Electronic supplementary information (ESI)

Development of a ruthenium aquo complex for utilization in synthesis and, in catalysis for selective hydration of nitriles and alkynes†

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Table S1. Selected bond distances and bond angles for **1a**.

Bond distances (Å)			
Ru1-N1	2.0636(17)	C3-N1	1.433(3)
Ru1-N2	1.9908(18)	C1-N1	1.305(3)
Ru1-N3	2.0741(19)	C1-C2	1.425(3)
Ru1-N4	1.9750(18)	C2-N2	1.295(3)
Ru1-N5	2.0777(19)	C10-N2	1.437(3)
Ru1-O3	2.1358(16)		
Bond angles (°)			
N1-Ru1-N4	172.67(7)	N1-Ru1-N2	77.67(7)
N2-Ru1-O3	175.98(7)	N3-Ru1-N4	79.24(8)
N3-Ru1-N5	158.06(8)	N4-Ru1-N5	79.11(8)

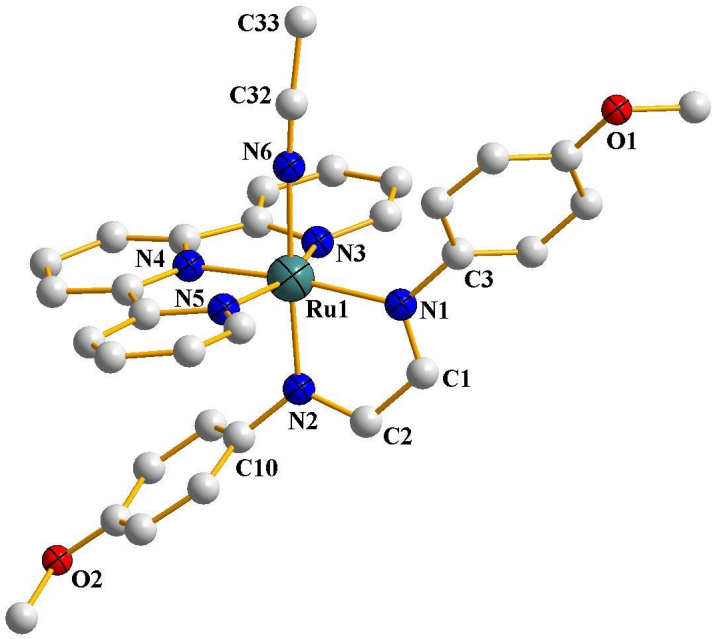


Fig. S1 Crystal structure of complex **1b**. The perchlorate ions and hydrogen atoms are omitted for clarity.

Table S2. Selected bond distances and bond angles for **1b**.

Bond distances (Å)			
Ru1-N1	2.065(8)	C3-N1	1.443(13)
Ru1-N2	2.005(8)	C1-N1	1.301(14)
Ru1-N3	2.083(9)	C1-C2	1.425(16)
Ru1-N4	1.979(8)	C2-N2	1.295(13)
Ru1-N5	1.984(7)	C10-N2	1.449(13)
Ru1-N6	2.039(9)		
Bond angles (°)			
N1-Ru1-N4	170.6(3)	N3-Ru1-N4	79.8(4)
N2-Ru1-N6	174.3(3)	N4-Ru1-N5	79.4(3)
N3-Ru1-N5	159.1(3)	Ru1-N6-C32	175.9(10)
N1-Ru1-N2	77.2(4)	N6-C32-C33	178.2(16)

Table S3. Selected bond distances and bond angles for **1d**.

Bond distances (Å)			
Ru1-N1	2.066(8)	C3-N1	1.414(14)
Ru1-N2	2.050(8)	C1-N1	1.290(14)
Ru1-N3	2.075(8)	C1-C2	1.394(16)
Ru1-N4	1.987(8)	C2-N2	1.272(14)
Ru1-N5	2.061(8)	C10-N2	1.446(14)
Ru1-N6	2.099(9)		
Bond angles (°)			
N1-Ru1-N4	175.0(3)	N1-Ru1-N2	76.8(4)
N2-Ru1-N6	170.0(4)	N3-Ru1-N4	79.2(3)
N3-Ru1-N5	157.6(3)	N4-Ru1-N5	78.5(3)

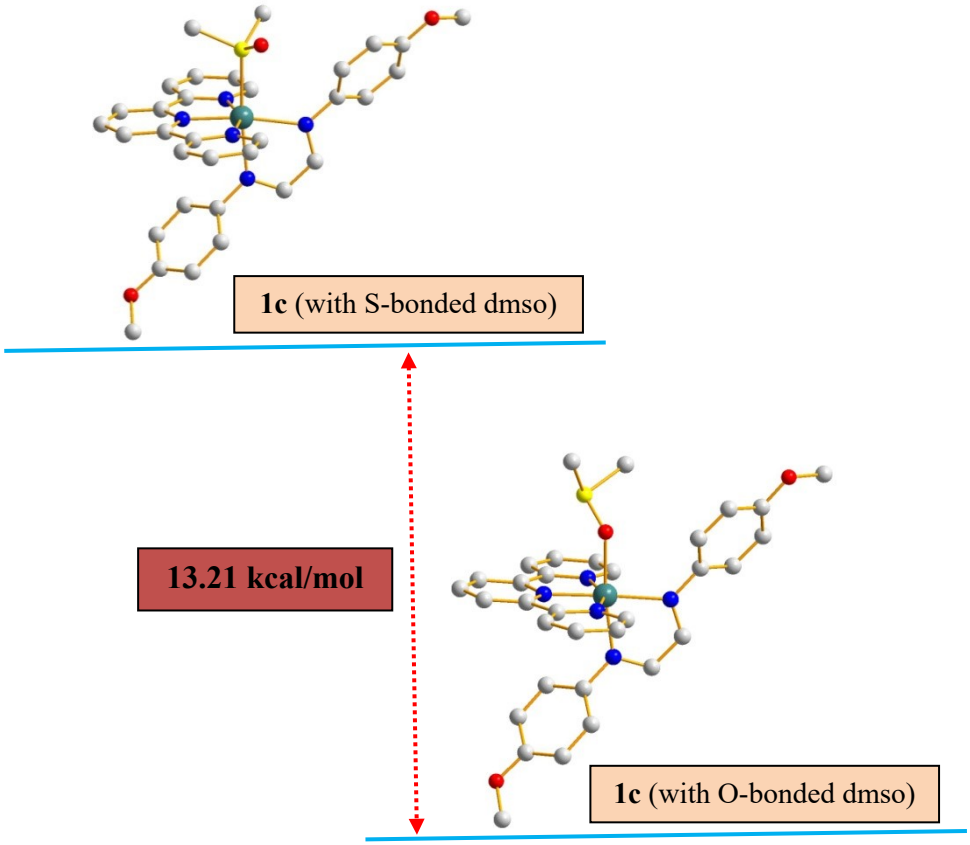


Fig. S2. Energy difference between linkage isomers of **1c**.

