

Citation

Akabar, N. and Chaturvedi, V. and Shillito, G.E. and Schwehr, B.J. and Gordon, K.C. and Huff, G.S. and Sutton, J.J. et al. 2019. Photophysical and biological investigation of phenol substituted rhenium tetrazolato complexes. Dalton Transactions. 48 (41): pp. 15613-15624. <http://doi.org/10.1039/c9dt02198a>

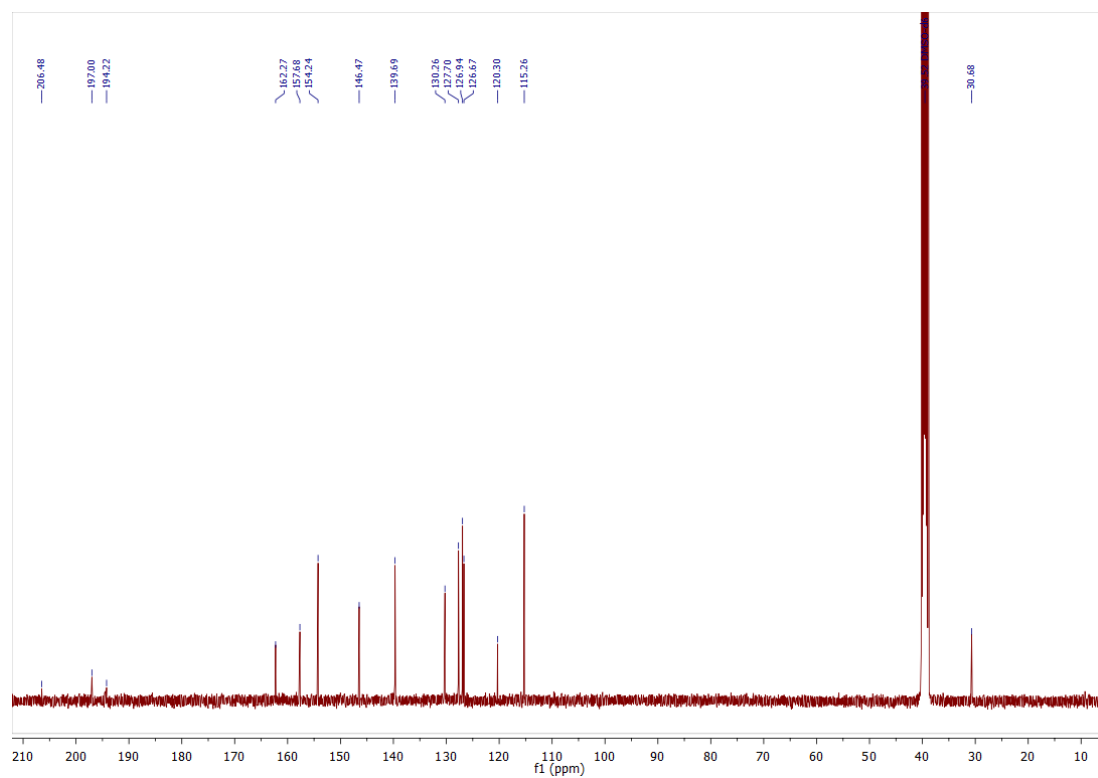
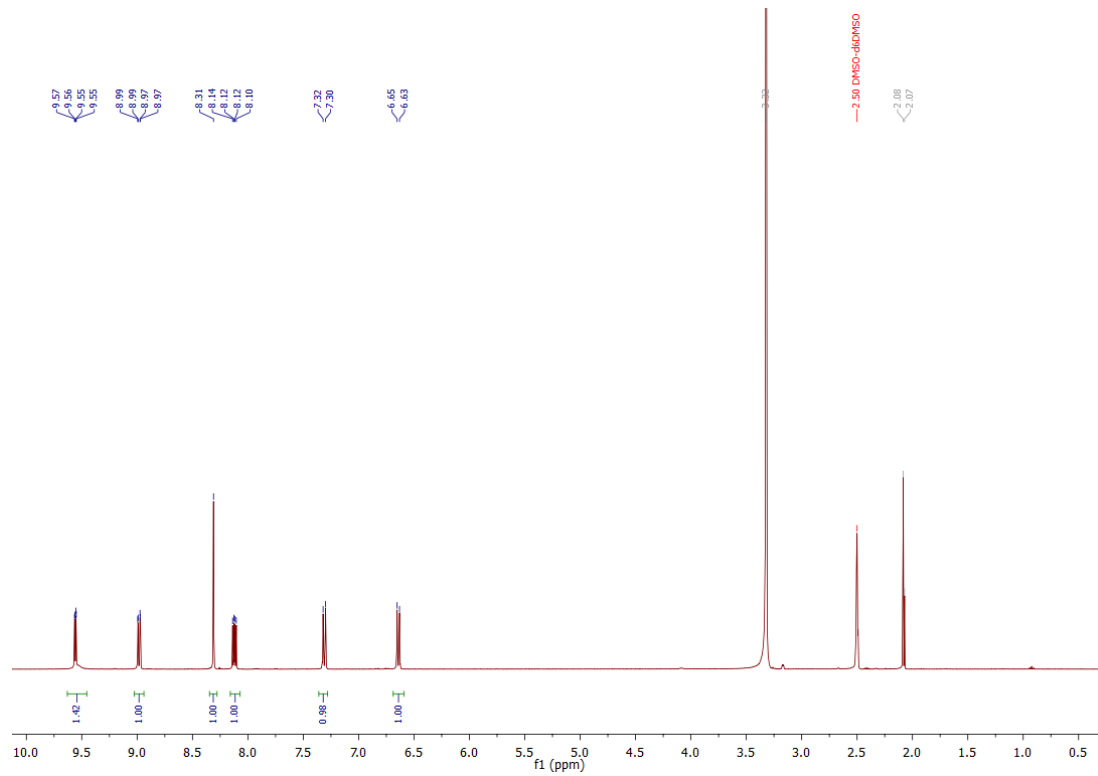
Photophysical and Biological Investigation of Phenol and Methoxy Substituted Rhenium Tetrazolato Complexes

Nurshadrina Akabar,^a Vishal Chaturvedi,^b Georgina E. Shillito,^c Bradley J. Schwehr,^a Keith C. Gordon,^c Gregory S. Huff,^c Joshua J. Sutton,^c Brian W. Skelton,^d Alexandre N. Sobolev,^d Stefano Stagni,^e Delia J. Nelson,^b and Massimiliano Massi^{a,*}

