Supporting Information

Synthesis, Spectroscopy, and Electrochemistry of Manganese(I) and Rhenium(I) Quinoline Oximes

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X-Ray Diffraction. Crystals were grown by slow diffusion of pentane into concentrated solutions of the complexes dissolved in THF. Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Mo K_α radiation (λ = 0.71073 Å) from an IμS micro-source. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2014 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

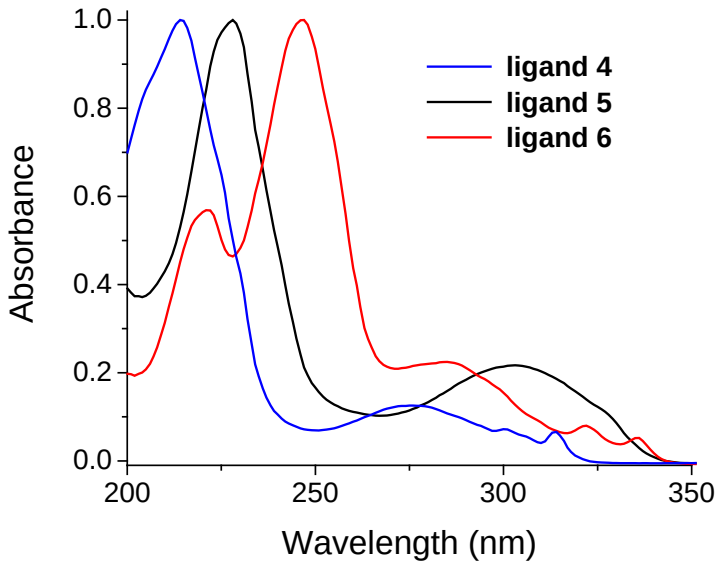


Figure S1. UV-Visible spectra of ligands in MeCN. Spectra normalized at the highest value.

Table S1. Summary of UV-Visible spectra.

Molecule	λ_{peak} (nm)	Extinction Coefficient (M^{-1} cm^{-1})
Re-4im	421	4900
	302	9400
	217	40500
Mn-5	388	3400
	295	7600
	217	42900
Re-5	382	4300
	296	7500
	242	16200
Mn-6	458	2900
	322	6400
	300	7100
	256	22500
Re-6	412	4900
	332	7200
	256	20700
	205	36600