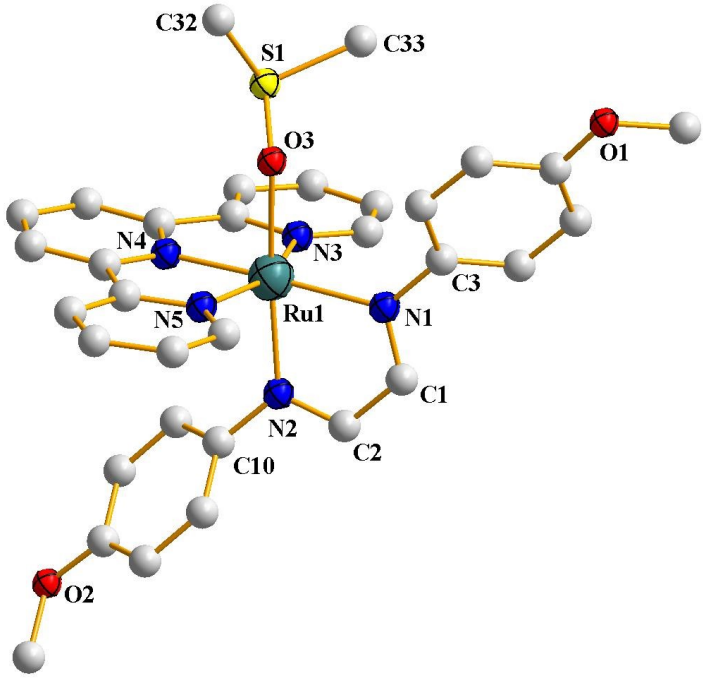


Fig. S3. DFT-optimized structure of **1c**. The hydrogen atoms are omitted for clarity.

Table S4. Some computed bond distances and bond angles for complex **1c**.

Bond distances (Å)			
Ru1-N1	2.151	C1-N1	1.313
Ru1-N2	2.086	C3-N1	1.417
Ru1-N3	2.133	C1-C2	1.427
Ru1-N4	2.007	C2-N2	1.313
Ru1-N5	2.116	C10-N2	1.422
Ru1-O3	2.195	S1-C32	1.816
O3-S1	1.526	S1-C33	1.822
Bond angles (°)			
N1-Ru1-N2	77.799	N3-Ru1-N4	78.427
N2-Ru1-O3	170.139	N4-Ru1-N5	79.034
N1-Ru1-N4	176.902	N3-Ru1-N5	157.445
Ru1-O3-S1	126.135		

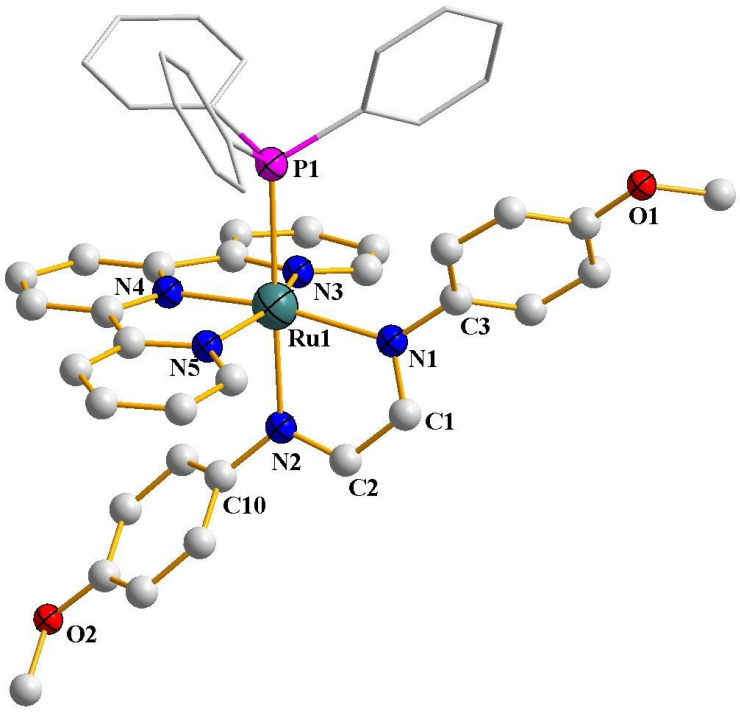


Fig. S4. DFT-optimized structure of **1e**. The hydrogen atoms are omitted for clarity.

Table S5. Some computed bond distances and bond angles for complex **1e**.

Bond distances (Å)			
Ru1-N1	2.211	C1-N1	1.312
Ru1-N2	2.171	C3-N1	1.422
Ru1-N3	2.137	C1-C2	1.431
Ru1-N4	2.006	C2-N2	1.304
Ru1-N5	2.133	C10-N2	1.423
Ru1-P1	2.551		
Bond angles (°)			
N1-Ru1-N2	76.522	N3-Ru1-N4	78.376
N2-Ru1-P1	178.154	N4-Ru1-N5	78.674
N1-Ru1-N4	170.360	N3-Ru1-N5	156.279

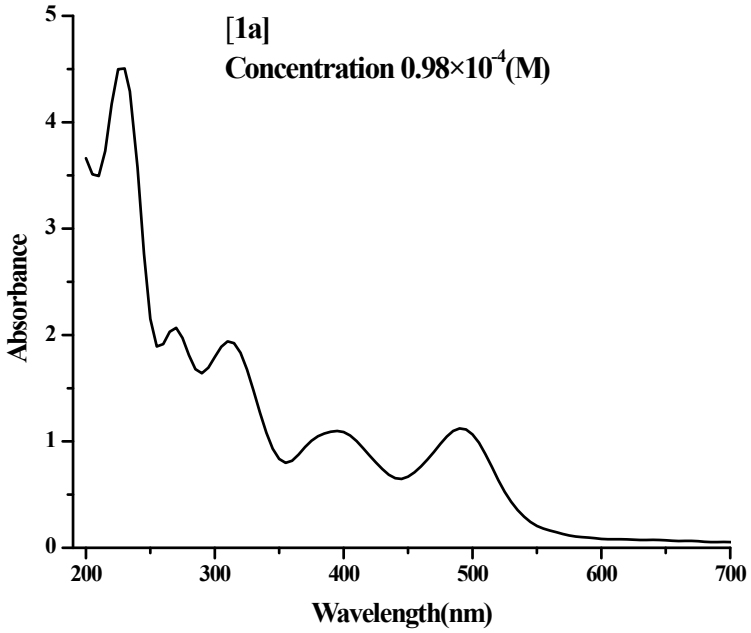


Fig. S5. Electronic absorption spectrum of complex **1a** in aqueous solution.