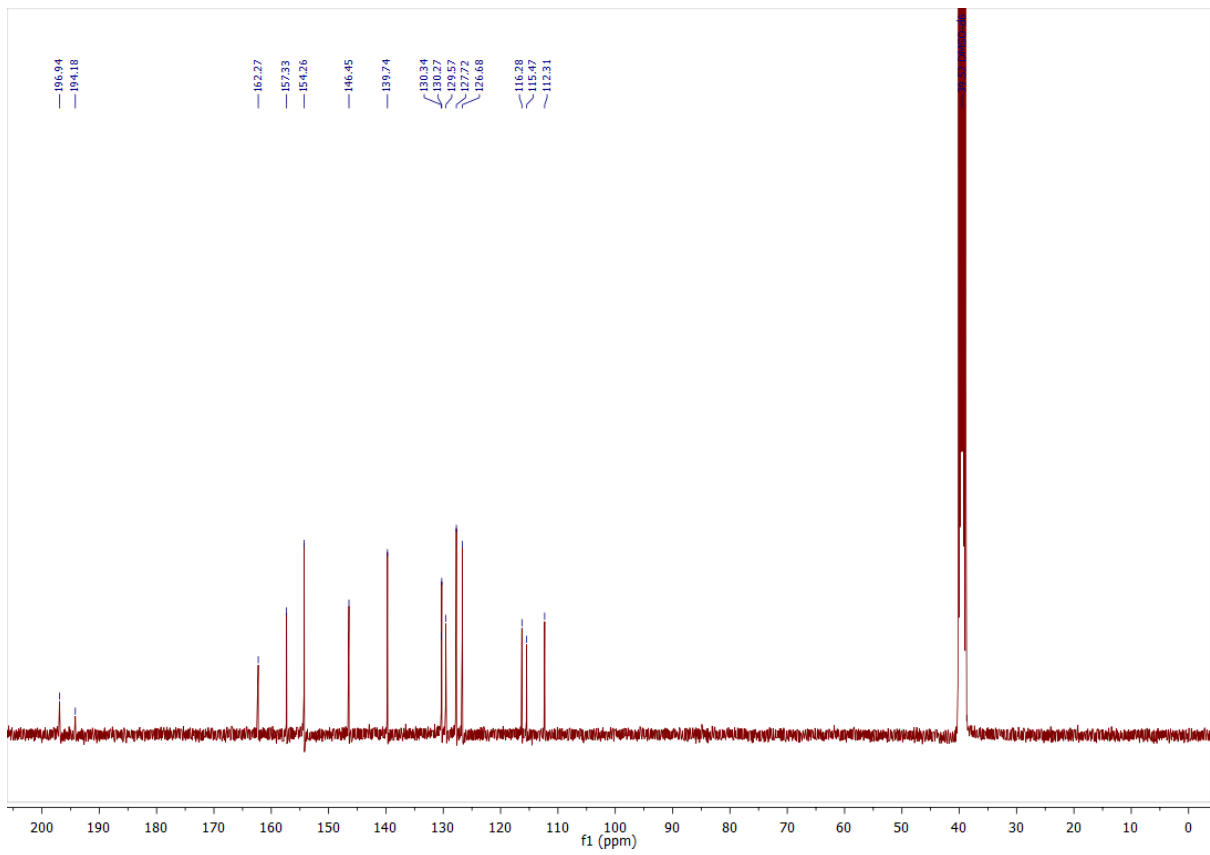
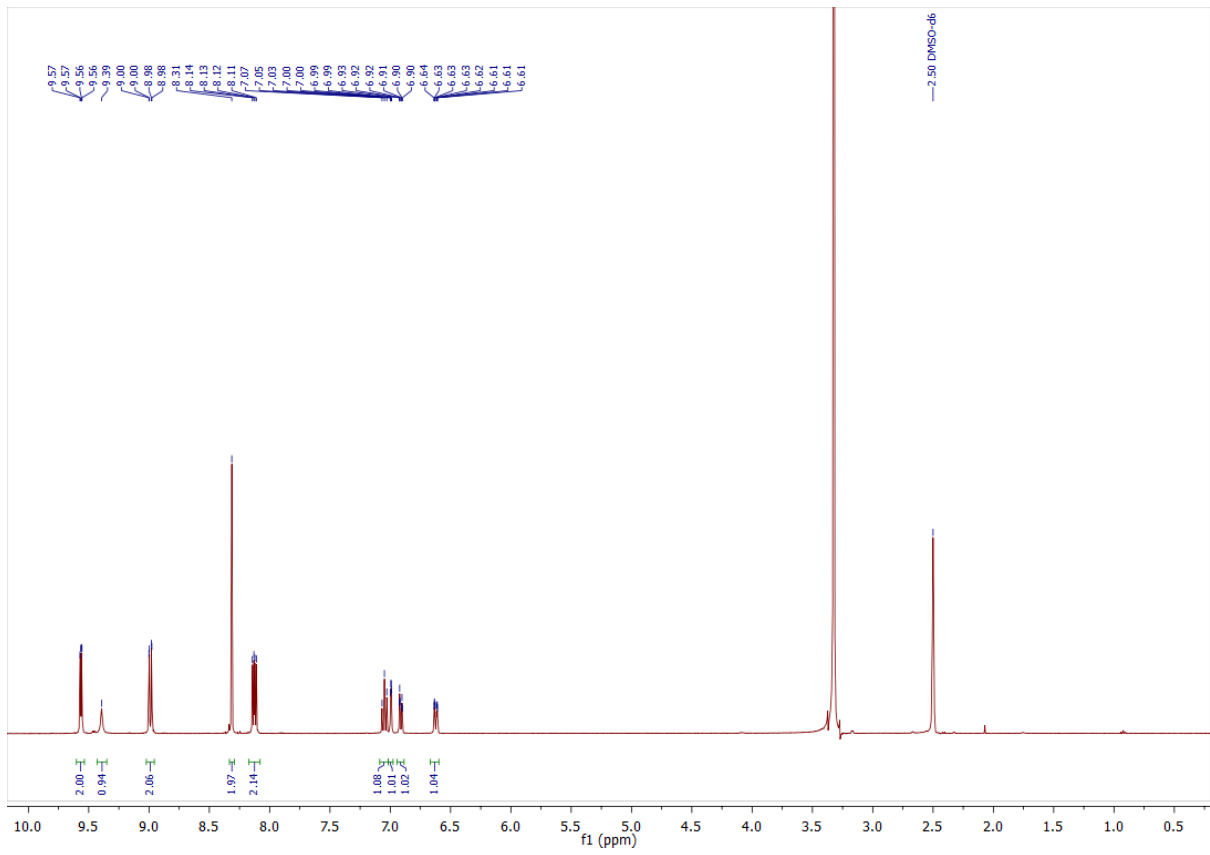
Supplementary Information