^{1}H NMR spectroscopy

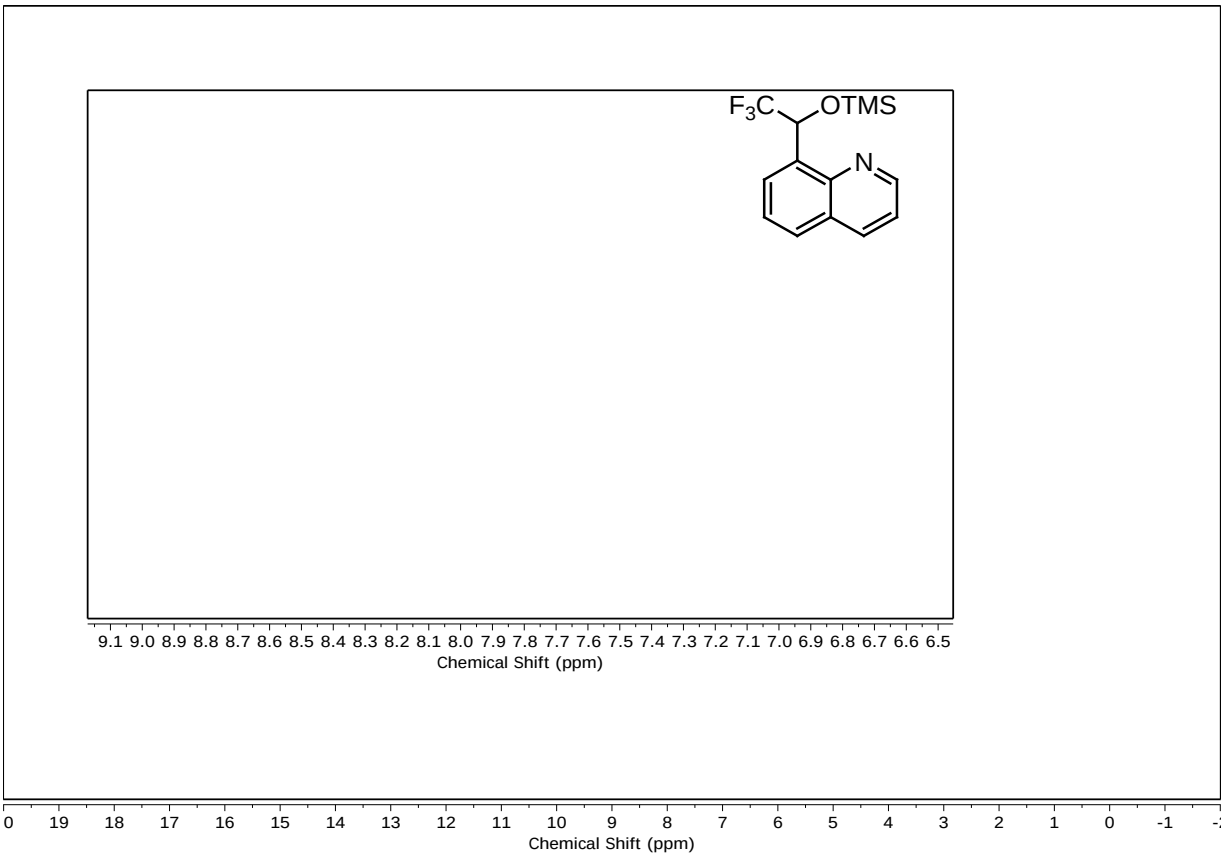


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of Compound **1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.13 (t, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.61 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.40 (dd, *J* = 8.3, 4.1 Hz, 1H), 6.81 (q, *J* = 6.6 Hz, 1H), 0.12 (s, 9H).