Table S6. Computed parameters from TDDFT calculations on complex **1a** for electronic spectral properties in aqueous solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 → L H-1 → L H → L	0.44216 0.37240 0.39467	2.5721	0.4901	482	MLCT/LLCT ILCT ILCT	492
2	H-4 → L H-4 → L+1 H-3 → L+1 H-2 → L H-2 → L+1 H-1 → L+1 H-1 → L+2 H-1 → L+5 H → L+5	0.43694 0.10291 0.24545 0.12469 0.11714 0.10428 0.10440 0.27243 0.20279	3.1122	0.0277	389	MLCT/ILCT/ LLCT MLCT/ILCT MLCT/ILCT MLCT/LLCT MLCT/LLCT/ ILCT LLCT LLCT LMCT/LLCT/ILCT LMCT/LLCT/ILCT	395
3	H-5 → L+1 H → L+3 H → L+4 H → L+5	0.40042 0.34558 0.37591 0.10524	3.9929	0.2109	310	LLCT LLCT LLCT LMCT/LLCT/ILCT	312
4	H-8 → L+1 H-5 → L+2 H-3 → L+3 H-3 → L+4 H-2 → L+4 H-1 → L+4	0.13454 0.48720 0.26888 0.27855 0.10789 0.21551	4.5044	0.0880	275	ILCT LLCT MLCT/ILCT MLCT/ILCT MLCT/ILCT/LLCT LLCT	269
5	H-12 → L H-11 → L H-10 → L+1 H-5 → L+4 H-1 → L+9	0.35228 0.23171 0.13218 0.27703 0.36093	5.1824	0.0136	239	ILCT/LMCT ILCT/LMCT LLCT LLCT ILCT/LLCT	227

Table S7. Compositions of the molecular orbitals of complex **1a** associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments			
	Ru	trpy	L-OCH_3	H_2O
HOMO (H)	5	1	94	0
H-1	9	2	89	0
H-2	73	14	12	1
H-3	77	17	5	1
H-4	66	11	23	0
H-5	0	0	99	1
H-8	2	95	3	0
H-10	0	1	99	0
H-11	1	3	95	1
H-12	0	1	98	1
LUMO (L)	10	2	88	0
L+1	6	93	0	1
L+2	1	99	0	0
L+3	3	96	0	1
L+4	3	97	0	0
L+5	52	12	18	18
L+9	11	3	72	14

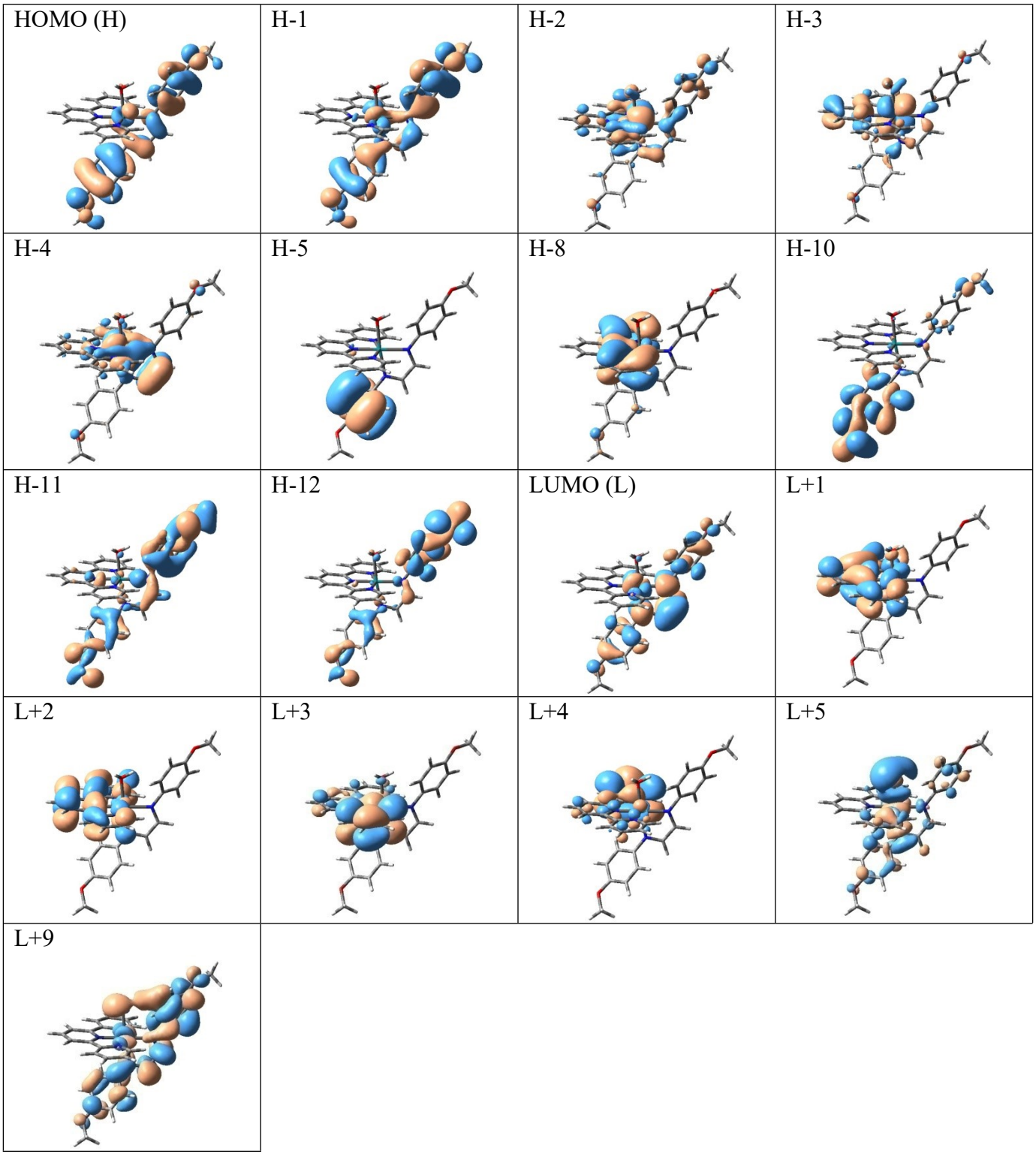


Fig. S6. Contour plots of the molecular orbitals of complex **1a**, which are associated with the electronic spectral transitions (See **Table S6**).

Table S8. Computed parameters from TDDFT calculations on complex **1b** for electronic spectral properties in acetonitrile solution.