^1H and ^{13}C NMR spectra

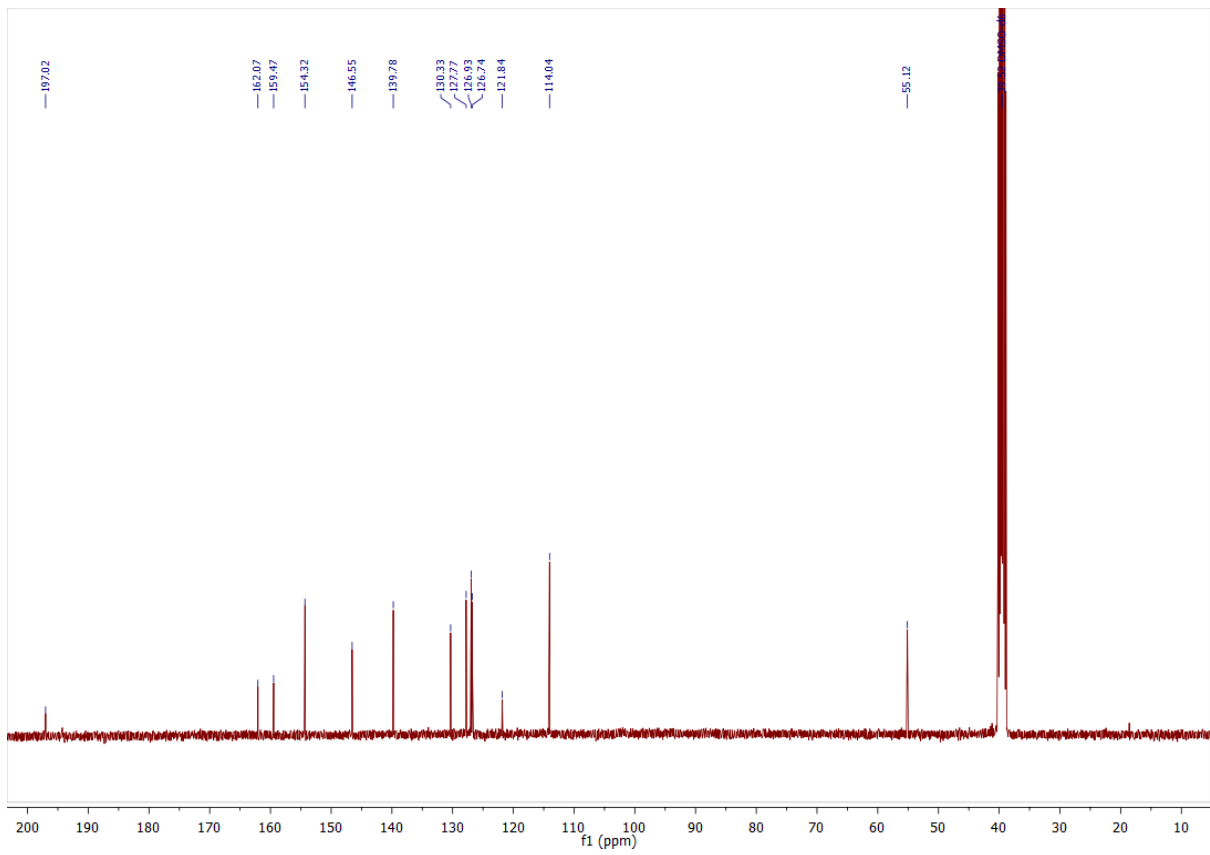
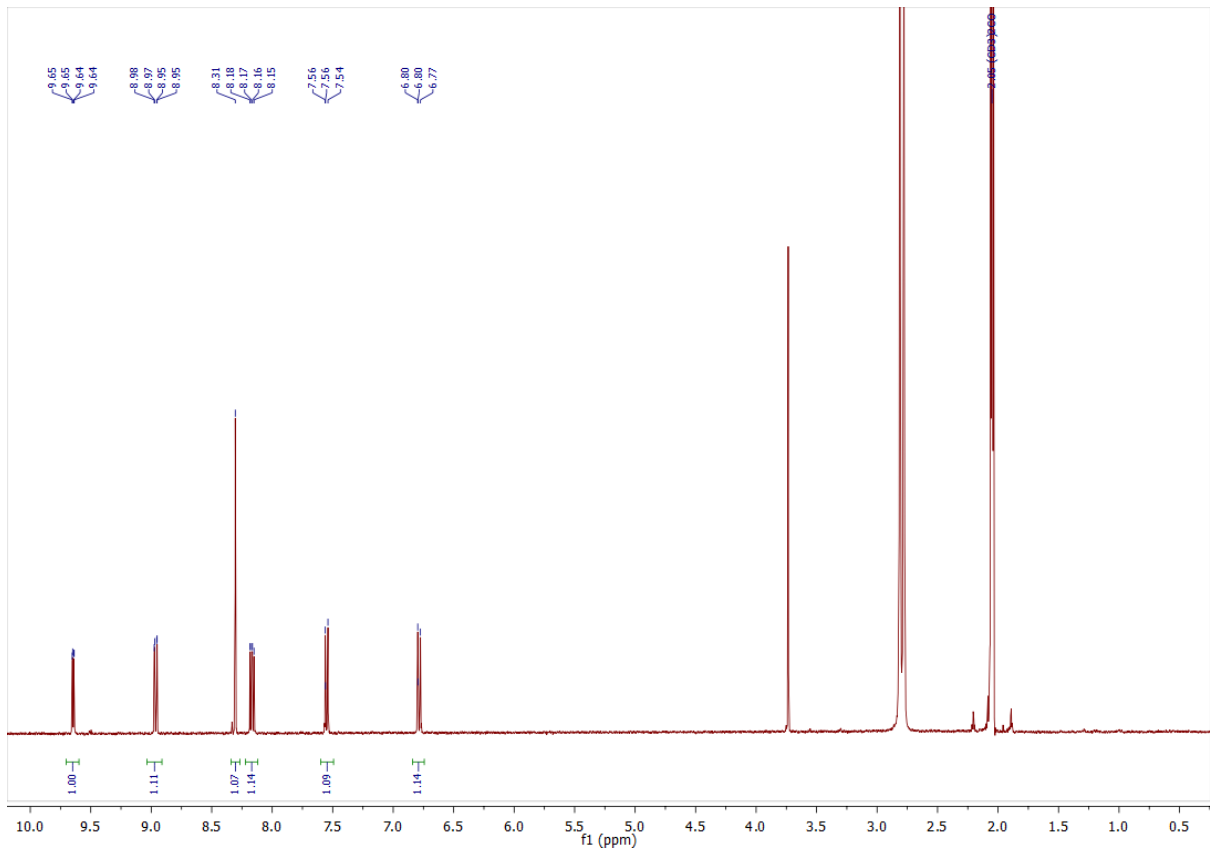
Re4OH



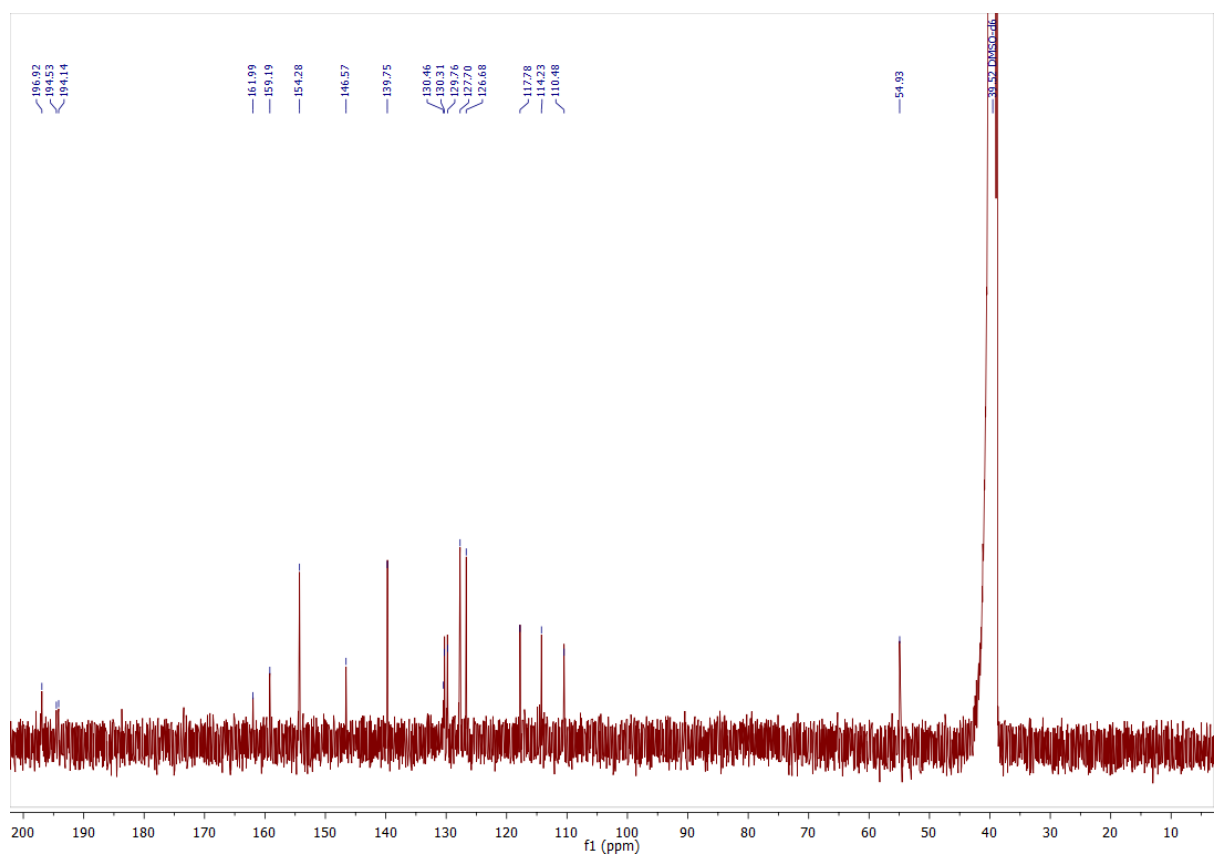
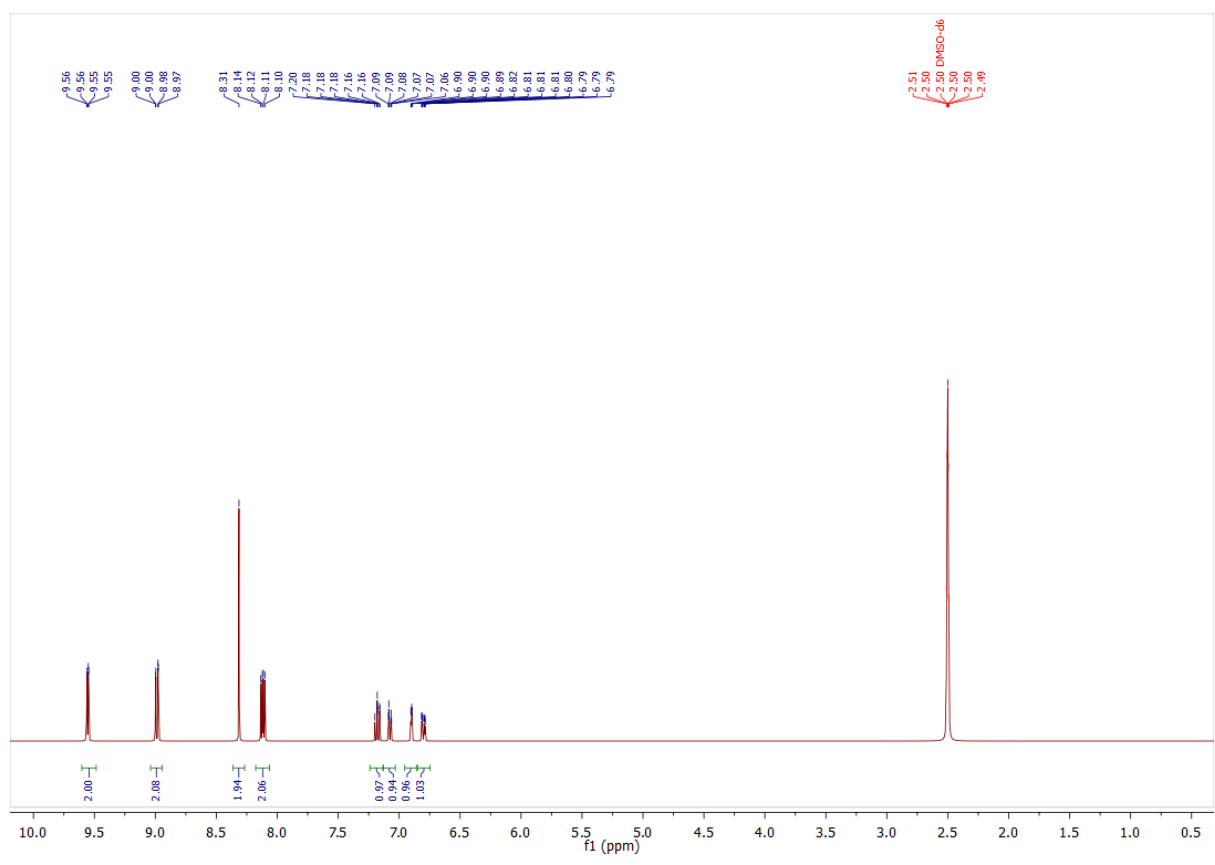
Re3OH