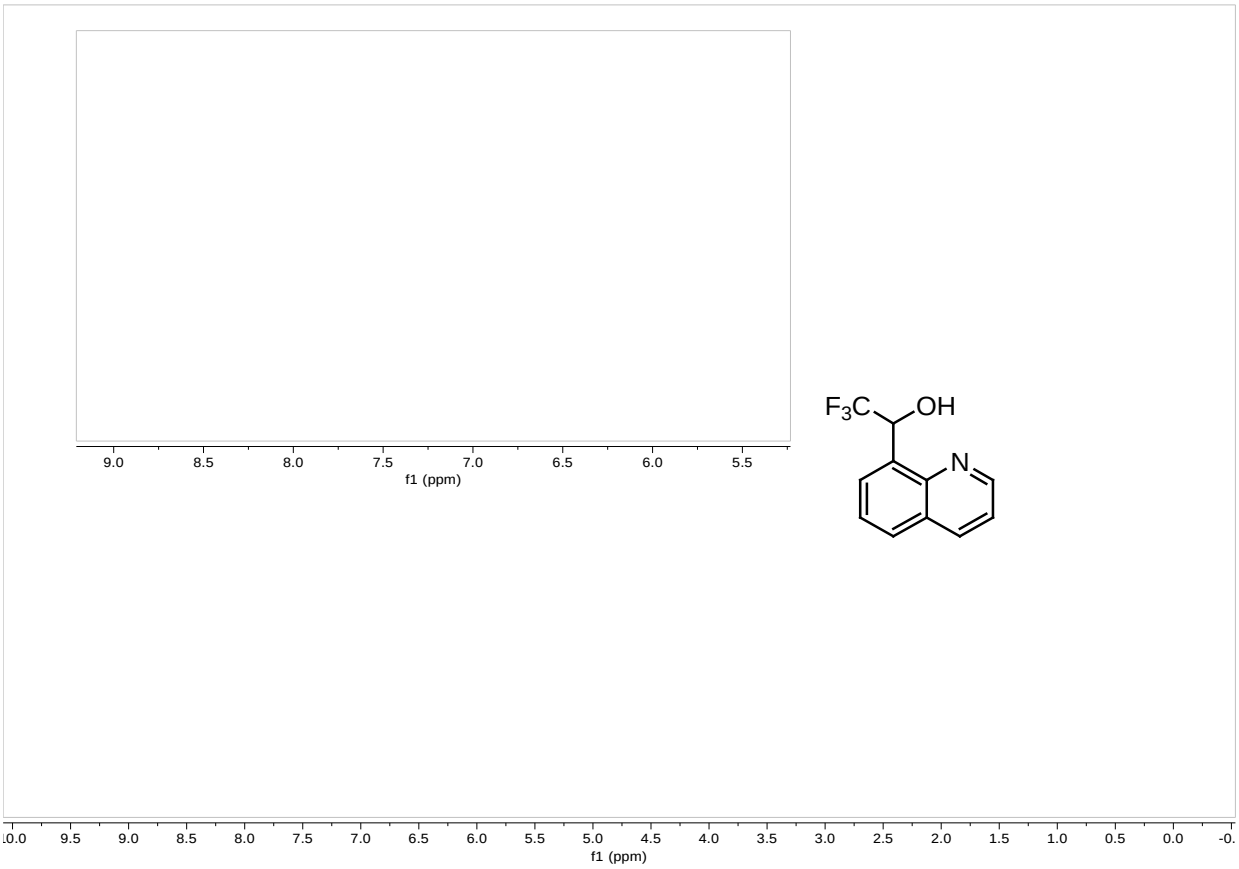


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of Compound **2**. δ 9.01 (s, 1H), 8.87 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.29 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.70 (ddt, *J* = 7.1, 1.6, 0.8 Hz, 1H), 7.62 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.52 (dd, *J* = 8.3, 4.3 Hz, 1H), 5.49 (q, *J* = 7.8 Hz, 1H).

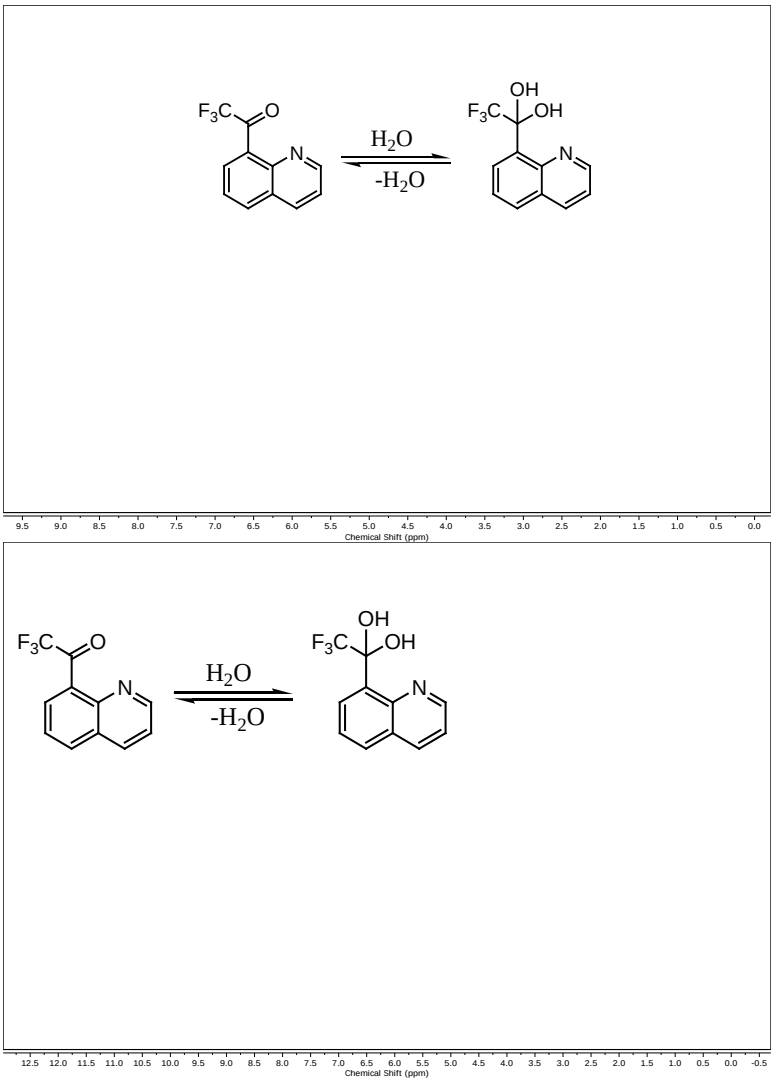


Figure S4. ^{1}H NMR (500 MHz, CD_3CN) spectrum (top) and ^{1}H NMR (300 MHz, CD_3OD) spectrum (bottom) of Compound **3**. CD_3CN: δ (ketone) 8.99 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.45 (d, *J* = 1.8 Hz, 1H), 8.44 (d, *J* = 1.7 Hz, 1H), 8.26 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.03 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H). δ (hydrated ketone) 8.92 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.49 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.47 (s, 2H), 8.20 (d, *J* = 7.4 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.75 (dd, *J* = 8.2, 7.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 4.3 Hz, 1H). CD_3OD: δ 8.90 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.51 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 8.4, 4.3 Hz, 1H), 5.49 (s, 1H).