Excited state	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 → L H-1 → L H → L	0.49112 0.28458 0.40475	2.5632	0.4854	484	MLCT/LLCT ILCT ILCT	481
2	H-4 → L H-3 → L+1 H-2 → L	0.63154 0.10707 0.24464	3.0572	0.0456	405	MLCT/ILCT/LLCT MLCT/ILCT MLCT/LLCT	405
3	H-5 → L+1 H → L+3	0.44630 0.50881	4.0032	0.2295	310	LLCT LLCT	304
4	H-8 → L+1 H-5 → L+2 H-3 → L+3 H-3 → L+4 H-2 → L+4 H-1 → L+4	0.12636 0.48345 0.34287 0.18001 0.14342 0.21724	4.5065	0.0979	275	ILCT LLCT MLCT/LLCT/ILCT MLCT/ILCT/LLCT MLCT/ILCT/LLCT LLCT	273
5	H-12 → L H-2 → L+7 H-2 → L+8 H-2 → L+9 H-1 → L+7 H-1 → L+8 H-1 → L+9 H→ L+10	0.15867 0.33532 0.19579 0.16477 0.19995 0.30896 0.21252 0.19191	5.1735	0.0187	240	ILCT/LMCT IMCT/MLCT/LLCT/ILCT MLCT/LLCT MLCT/LLCT LMCT/LLCT/ ILCT ILCT/ LLCT ILCT/ LLCT LLCT/ ILCT	232

Table S9. Compositions of the molecular orbitals of complex **1b** associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments			
	Ru	trpy	L-OCH_3	CH_3CN
HOMO (H)	4	0	96	0
H-1	6	1	93	0
H-2	73	14	9	4
H-3	74	16	5	5
H-4	69	12	18	1
H-5	0	1	99	0
H-8	2	94	4	
H-12	0	1	99	0
LUMO (L)	8	3	89	2
L+1	5	94	1	0
L+2	1	98	0	1
L+3	1	99	0	0
L+4	3	97	0	0
L+7	55	15	26	4
L+8	4	2	80	14
L+9	4	2	77	17
L+10	6	1	15	78

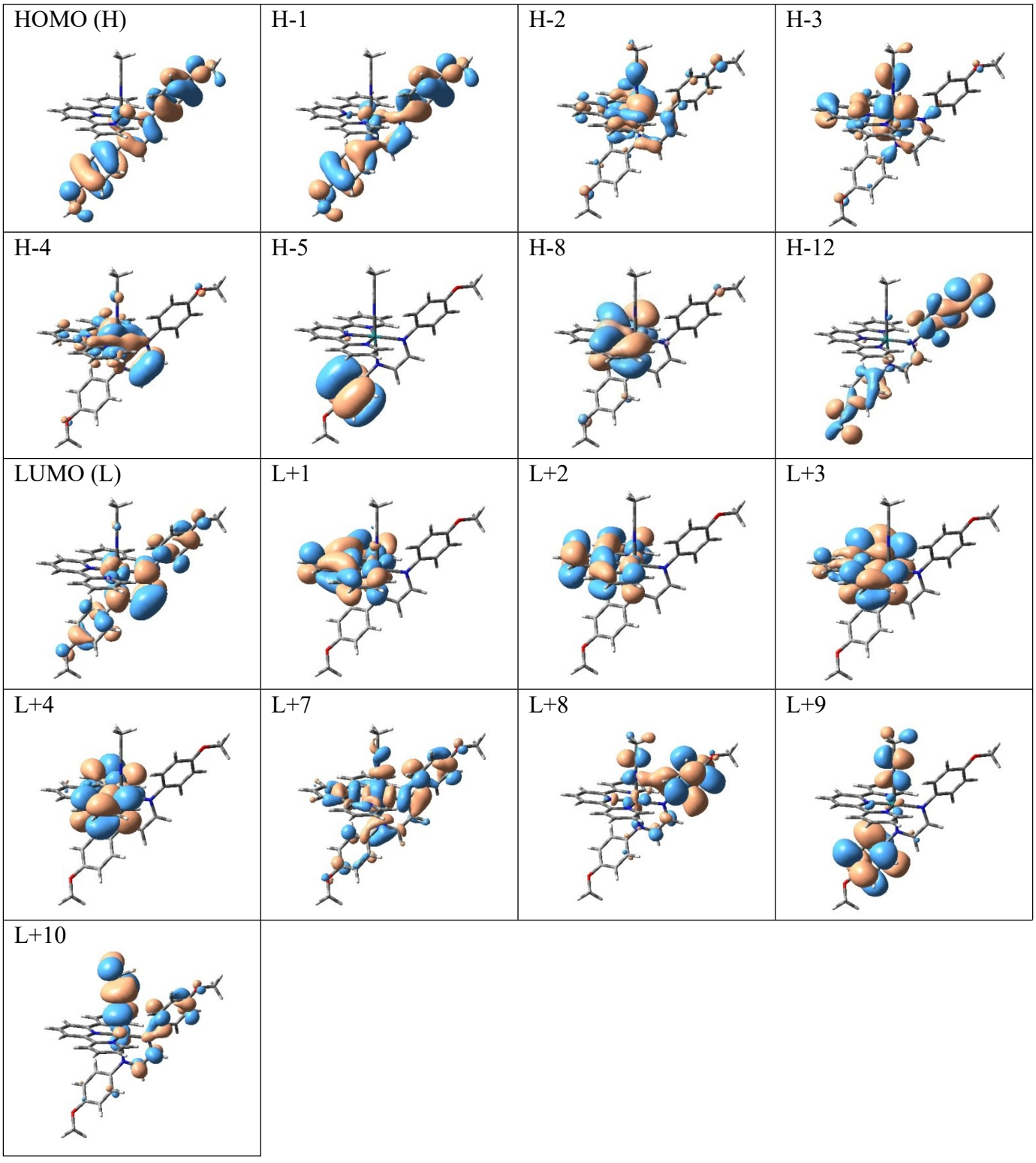


Fig. S7. Contour plots of the molecular orbitals of complex **1b**, which are associated with the electronic spectral transitions (See **Table S8**).

