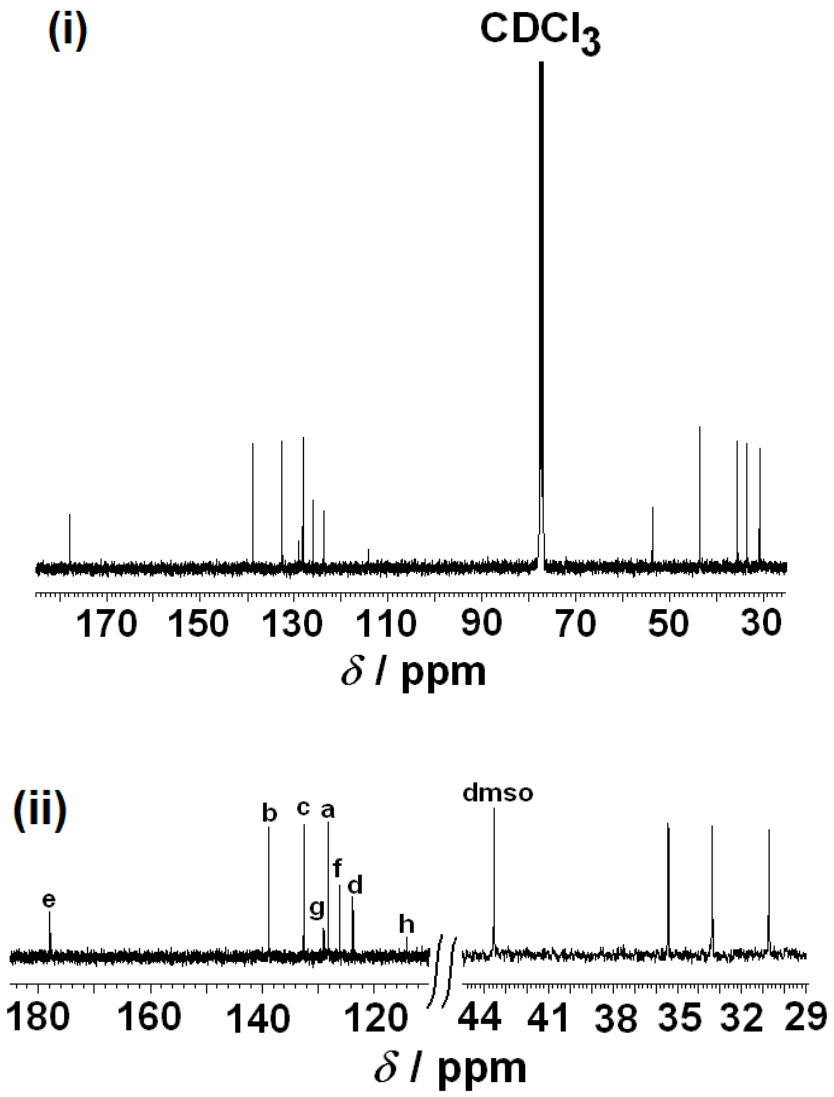


Fig. S2(c) ^{13}C NMR spectrum of [**1**]ClO_4 in $CDCl_3$: (i) full, (ii) expanded.