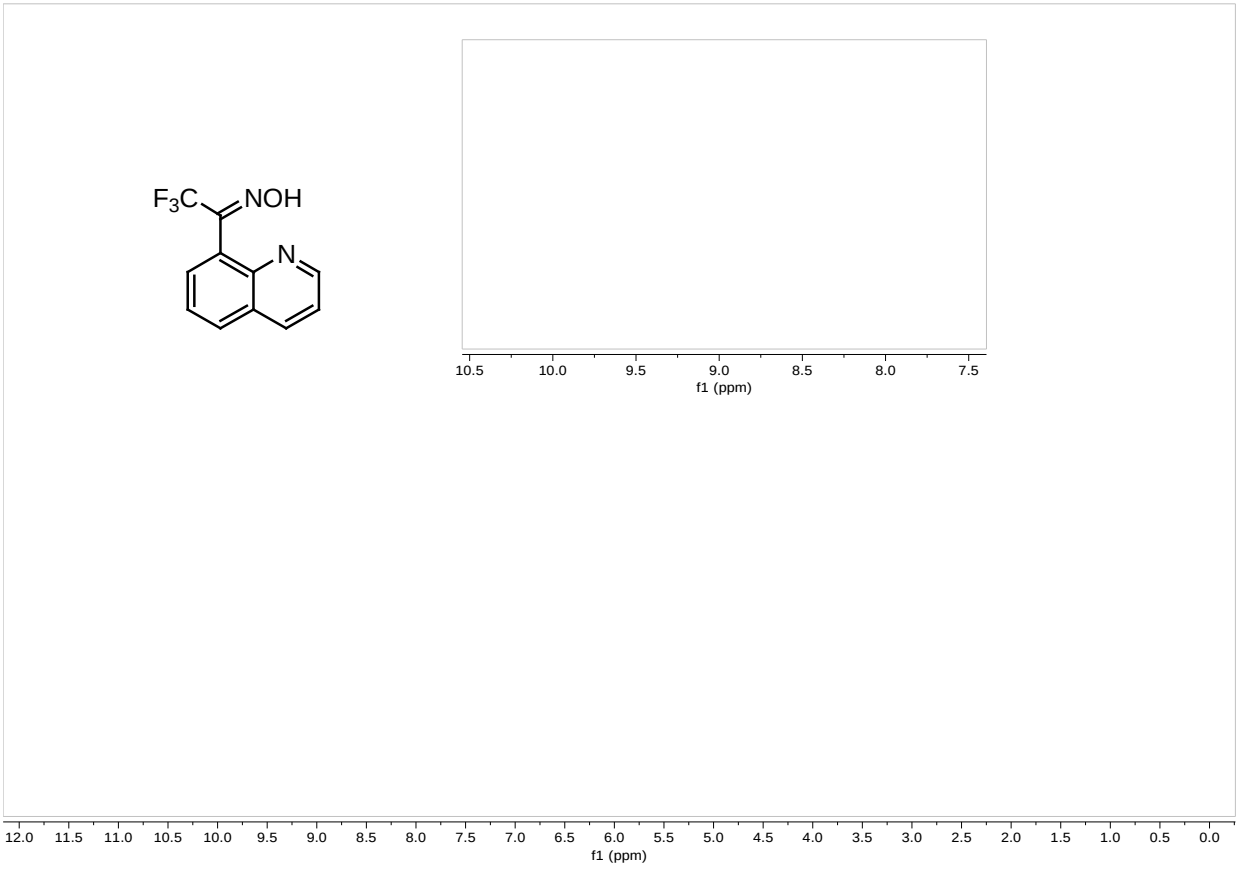


Figure S5. ^{1}H NMR (500 MHz, CD_3CN) spectrum of Compound **4**. δ 10.16 (br s, 0.6H), 8.95 (m, 1H), 8.39 (ddt, *J* = 8.4, 1.8, 0.5 Hz, 1H), 8.14 – 8.10 (m, 1H), 7.85 – 7.73 (m, 0.4H), 7.73 – 7.66 (m, 1.6H), 7.60 (m, 1H).