Re4OMe



Re3OMe



Bond lengths and angles

Table S1. Selected bond lengths [Å] and angles (°) for complex **Re4OH**.

Re(1)-C(103)	1.938(6)
Re(1)-C(102)	1.921(6)
Re(1)-C(101)	1.931(6)
Re(1)-N(11)	2.162(4)
Re(1)-N(2)	2.169(4)
Re(1)-N(21)	2.181(4)
C(103)-Re(1)-C(102)	88.8(2)
C(103)-Re(1)-C(101)	90.7(2)
C(102)-Re(1)-C(101)	90.3(2)
C(103)-Re(1)-N(11)	94.77(19)
C(102)-Re(1)-N(11)	173.06(18)
C(101)-Re(1)-N(11)	95.65(18)
C(103)-Re(1)-N(2)	177.10(19)
C(102)-Re(1)-N(2)	92.43(19)
C(101)-Re(1)-N(2)	91.9(2)
N(11)-Re(1)-N(2)	83.78(14)
C(103)-Re(1)-N(21)	95.09(18)
C(102)-Re(1)-N(21)	97.83(19)
C(101)-Re(1)-N(21)	170.13(19)
N(11)-Re(1)-N(21)	75.93(14)
N(2)-Re(1)-N(21)	82.13(14)

Table S2. Selected bond lengths [Å] and angles (°) for complex **Re3OH**.

Re(1)-C(3)	1.924(3)
Re(1)-C(2)	1.924(3)
Re(1)-C(1)	1.926(3)
Re(1)-N(11)	2.171(2)
Re(1)-N(2)	2.174(2)
Re(1)-N(21)	2.177(2)
C(3)-Re(1)-C(2)	88.47(11)
C(3)-Re(1)-C(1)	88.54(12)
C(2)-Re(1)-C(1)	88.77(12)
C(3)-Re(1)-N(11)	97.49(10)
C(2)-Re(1)-N(11)	95.48(10)
C(1)-Re(1)-N(11)	172.70(10)
C(3)-Re(1)-N(2)	92.94(10)
C(2)-Re(1)-N(2)	174.93(10)
C(1)-Re(1)-N(2)	96.13(11)
N(11)-Re(1)-N(2)	79.51(8)
C(3)-Re(1)-N(21)	173.14(10)
C(2)-Re(1)-N(21)	93.89(9)
C(1)-Re(1)-N(21)	97.94(10)
N(11)-Re(1)-N(21)	75.89(8)
N(2)-Re(1)-N(21)	84.17(8)

Table S3. Hydrogen bonds for complex **Re3OH** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
---------	--------	----------	----------	--------

O(53)- H(53)...N(3) ¹	0.886(18)	2.004(18)	2.888(3)	176(3)
-------------------------------------	-----------	-----------	----------	--------

Symmetry transformations used to generate equivalent atoms: ¹ 2-x,1-y,-z

Table S4. Selected bond lengths [Å] and angles (°) for complex **Re4OMe**.

Re(1)-C(3)	1.9215(14)
Re(1)-C(2)	1.9238(15)
Re(1)-C(1)	1.9237(14)
Re(1)-N(2)	2.1645(12)
Re(1)-N(21)	2.1752(12)
Re(1)-N(11)	2.1813(11)
C(3)-Re(1)-C(2)	87.25(6)
C(3)-Re(1)-C(1)	88.28(6)
C(2)-Re(1)-C(1)	89.02(6)
C(3)-Re(1)-N(2)	91.46(5)
C(2)-Re(1)-N(2)	177.98(5)
C(1)-Re(1)-N(2)	89.40(5)
C(3)-Re(1)-N(21)	171.62(6)
C(2)-Re(1)-N(21)	98.24(5)
C(1)-Re(1)-N(21)	98.10(5)
N(2)-Re(1)-N(21)	83.22(4)
C(3)-Re(1)-N(11)	97.36(5)
C(2)-Re(1)-N(11)	97.99(5)
C(1)-Re(1)-N(11)	171.18(5)
N(2)-Re(1)-N(11)	83.70(4)
N(21)-Re(1)-N(11)	75.68(4)
N(2)-N(1)-C(5)	103.46(11)
N(3)-N(2)-N(1)	111.07(11)
N(3)-N(2)-Re(1)	122.35(8)
N(1)-N(2)-Re(1)	126.07(9)

Table S5. Selected bond lengths [Å] and angles (°) for complex **Re3OMe**.