Table S10. Computed parameters from TDDFT calculations on complex **1c** for electronic spectral properties in acetonitrile solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-2 →L	0.54729	2.5655	0.5531	483.28	MLCT/LLCT	486
	H-1 →L	0.15447				ILCT/MLCT	
	H →L	0.39826				ILCT	
2	H-4 →L	0.46758	3.0525	0.0242	406.18	MLCT/ILCT	403
	H-3 →L	0.21236				MLCT/LLCT	
	H-3 →L+1	0.10453				MLCT/ILCT	
	H-3 →L+2	0.11788				MLCT/ILCT	
	H-2 →L+1	0.32982				MLCT/LLCT/ILCT	
	H-1 →L+2	0.25499				LLCT/MLCT	
3	H-5 →L+1	0.31171	4.0151	0.1169	308.80	LLCT	309
	H-2 →L+3	0.10529				MLCT/ILCT/LLCT	
	H-2 →L+9	0.16964				MLCT/LLCT/ILCT	
	H-1 →L+3	0.35149				LLCT/MLCT	
	H-1 →L+4	0.20294				LLCT/MLCT	
	H-1 →L+5	0.17985				MLCT/ILCT/LLCT/LMCT	
	H-1 →L+9	0.16712				MLCT/ILCT	
	H →L+3	0.11691				LLCT	
	H →L+4	0.14905				LLCT	
	H →L+9	0.12275				ILCT	
4	H-6 →L+2	0.10232	4.4551	0.1444	278.30	LLCT	271
	H-5 →L+2	0.35304				LLCT	
	H-2 →L+5	0.40564				MLCT/ILCT/LLCT/LMCT	
	H-1 →L+5	0.11118				MLCT/ILCT/LLCT/LMCT	
	H →L+5	0.37918				LMCT/LLCT/ILCT	
5	H-15 →L	0.31982	5.2754	0.0546	235.02	LLCT	216
	H-13→L	0.15501				ILCT/LLCT	
	H-4 →L+7	0.28094				MLCT/ILCT/LLCT/LMCT	
	H-3 →L+7	0.41276				MLCT/ILCT/LLCT/LMCT	
	H-3 →L+9	0.10248				MLCT/LLCT	
	H-2 →L+7	0.15762				MLCT/ILCT/LLCT/LMCT	
	H-2 →L+8	0.13455				MLCT/ILCT/LLCT	
	H-2 →L+9	0.11581				MLCT/ILCT/LLCT	

Table S11. Compositions of the molecular orbitals of complex **1c** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	trpy	L-OCH_3	DMSO
HOMO (H)	6	1	93	0
H-1	14	2	83	1
H-2	70	12	14	4
H-3	70	13	9	7
H-4	68	10	22	0
H-5	0	1	99	0
H-6	1	0	97	2
H-13	1	11	66	22
H-15	1	90	5	4
LUMO (L)	10	3	87	0
L+1	7	91	1	1
L+2	2	97	1	0
L+3	2	96	0	2
L+4	2	97	1	0
L+5	57	11	17	15
L+7	56	24	14	6
L+8	4	2	85	9
L+9	0	2	97	1

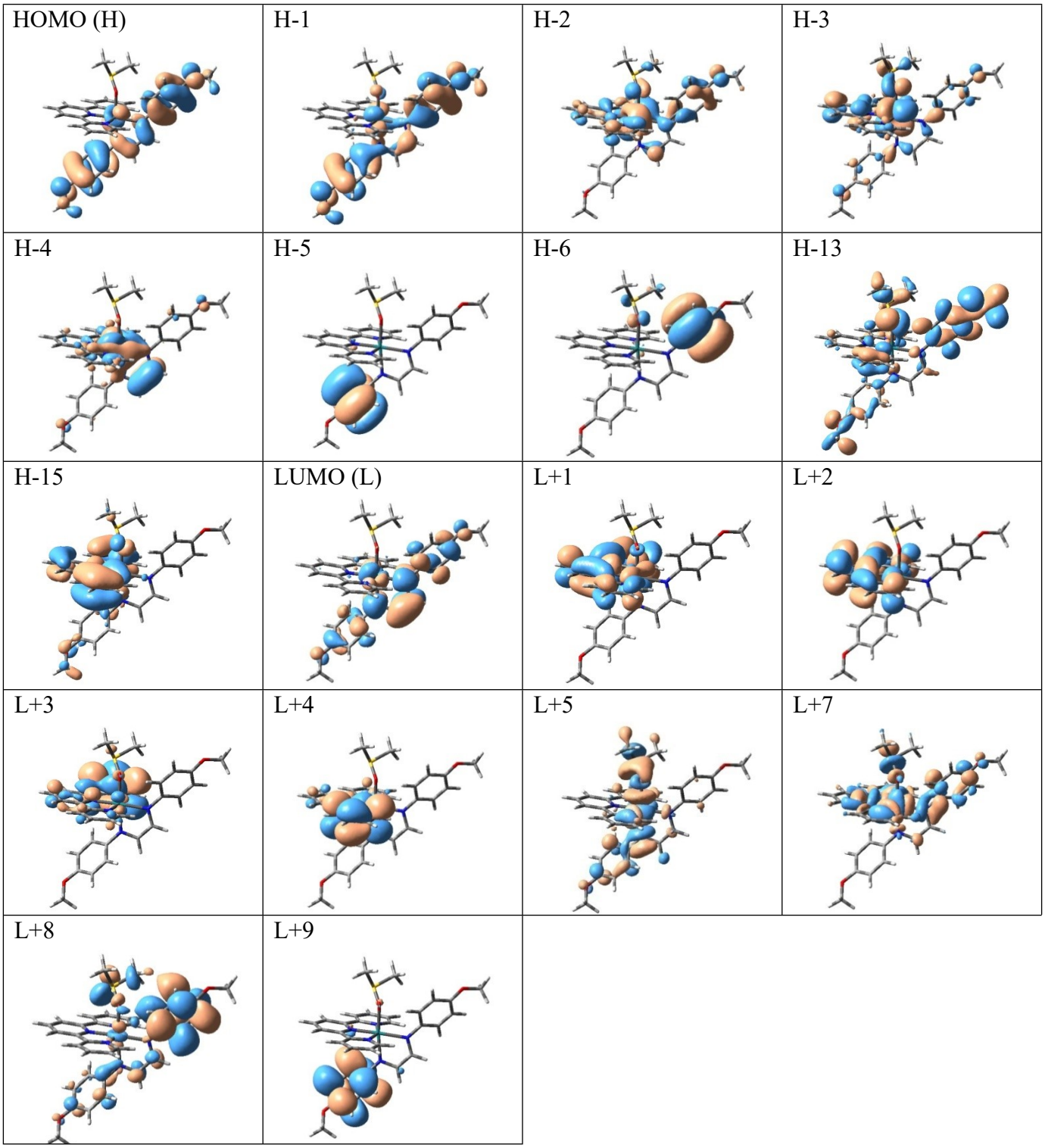


Fig. S8. Contour plots of the molecular orbitals of complex **1c**, which are associated with the electronic spectral transitions (See **Table S10**).