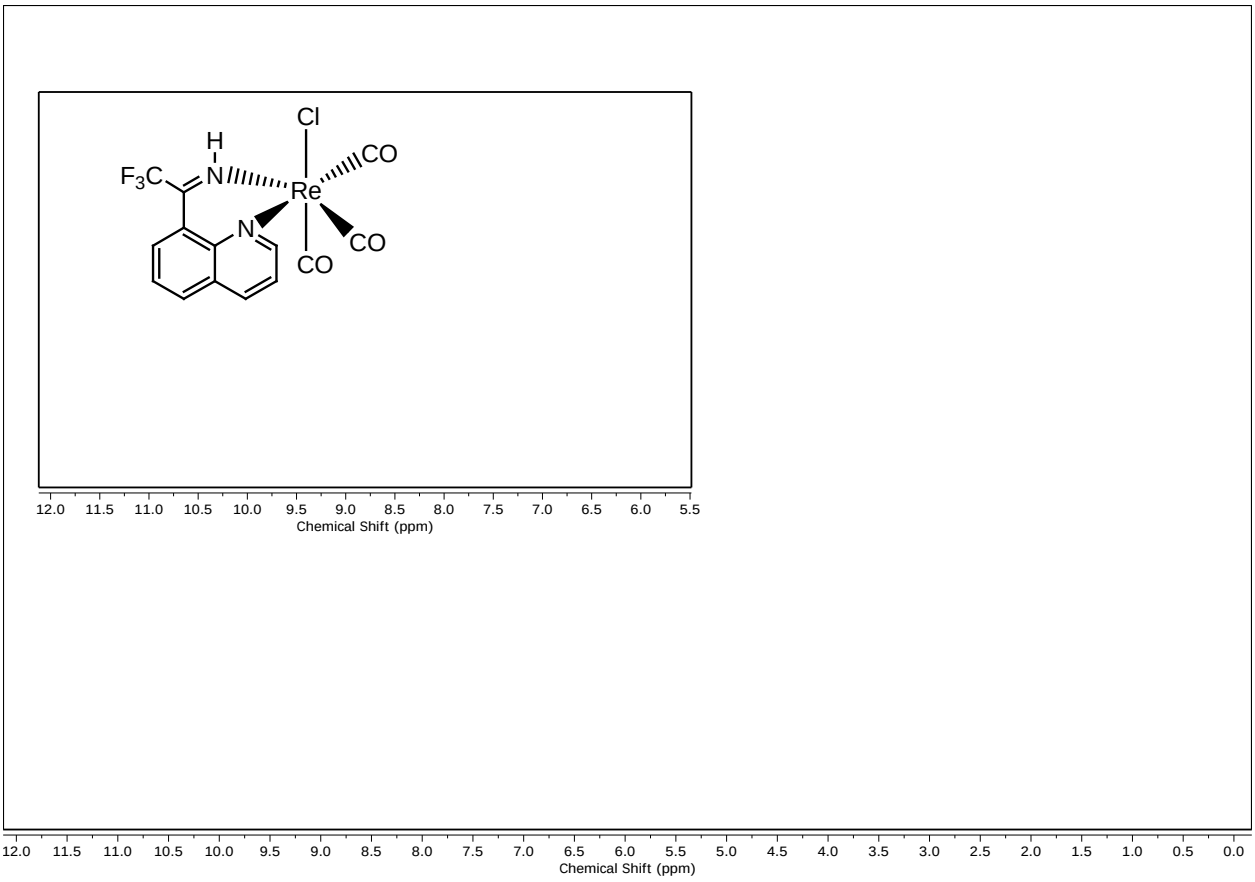


Figure S6. ^{1}H NMR (500 MHz, CD_3CN) spectrum of **Re-4im**. δ 9.69 (dd, *J* = 5.2, 1.7 Hz, 1H), 8.72 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.49 – 8.41 (m, 2H), 7.91 (t, *J* = 7.9 Hz, 1H), 7.70 (dd, *J* = 8.2, 5.2 Hz, 1H), 5.96 (t, *J* = 53.2 Hz, 1H).