Re(1)-C(3)	1.929(4)
Re(1)-C(2)	1.918(4)
Re(1)-C(1)	1.922(4)
Re(1)-N(21)	2.165(3)
Re(1)-N(2)	2.171(3)
Re(1)-N(11)	2.187(3)
C(2)-Re(1)-C(1)	89.50(14)
C(2)-Re(1)-C(3)	86.97(15)
C(1)-Re(1)-C(3)	89.39(14)
C(2)-Re(1)-N(21)	98.24(13)
C(1)-Re(1)-N(21)	96.41(12)
C(3)-Re(1)-N(21)	172.21(13)
C(2)-Re(1)-N(2)	178.32(13)
C(1)-Re(1)-N(2)	90.43(12)
C(3)-Re(1)-N(2)	91.35(13)
N(21)-Re(1)-N(2)	83.43(10)
C(2)-Re(1)-N(11)	96.27(12)
C(1)-Re(1)-N(11)	170.90(12)
C(3)-Re(1)-N(11)	97.92(12)
N(21)-Re(1)-N(11)	75.83(10)
N(2)-Re(1)-N(11)	84.01(10)

Table S6: TDDFT calculations (B3LYP/LANL2DZ 6-31G(d), MeCN solvent field) for the lowest singlet states with $f > 0.01$ in the four identified configurations of **Re3OH** and **Re3OMe**. MO contribution of $< 15\%$ are not tabulated.

	Re3OH							
	State	λ / nm	f	MO contribution (%)	Mulliken analysis			
					Re(CO) ₃	phen	tetrazole	phenyl
Config #1	4	365	0.081	H-2→L (83)	-68	77	-4	-4
	5	355	0.011	H-4→L (86)	-85	90	-1	-5
	6	348	0.043	H-1→L+1 (71)	-41	96	-10	-44
	7	337	0.018	H-3→L (16) H-2→L+1 (76)	-65	79	-6	-8
Config #2	1	420	0.025	H→L (92)	-6	93	-21	-65
	4	375	0.033	H-1→L (74)	-30	89	-9	-49
	6	348	0.010	H-1→L+1 (74)	-38	94	-10	-47
	8	335	0.068	H-3→L (68) H-2→L+1 (21)	-47	83	-8	-29
Config #3	4	363	0.062	H-2→L (78)	-70	77	-1	-6
	6	350	0.046	H-2→L (15) H-1→L+1 (67)	-45	93	-6	-42
	8	334	0.024	H-2→L+1 (91)	-73	75	-1	0
Config #4	1	420	0.025	H→L (92)	-6	93	-21	-65
	4	375	0.033	H-1→L (74)	-30	89	-9	-49
	6	348	0.010	H-1→L+1 (74)	-38	94	-10	-47
	8	335	0.068	H-3→L (68) H-2→L+1 (21)	-47	83	-8	-29

	Re3OMe							
	State	λ / nm	f	MO contribution (%)	Mulliken analysis			
					Re(CO) ₃	phen	tetrazole	phenyl
Config #1	4	366	0.074	H-2→L (82)	-68	78	-4	-6
	6	351	0.059	H-4→L (18) H-1→L+1 (57)	-53	93	-9	-32
	7	337	0.018	H-2→L+1 (78)	-65	79	-6	-8
Config #2	1	426	0.020	H→L (92)	-4	93	-19	-69
	3	382	0.011	H-2→L (77) H-1→L (20)	-72	87	-4	-11
	4	378	0.032	H-2→L (22) H-1→L (64)	-39	89	-10	-39
	6	350	0.010	H-1→L+1 (86)	-34	95	-12	-48
	8	335	0.068	H-3→L (68) H-2→L+1 (20)	-47	83	-8	-29
Config #3	4	363	0.051	H-2→L (72)	-66	79	-3	-10
	6	352	0.061	H-4→L (34) H-2→L (24) H-1→L+1 (39)	-64	89	-4	-21
	8	334	0.023	H-2→L+1 (91)	-73	74	-1	0
Config #4	1	426	0.020	H→L (92)	-4	93	-19	-69
	3	382	0.011	H-2→L (77) H-1→L (20)	-72	87	-4	-11
	4	378	0.032	H-2→L (22) H-1→L (64)	-39	89	-10	-39
	6	350	0.010	H-1→L+1 (86)	-34	95	-12	-48
	8	335	0.068	H-3→L (68)	-47	83	-8	-29

				H-2→L+1 (20)				
--	--	--	--	--------------	--	--	--	--

Table S7: TDDFT calculations (B3LYP/LANL2DZ 6-31G(d), MeCN solvent field) for the lowest singlet states with $f > 0.01$ in the four identified configurations of **Re4OH** and **Re4OMe**. MO contribution of $< 15\%$ are not tabulated.

	Re4OH							
	State	λ / nm	f	MO contribution (%)	Mulliken analysis			
					Re(CO) ₃	phen	tetrazole	phenyl
Config #1	4	367	0.074	H-2→L (86)	-72	77	-4	-1
	6	346	0.066	H-2→L (10) H-1→L+1 (80)	-73	92	-7	-12
	7	337	0.022	H-2→L+1 (93)	-72	77	-5	0
Config #2	1	455	0.012	H→L (98)	-2	93	-27	-64
	4	369	0.064	H-2→L (20) H-1→L (70)	-70	83	-4	-8
	6	344	0.045	H-2→L+1 (54) H-1→L+1 (37)	-77	87	-4	-6
	7	340	0.019	H-2→L+1 (38) H-1→L+1 (56)	-76	88	-5	-7
Config #3	4	363	0.060	H-2→L (81)	-75	76	0	-1
	5	355	0.010	H-3→L (87)	-89	90	0	-1
	6	344	0.051	H-1→L+1 (83)	-72	93	-5	-16
Config #4	1	455	0.012	H→L (98)	-2	93	-27	-64
	4	369	0.064	H-2→L (20) H-1→L (70)	-70	83	-4	-8
	6	344	0.045	H-2→L+1 (54) H-1→L+1 (37)	-77	87	-4	-6
	7	340	0.019	H-2→L+1 (38) H-1→L+1 (56)	-76	88	-5	-7

	Re4OMe							
	State	λ / nm	f	MO contribution (%)	Mulliken analysis			
					Re(CO) ₃	phen	tetrazole	phenyl
Config #1	4	367	0.072	H-2→L (85)	-72	77	-4	-1
	6	347	0.072	H-1→L+1 (77)	-74	91	-7	-10
	7	337	0.022	H-2→L+1 (93)	-72	77	-5	0
Config #2	1	459	0.010	H→L (98)	-1	94	-25	-67
	4	370	0.066	H-2→L (17) H-1→L (74)	-68	82	-5	-9
	6	344	0.042	H-2→L+1 (52) H-1→L+1 (40)	-77	87	-5	-6
Config #3	2	425	0.001	H→L+1 (98)	-9	98	-27	-63
	4	363	0.057	H-2→L (80)	-74	77	0	-2
	6	346	0.055	H-2→L (14) H-1→L+1 (80)	-72	91	-5	-15
	7	334	0.023	H-2→L+1 (92)	-73	74	-1	0
Config #4	1	459	0.010	H→L (98)	-1	94	-25	-67
	4	370	0.066	H-2→L (17) H-1→L (74)	-68	82	-5	-9
	6	344	0.042	H-2→L+1 (52)	-77	87	-5	-6

				H-1→L+1 (40)				
--	--	--	--	--------------	--	--	--	--

Table S8: TDDFT calculations (B3LYP/LANL2DZ 6-31G(d), MeCN solvent field) for the lowest singlet states with $f > 0.01$ in the four identified configurations of the deprotonated phenol complexes (**Re3O⁻** and **Re4O⁻**). MO contribution of $< 15\%$ are not tabulated.