Table S12. Computed parameters from TDDFT calculations on complex **1d** for electronic spectral properties in acetonitrile solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 → L H-1 → L H → L	0.34955 0.42985 0.41819	2.5341	0.5379	489	MLCT/LLCT ILCT ILCT	493
2	H-4 → L H-4 → L+1 H-3 → L+1 H-2 → L H-1 → L+1 H-1 → L+2	0.49666 0.10156 0.34931 0.23312 0.12310 0.11789	3.0361	0.0214	408	MLCT/LLCT/ILCT MLCT/LLCT MLCT/ILCT MLCT/LLCT LLCT LLCT	410
3	H-5 → L+1 H → L+3 H → L+5	0.54863 0.31981 0.17420	3.9620	0.2109	313	LLCT LLCT LLCT	310
4	H-10 → L H-8 → L+1 H-5 → L+2 H-3 → L+3 H-2 → L+4 H-1 → L+4	0.10579 0.27445 0.52526 0.10395 0.17197 0.14673	4.4638	0.0947	278	ILCT/LLCT/LMCT LLCT LLCT MLCT/ILCT MLCT/LLCT/ILCT LLCT	272
5	H-13 → L H-3 → L+8 H-1 → L+11 H-1 → L+12 H → L+12	0.13239 0.13449 0.15755 0.21121 0.54779	5.1140	0.0335	242	ILCT/LMCT MLCT/LLCT ILCT ILCT ILCT	235

Table S13. Compositions of the molecular orbitals of complex **1d** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	trpy	L-OCH_3	4-picoline
HOMO (H)	5	1	94	0
H-1	7	1	92	0
H-2	73	14	10	3
H-3	76	16	4	4
H-4	70	10	19	1
H-5	0	1	99	0
H-8	0	1	7	92
H-10	0	26	72	2
H-13	0	1	99	0
LUMO (L)	10	1	89	0
L+1	6	92	1	1
L+2	1	98	0	1
L+3	1	98	0	1
L+4	3	96	0	1
L+5	4	0	1	95
L+8	1	42	5	52
L+11	2	1	97	0
L+12	5	3	92	0

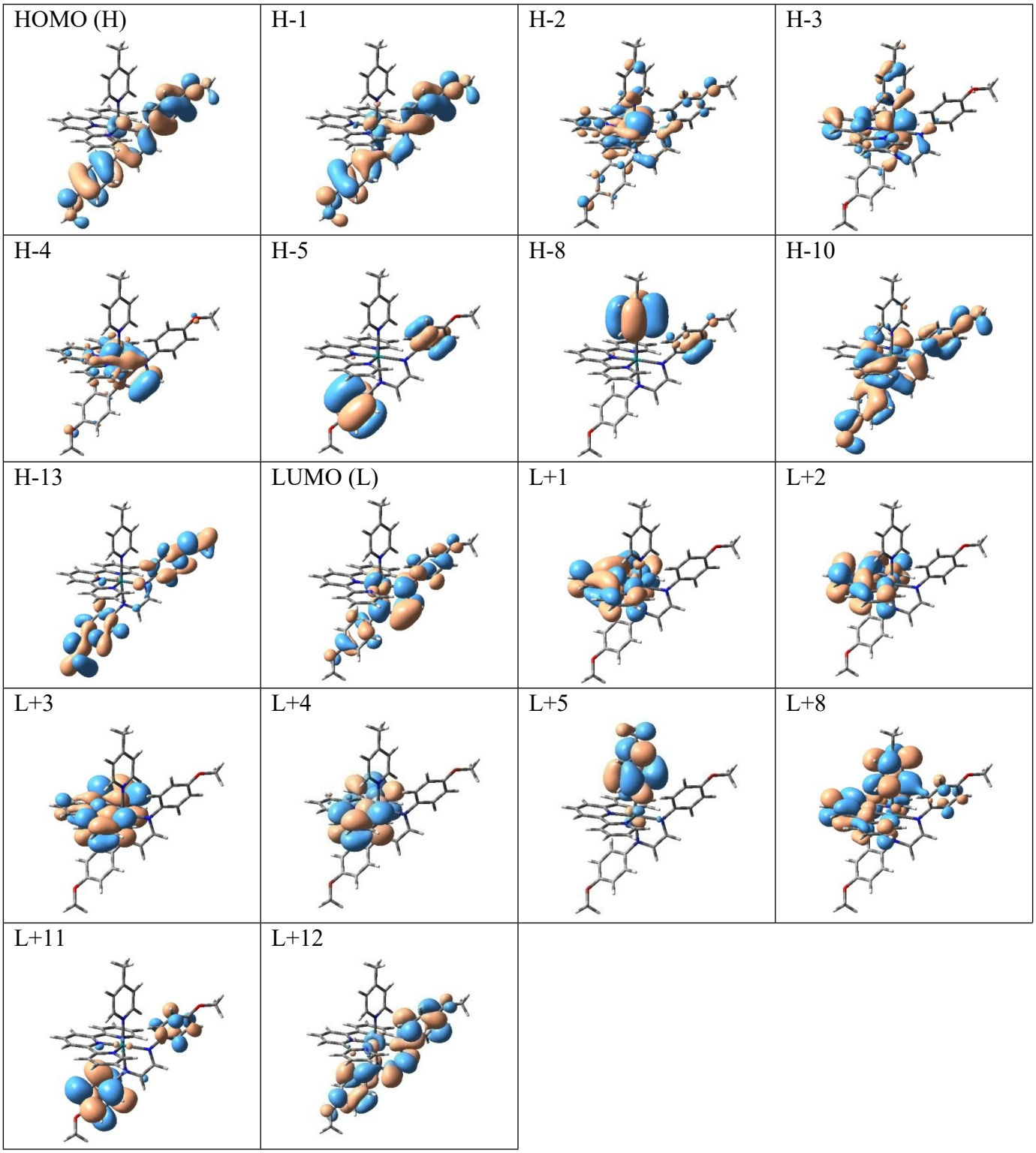


Fig. S9. Contour plots of the molecular orbitals of complex **1d**, which are associated with the electronic spectral transitions (See **Table S12**).

Table S14. Computed parameters from TDDFT calculations on complex **1e** for electronic spectral properties in acetonitrile solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 →L	0.44901	2.4677	0.3669	502.43	MLCT/LLCT	485
	H-2 →L	0.21785				MLCT/LLCT	
	H-1 →L	0.24486				ILCT	
	H →L	0.41560				ILCT	
2	H-5 →L	0.46758	3.1130	0.0205	398.28	LLCT	406
	H-3 →L+1	0.21236				MLCT/LLCT	
	H-3 →L+2	0.10453				MLCT/LLCT	
	H-2 →L+1	0.11788				MLCT/ILCT	
	H-2 →L+2	0.32982				MLCT/ILCT	
	H-1 →L+2	0.25499				LLCT	
	H →L+2					LLCT	
3	H-3 →L+5	0.31171	4.0540	0.1060	305.83	MLCT/LLCT/ILCT/LMCT	307
	H-3 →L+9	0.10529				MLCT/LLCT/ILCT	
	H-1 →L+4	0.16964				LLCT	
	H-1 →L+5	0.35149				LLCT/ILCT/LMCT	
	H →L+3	0.20294				LLCT	
	H →L+4	0.17985				LLCT	
	H →L+5	0.16712				LLCT/ILCT/LMCT	
4	H-11 →L+2	0.10963	4.4670	0.0534	277.56	LLCT	271
	H-10 →L+2	0.24403				LLCT	
	H-4 →L+3	0.39297				MLCT/LLCT/ILCT	
	H-4 →L+5	0.18952				MLCT/LLCT/ILCT/LMCT	
	H-2 →L+3	0.31114				MLCT/ILCT	
	H-2 →L+5	0.25729				MLCT/LLCT/LMCT	
	H-1 →L+3	0.15528				LLCT	
5	H-7→L+4	0.10637	4.9812	0.0337	248.90	MLCT/LLCT	227
	H-7→L+5	0.13913				MLCT/LLCT/ILCT/LMCT	
	H-4 →L+6	0.53488				MLCT/LLCT/ILCT	
	H-2 →L+6	0.23400				MLCT/ILCT	
	H-2 →L+8	0.11942				MLCT/LLCT/ILCT/LMCT	