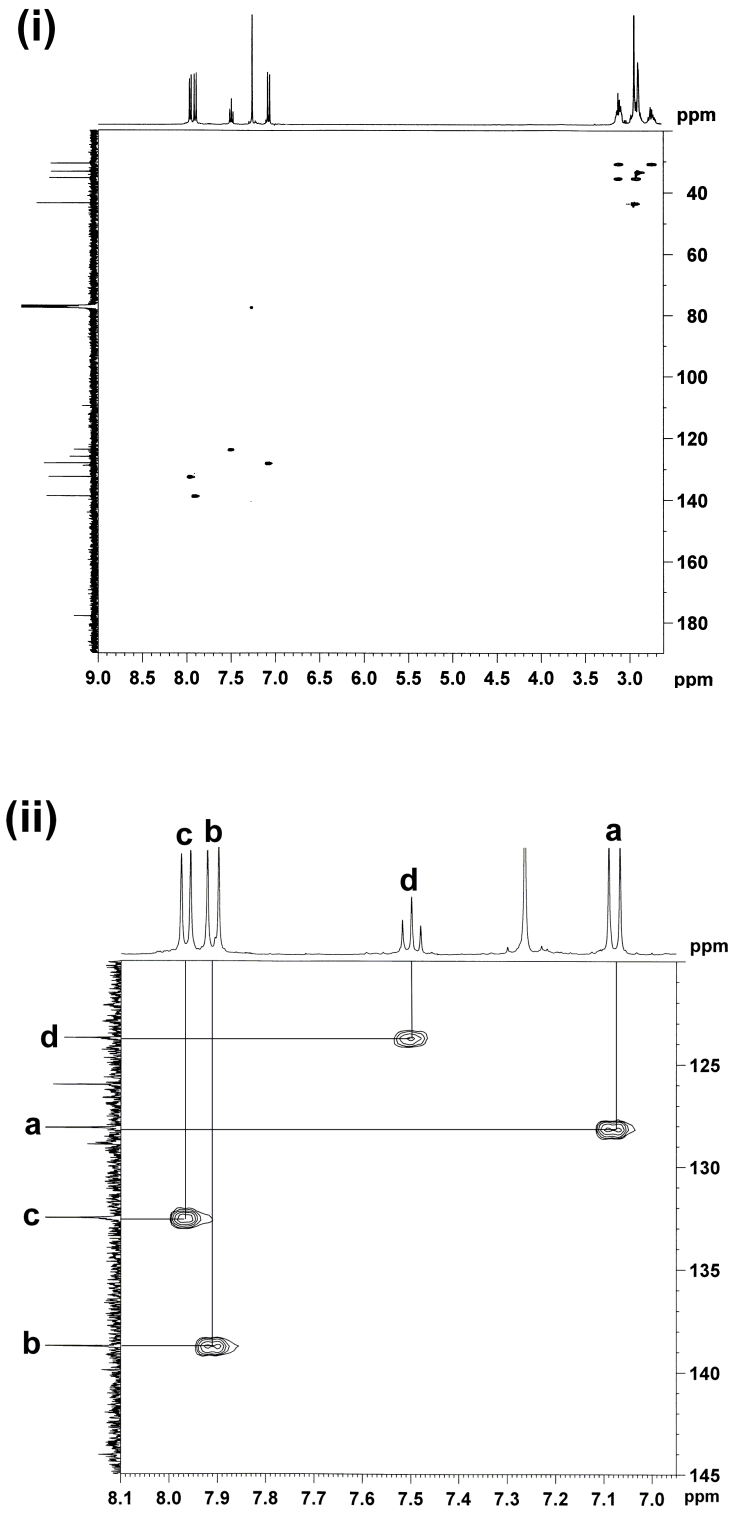


Fig. S2(d) ^{1}H-^{13}C HSQC NMR spectrum of [**1**]ClO_4 in $CDCl_3$: (i) full, (ii) expanded aromatic region.

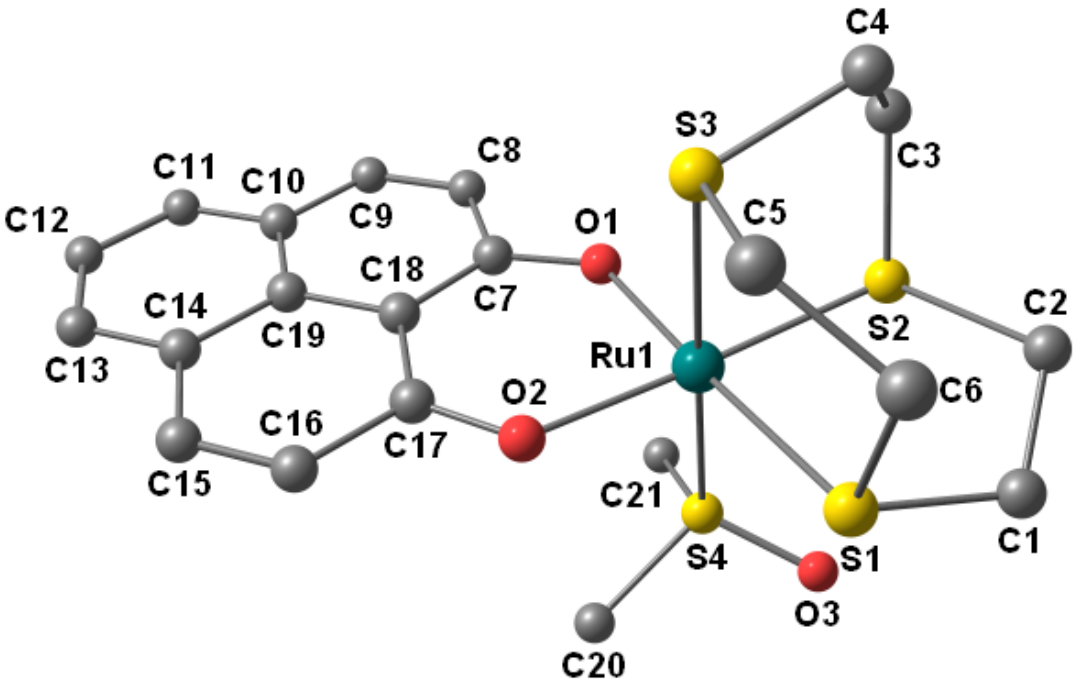


Fig. S3 DFT optimised structure of $\mathbf{1}^{+}$ (κ-S).