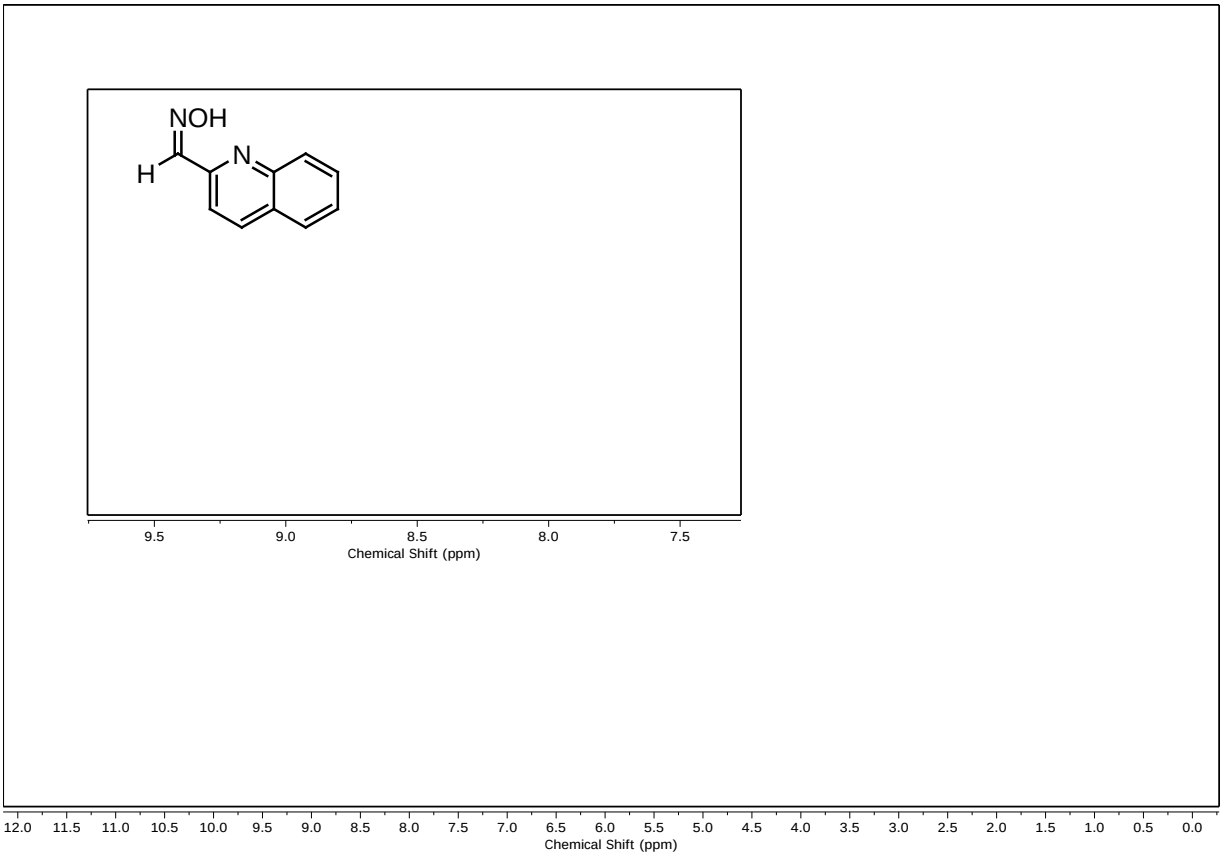


Figure S7. ^{1}H NMR (500 MHz, CD_3CN) spectrum of Compound **5**. δ 10.66 (br s, 1H), 9.60 (d, *J* = 3.2 Hz, 1H), 8.31 (d, *J* = 8.6 Hz, 1H), 8.31 (s, 1H), 8.07 (dq, *J* = 8.5, 0.9 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.81 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.66 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H).