	Re3O⁻							
	State	λ / nm	f	MO contribution (%)	Mulliken analysis			
					Re(CO) ₃	phen	tetrazole	phenyl
Config #1	11	370	0.070	H-4→L (85)	-71	79	-7	-2
	16	351	0.073	H-5→L (17) H-3→L+1 (66)	-75	92	-7	-10
	17	344	0.063	H→L+7 (95)	7	4	36	-46
	18	341	0.022	H-4→L+1 (94)	-74	83	-8	0
Config #2	11	374	0.065	H-4→L (22) H-3→L (70)	-68	84	-6	-10
	15	349	0.024	H→L+6 (93)	36	4	34	-75
	18	344	0.021	H-4→L+1 (59) H-3→L+1 (35)	-79	90	-5	-6
	19	339	0.025	H→L+7 (74) H→L+8 (22)	71	6	13	-90
	20	331	0.030	H→L+7 (21) H→L+8 (74)	38	3	28	-70
Config #3	12	365	0.053	H-4→L (79) H-3→L+1 (13)	-73	78	-1	-3
	16	349	0.044	H-4→L (17) H-3→L+1 (71)	-71	91	-5	-15
	17	345	0.066	H→L+6 (77) H→L+7 (19)	60	3	14	-77
	18	336	0.023	H-4→L+1 (92)	-75	77	-2	0
	19	331	0.035	H→L+6 (16) H→L+7 (65) H→L+8 (17)	34	3	28	-64
Config #4	11	374	0.065	H-4→L (22) H-3→L (70)	-68	84	-6	-10
	15	349	0.024	H→L+6 (93)	36	4	34	-75
	16	348	0.034	H-4→L+1 (33) H-3→L+1 (59)	-73	89	-7	-10
	18	344	0.021	H-4→L+1 (59) H-3→L+1 (35)	-79	90	-5	-6
	19	339	0.025	H→L+7 (74) H→L+8 (22)	71	6	13	-90

	Re4O ⁻							
	State	λ / nm	f	MO contribution (%)	Mulliken analysis			
					Re(CO) ₃	phen	tetrazole	phenyl
Config #1	5	479	0.030	H→L+3 (98)	88	5	-7	-87
	11	371	0.022	H→L+5 (91)	3	90	-12	-81
	12	368	0.085	H-4→L (64) H-3→L+1 (15)	-59	85	-11	-14
	13	357	0.029	H-5→L (91)	-89	90	0	0
	15	344	0.021	H-4→L+1 (94)	-71	82	-11	0
Config #2	7	417	0.019	H→L+4 (99)	87	8	-8	-87
	8	400	0.056	H-3→L (86)	-45	89	-21	-21
	12	368	0.014	H-3→L+1 (86)	-47	94	-22	-24
	15	349	0.015	H-4→L+1 (92)	-84	92	-6	-2
	16	343	0.015	H→L+6 (82) H→L+7 (17)	81	6	-2	-86
	18	336	0.049	H→L+6 (18) H→L+7 (79)	61	4	16	-82
	20	328	0.018	H-6→L (39) H-5→L+1 (56)	-60	87	-15	-12
21	327	0.031	H-6→L (50) H-5→L+1 (44)	-51	84	-19	-15	
Config #3	6	475	0.043	H→L+3 (99)	87	7	-8	-86
	12	363	0.076	H-5→L (15) H-4→L (71)	-71	80	-2	-7
	14	355	0.030	H-5→L (83)	-87	90	-2	0
	16	338	0.029	H-4→L+1 (16) H→L+6 (81)	62	17	-8	-71
	17	338	0.030	H-4→L+1 (77) H→L+6 (17)	-49	67	-3	-16
Config #4	7	418	0.022	H→L+4 (99)	86	7	-8	-87
	8	399	0.064	H-3→L (87)	-43	88	-22	-23
	12	368	0.014	H-3→L+1 (85)	-47	94	-22	-25
	15	350	0.018	H-4→L+1 (92)	-83	92	-7	-2
	16	341	0.017	H→L+6 (54) H→L+7 (45)	73	5	6	-84
	18	339	0.039	H-1→L+2 (15) H→L+6 (38) H→L+7 (45)	60	18	8	-86

Configuration #1

Configuration #2

Configuration #3

Configuration #4

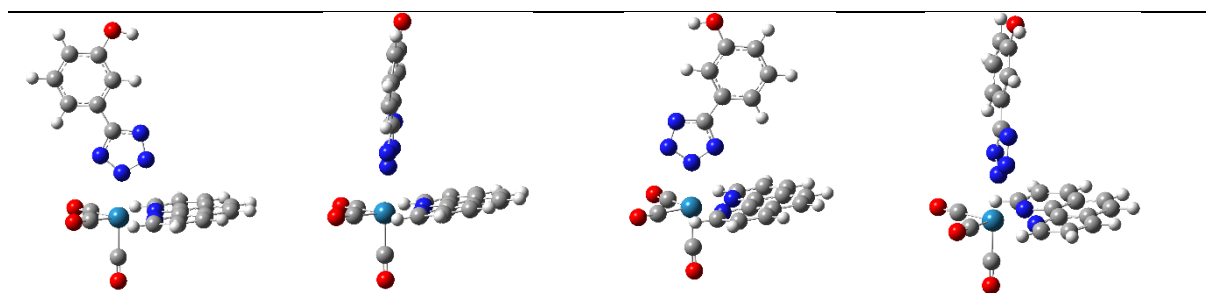
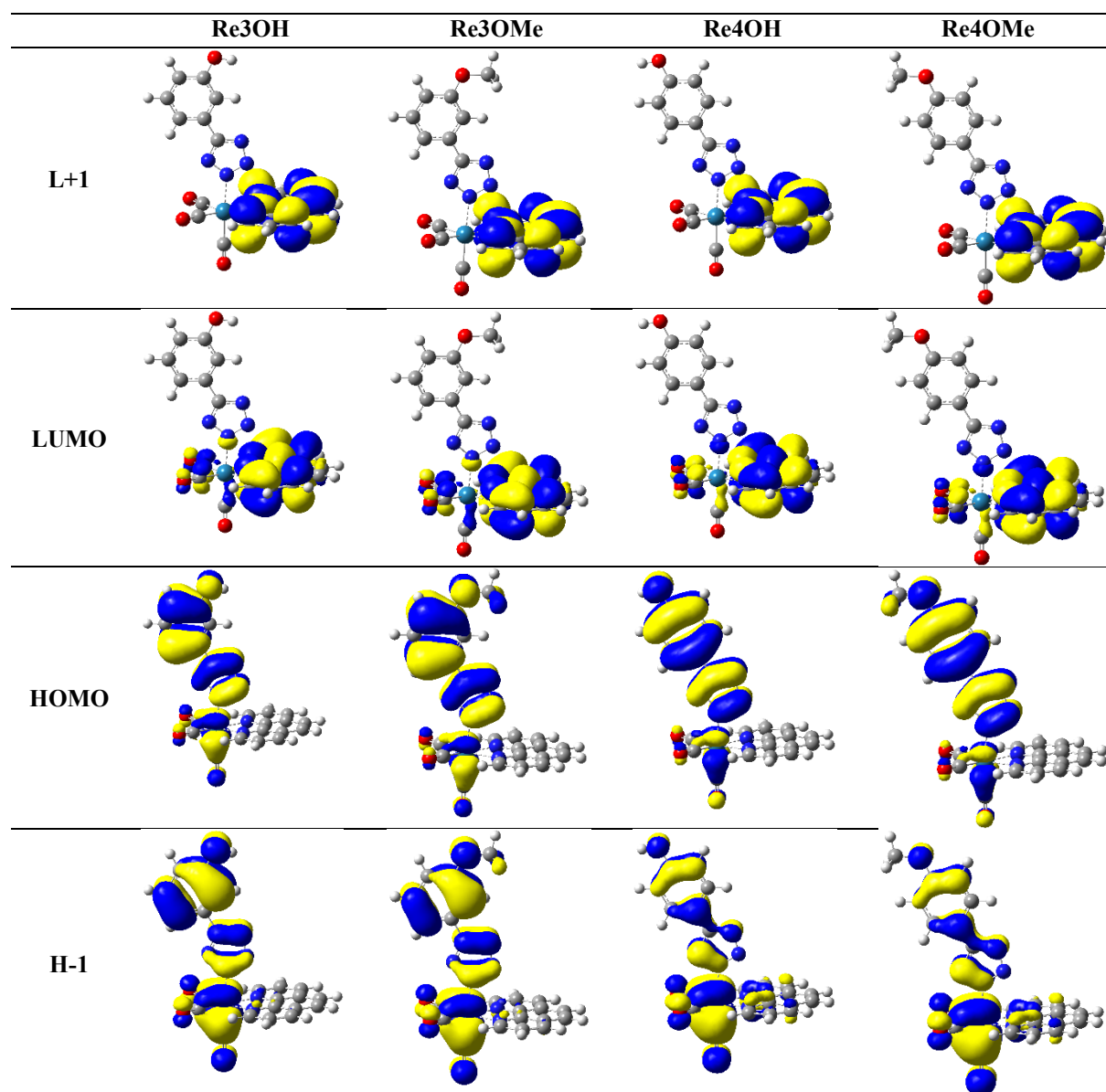


Figure S1: Illustration of the different structural configurations of the complexes in regard to the orientation of the tetrazole ligand.