Table S15. Compositions of the molecular orbitals of complex **1e** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	trpy	L-OCH_3	PPh_3
HOMO (H)	4	1	93	2
H-1	6	1	90	3
H-2	74	15	8	3
H-3	27	4	5	64
H-4	51	13	7	29
H-5	1	1	4	94
H-7	16	3	8	73
H-10	1	1	9	89
H-11	1	0	73	26
LUMO (L)	8	2	90	0
L+1	6	92	1	1
L+2	1	98	0	1
L+3	1	97	0	2
L+4	3	95	0	2
L+5	48	8	14	30
L+6	4	91	1	4
L+8	22	10	4	64
L+9	3	2	18	77

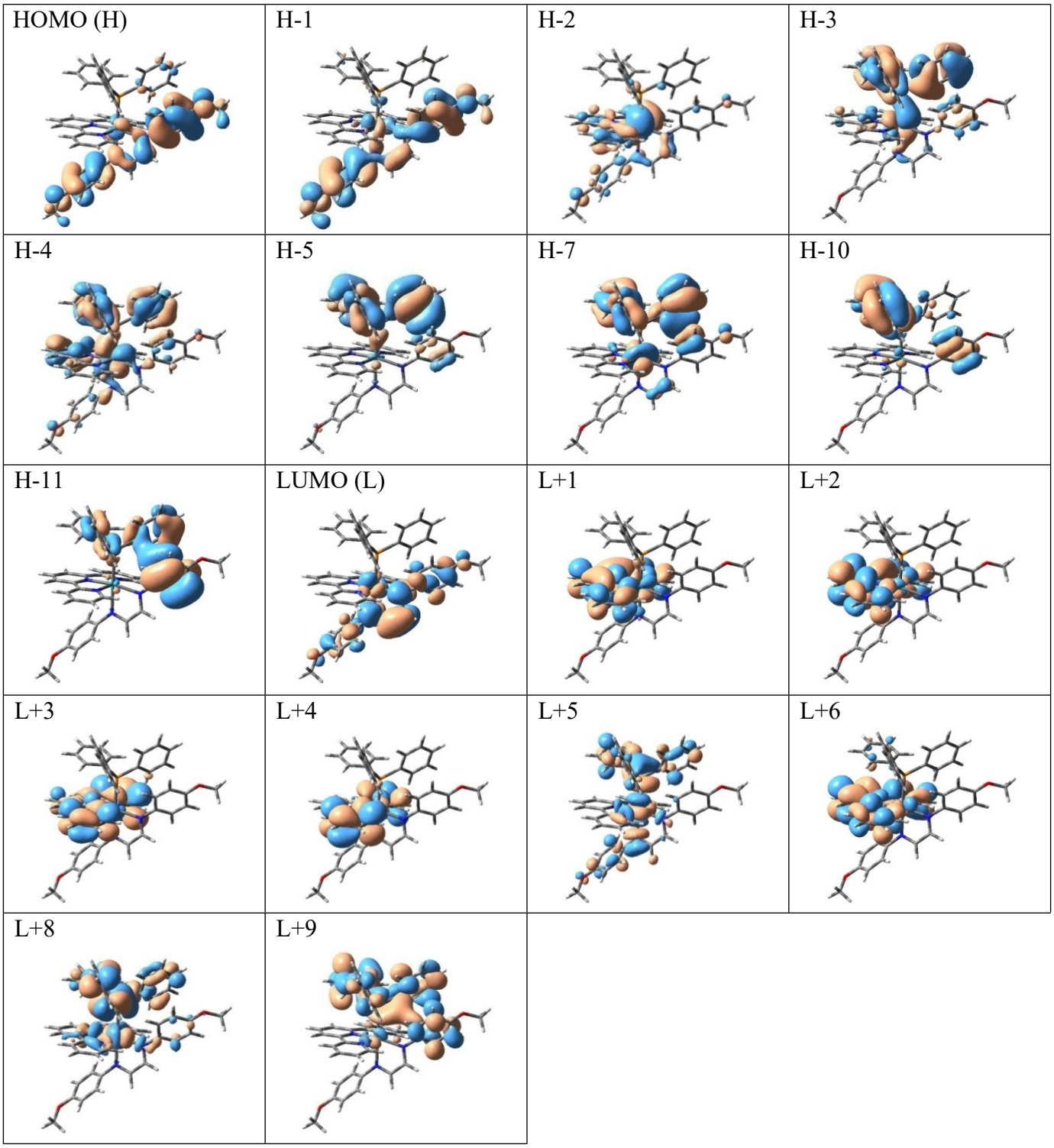


Fig. S10. Contour plots of the molecular orbitals of complex **1e**, which are associated with the electronic spectral transitions (See **Table S14**).