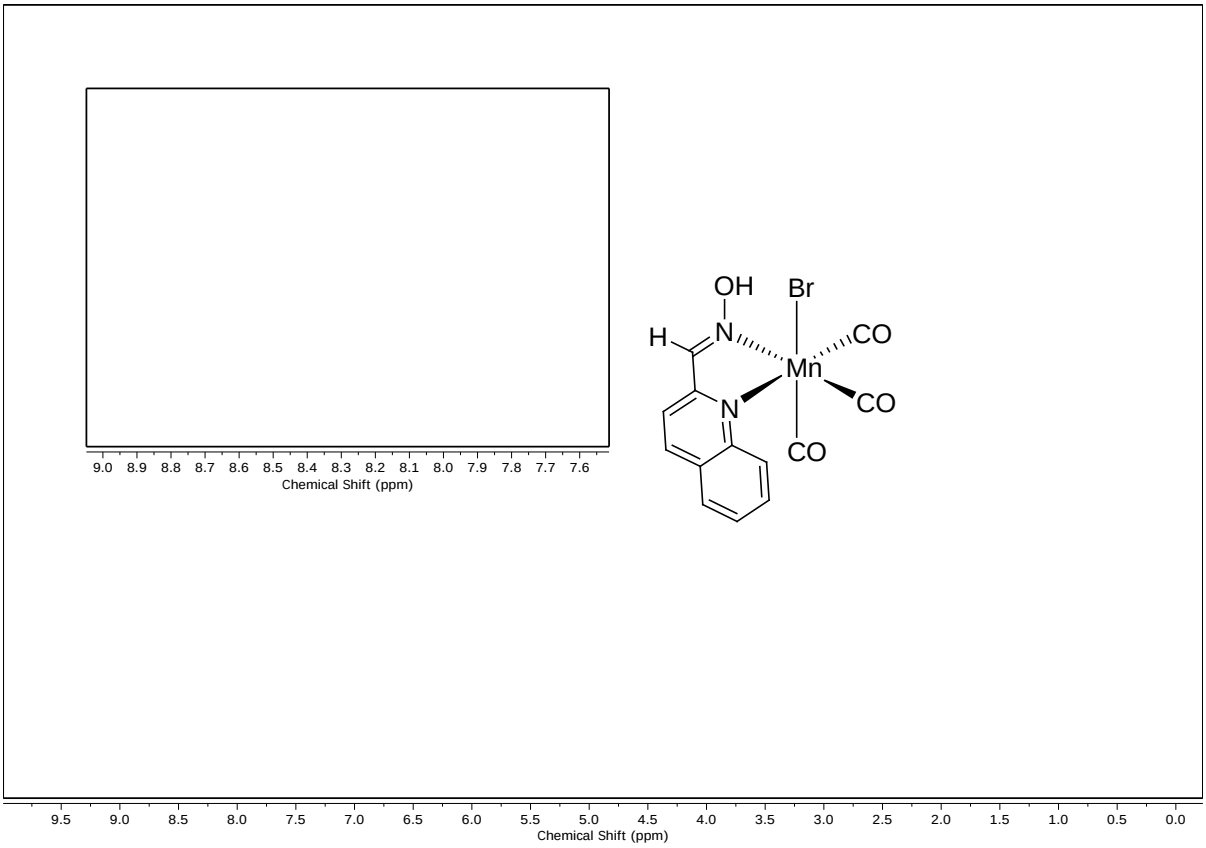


Figure S8. ^{1}H NMR (500 MHz, CD_3CN) spectrum of **Mn-5**. δ 8.86 (d, *J* = 8.9 Hz, 1H), 8.74 (s, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 8.17 – 8.11 (m, 1H), 8.08 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H).