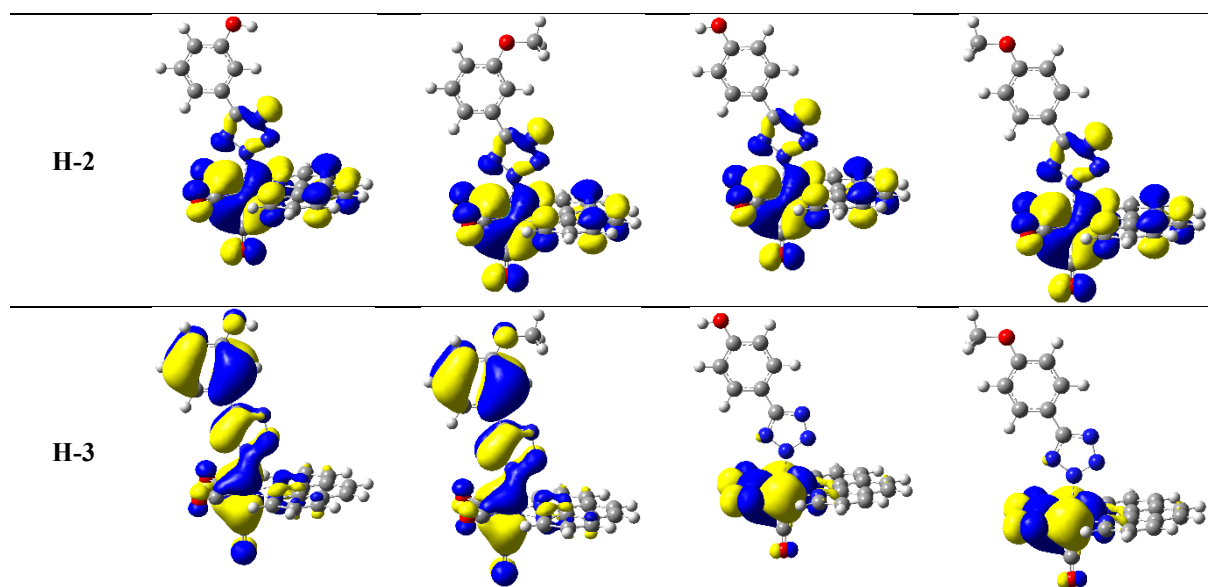


Figure S2: TDDFT predicted frontier molecular orbitals of the complexes. The structures shown correspond to configuration 1.

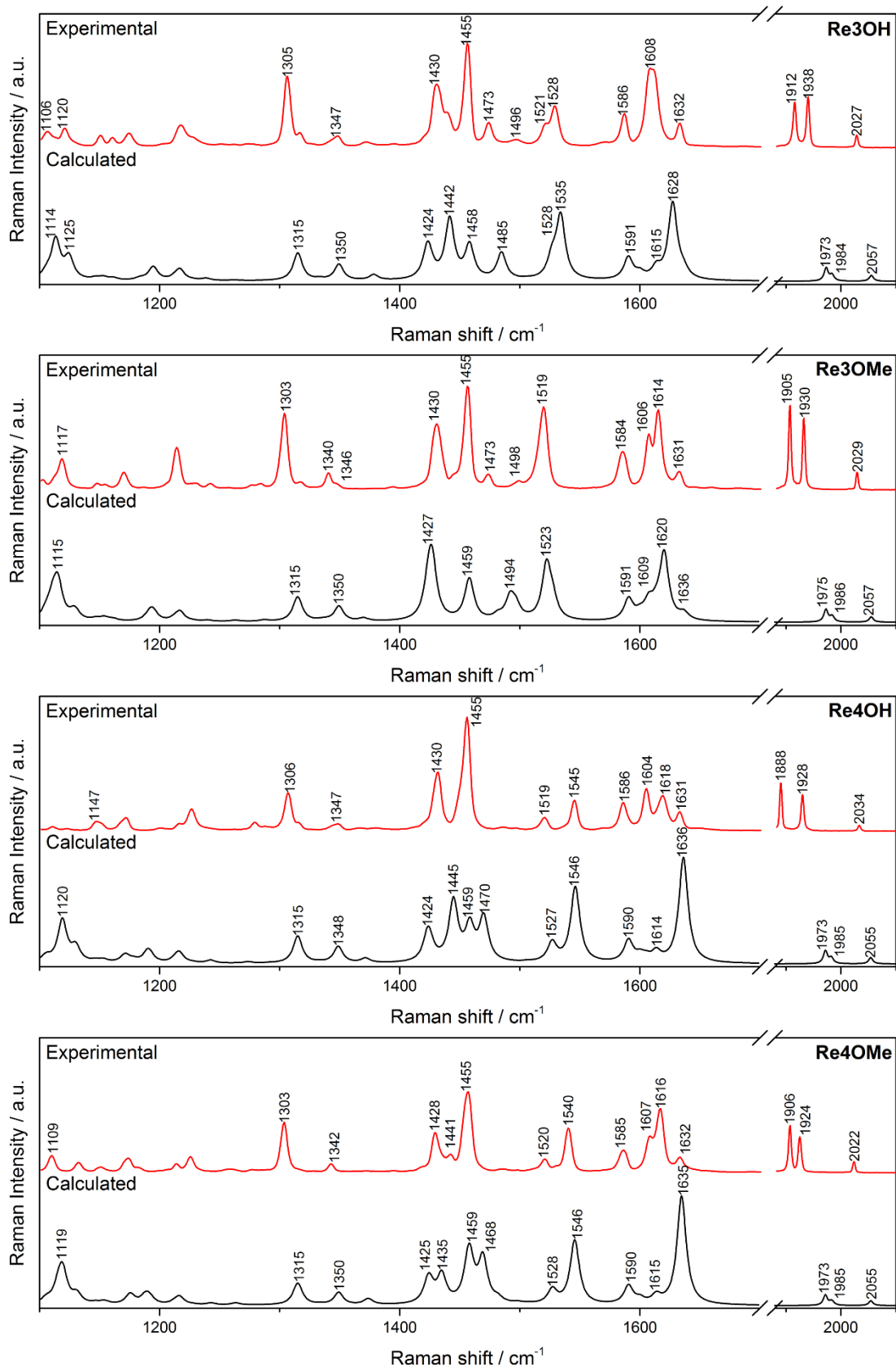


Figure S3: Comparison between the experimental (FT-Raman, solid sample, 1064 nm) and DFT predicted spectra. The DFT calculations were performed in vacuo and the presented spectra are an average of the spectra of the four configurations.