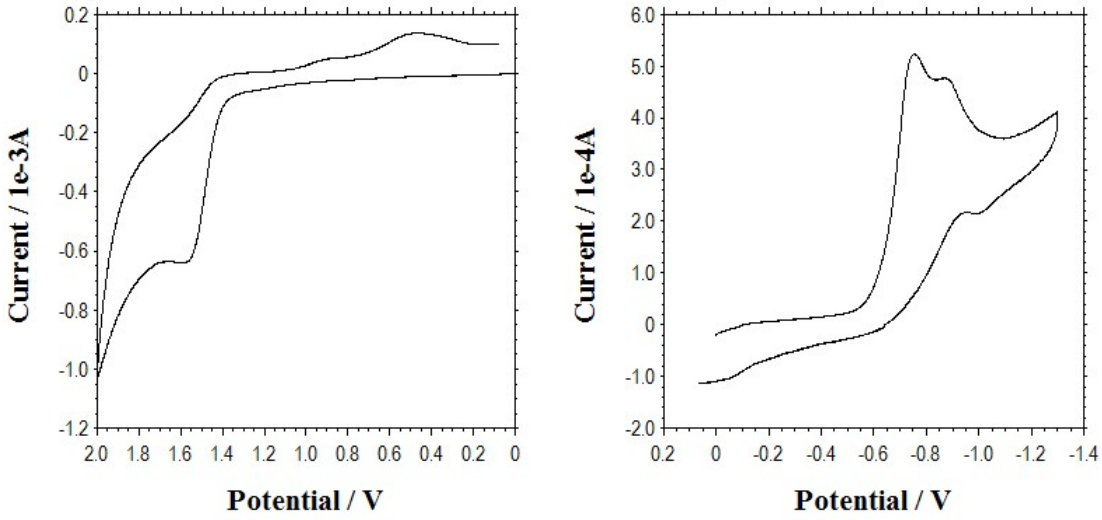
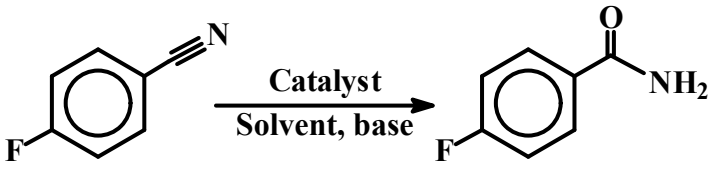


Fig. S11. Cyclic voltammograms of complex **1b** in acetonitrile solution (0.1 M TBHP) at a scan rate of 50 mVs^{-1}.

Table S16. Optimization of experimental parameters for catalytic hydration of nitrile to corresponding amide.[a]



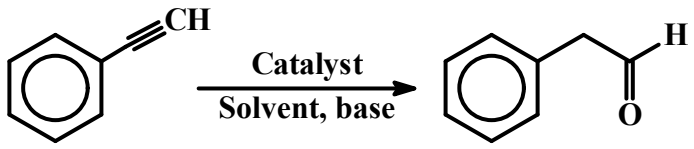
Entry	Catalyst	Mole % of catalyst	Solvent	base	Temp, ºC	Time, h	Yeild[b], %
1	**1a**	1	1:9 water-isopropanol	KO^{t}Bu	85	6	>99
2	**1a**	1	1:9 water-isopropanol	KO^{t}Bu	85	4	94
3	**1a**	0.5	1:9 water-isopropanol	KO^{t}Bu	85	6	70
4	**1a**	0.1	1:9 water-isopropanol	KO^{t}Bu	85	6	30
5	**1a**	1	1:9 water-n-propanol	KO^{t}Bu	85	6	35
6	**1a**	1	1:9 water-isopropanol	-	85	6	20
7	**1a**	1	1:9 water-isopropanol	KOH	85	6	>99
8	**1a**	1	1:9 water-isopropanol	KOH	85	4	>99
9	**1a**	0.5	1:9 water-isopropanol	KOH	85	4	90
10	**1a**	0.1	1:9 water-isopropanol	KOH	85	4	29
11	**1a**	0.5	1:9 water-isopropanol	KOH	rt	4	87
12	**1a**	0.5	1:9 water-isopropanol	KOH	rt[c]	6	98
13	**1a**	0.5	2:8 water-isopropanol	KOH	rt[c]	6	57
14	**1a**	0.5	isopropanol	KOH	rt[c]	6	77
15	**-**	-	1:9 water-isopropanol	KOH	rt	6	-
16	**1**	0.5	1:9 water-isopropanol	KOH	rt[c]	6	31

[a] Experimental condition: Substrate 4-Fluro Benzonitrile(0.5 mmol), Catalyst $[Ru(trpy)(L\text{-}OCH_3)(H_2O)](ClO_4)_2$, solvent (5 mL), Base (1 mol%)

[b] Conversion was determined by GC analysis.

[c] Room tempareture stirring.

Table S17. Optimization of experimental parameters for catalytic hydration of alkyne to corresponding aldehyde.[a]



Entry	Catalyst	Mole % of catalyst	Solvent	Base	Temp, ºC	Time, h	Yeild[b], %
1	**1a**	1	1:9 acetone-water	-	70	6	-
2	**1a**	1	1:9 acetone-water	-	85	6	19
3	**1a**	1	1:9 acetone-water	KOH	85	6	40
4	**1a**	1	1:9 water-n-propanol	KOH	85	6	25
5	**1a**	1	1:9 water-isopropanol	KOH	85	6	98
6	**1a**	1	1:9 water-isopropanol	KOH	rt[c]	6	71
7	**1a**	1	1:9 water-isopropanol	KOH	rt[c]	10	96
8	**1a**	1	1:9 water-isopropanol	KO^{t}Bu	rt	10	87
9	**-**	1	1:9 water-isopropanol	KOH	rt[c]	10	-
10	**1a**	1	isopropanol	KOH	rt[c]	10	53
11	**1a**	0.5	1:9 water-isopropanol	KOH	rt	10	41
12	**1a**	1.5	1:9 water-isopropanol	KOH	rt	6	95
13	**1**	1	1:9 water-isopropanol	KOH	rt[c]	10	61

[a] Reaction conditions: Catalyst $[Ru(trpy)(L\text{-}OCH_3)(H_2O)](ClO_4)_2$; Substrate Phenylacetylene (0.5 mmol), solvent (5.0 mL), Base (1 mol%).
[b] Determined by GCMS.
[c] Room tempareture stirring

Table S18. Crystallographic data for complexes **1a**, **1b** and **1d.**

complex	**1a**	**1b**	**1d**
empirical formula	$C_{33}H_{37}Cl_2N_5O_{13}Ru$	$C_{136}H_{126}Cl_8N_{26}O_{39}Ru_4$	$C_{37}Cl_2H_{40}N_6O_{13}Ru$
formula weight	883.64	3436.50	948.72
crystal system	Triclinic	Monoclinic	Orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$Pna2_1$
a (Å)	11.3948(10)	15.965(3)	30.054(3)
b (Å)	12.4038(10)	39.938(7)	11.0969(10)
c (Å)	14.2466(12)	12.631(2)	25.405(2)
α (◦)	83.522(3)	90	90
β (◦)	69.862(2)	107.142(4)	90
γ (◦)	82.487(3)	90	90
V (Å^3)	1869.3(3)	7696(2)	8472.6(13)
Z	2	2	8
D_{calcd} /mg m^{-3}	1.570	1.483	1.488
F (000)	904.0	3496.0	3888.0
crystal size (mm)	0.12 × 0.17 × 0.22	0.24 × 0.28 × 0.30	0.15 × 0.17 × 0.20
T (K)	273	273	273
μ (mm^{-1})	0.633	0.608	0.565
R1[a]	0.0328	0.1065	0.0612
wR2[b]	0.0886	0.2880	0.1491
GOF[c]	1.093	1.161	1.058

[a] $R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \Sigma \, |F_o|$.

[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.

[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.