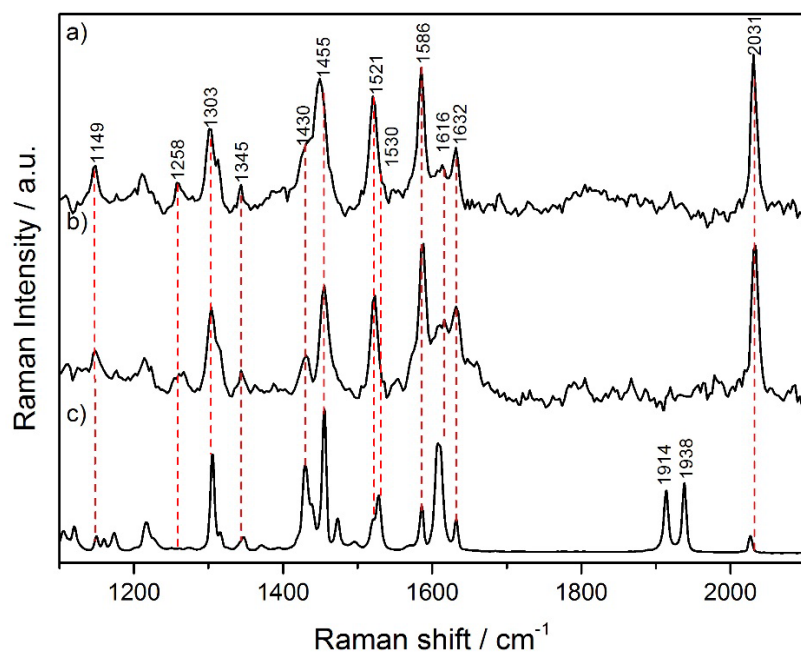


Figure S4: Raman spectra of **Re3OH**. 351 nm resonance spectra are shown in methanol (a) and methanol with 1 equivalent of KO^tBu (b). Panel c) shows the non-resonant 1064 nm spectrum from a solid state sample.

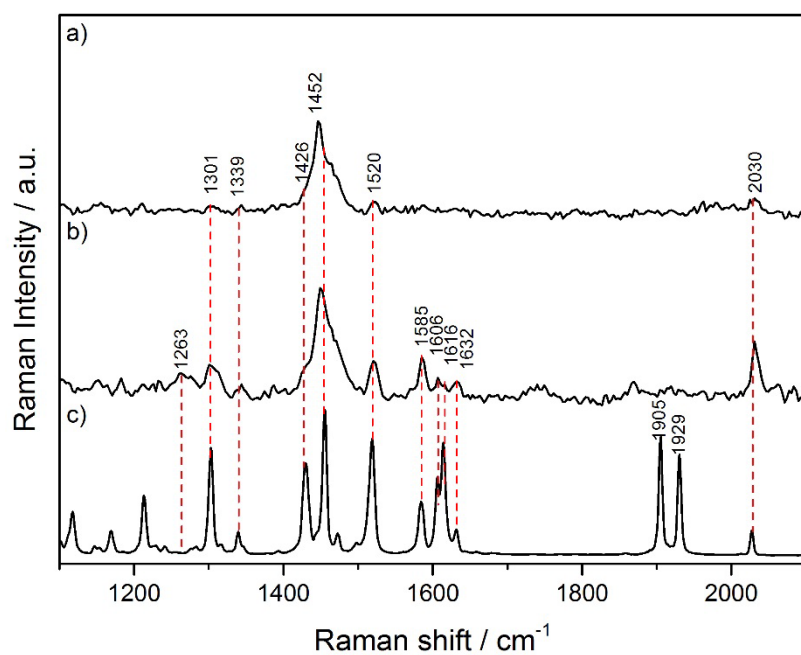


Figure S5: Raman spectra of **Re3OMe**. 351 nm resonance spectra are shown in methanol (a) and methanol with 1 equivalent of KO^tBu (b). Panel c) shows the non-resonant 1064 nm spectrum from a solid state sample.

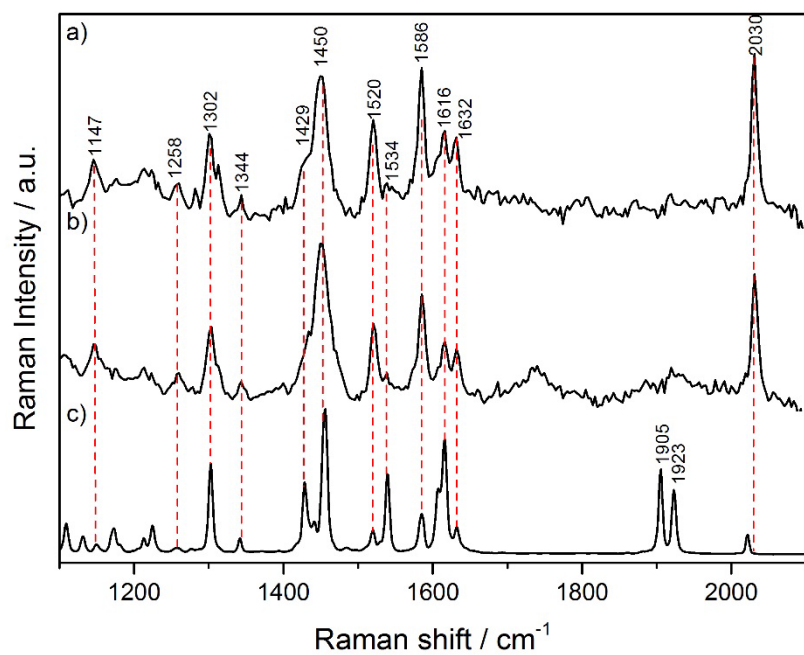


Figure S6: Raman spectra of **Re4OMe**. 351 nm resonance spectra are shown in methanol (a) and methanol with 1 equivalent of KO^tBu (b). Panel c) shows the non-resonant 1064 nm spectrum from a solid state sample.

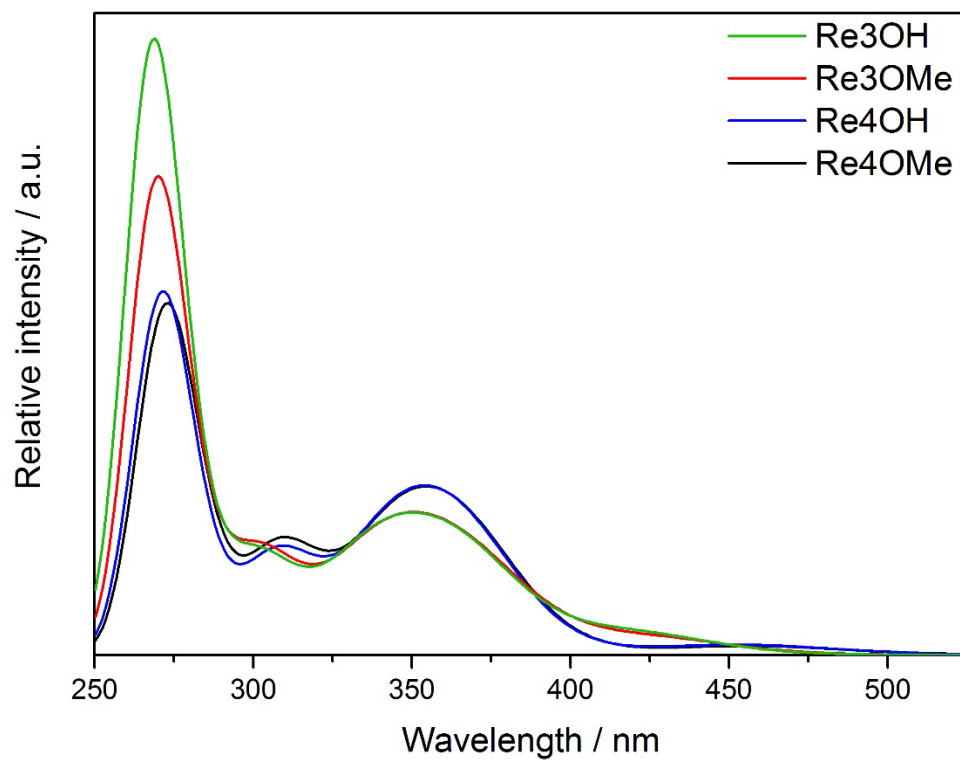


Figure S7: TDDFT predicted UV-vis spectra of the complexes. The spectra are an average obtained across the four configurations.