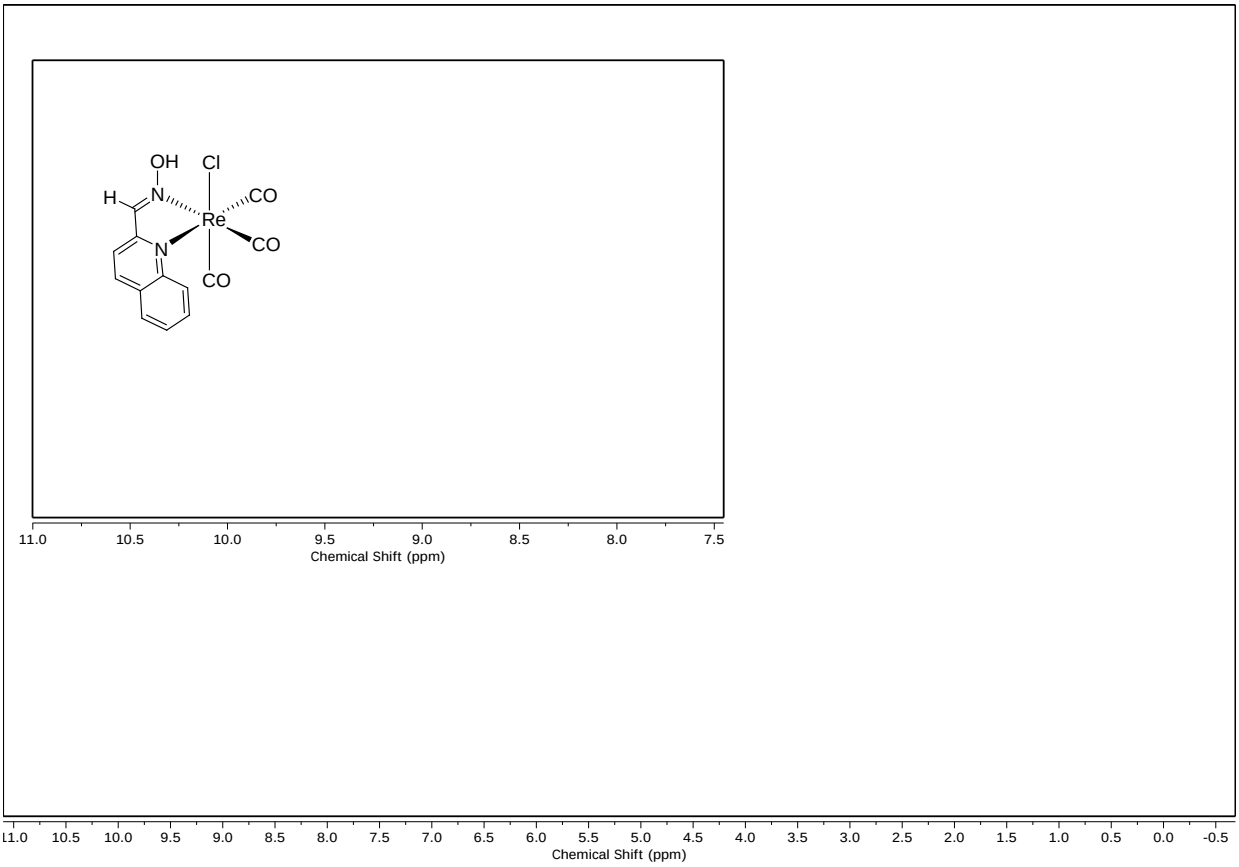


Figure S9. ^{1}H NMR (500 MHz, CD_3CN) spectrum of **Re-5**. δ 10.66 (br s, 1H), 9.07 (s, 1H), 8.72 (d, *J* = 5.8 Hz, 1H), 8.71 (d, *J* = 6.7 Hz, 1H), 8.17 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.10 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.89 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 1H).

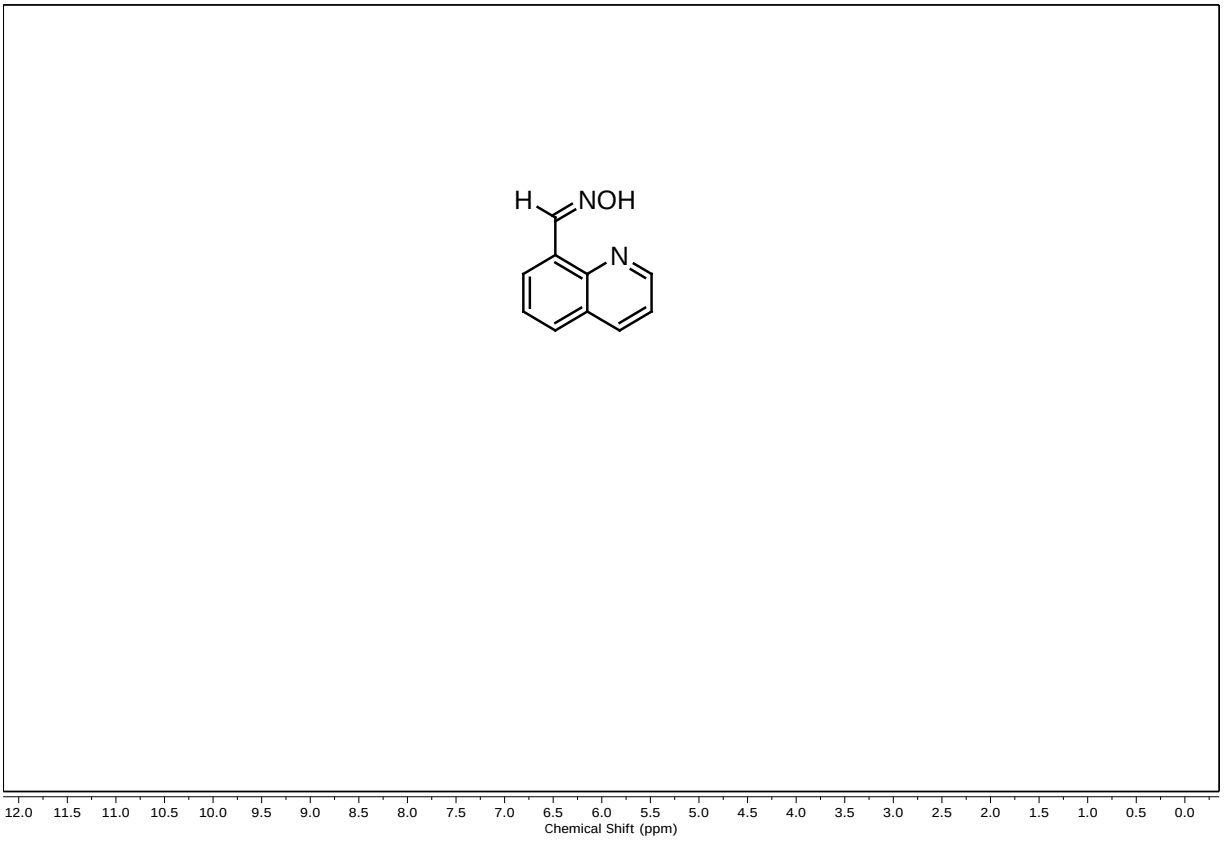


Figure S10. ^{1}H NMR (500 MHz, CD_3CN) spectrum of Compound **6**. δ 9.34 (s, 1H), 9.19 (s, 1H), 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.36 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.25 (dd, *J* = 7.3, 1.4 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 8.3, 4.1 Hz, 1H).

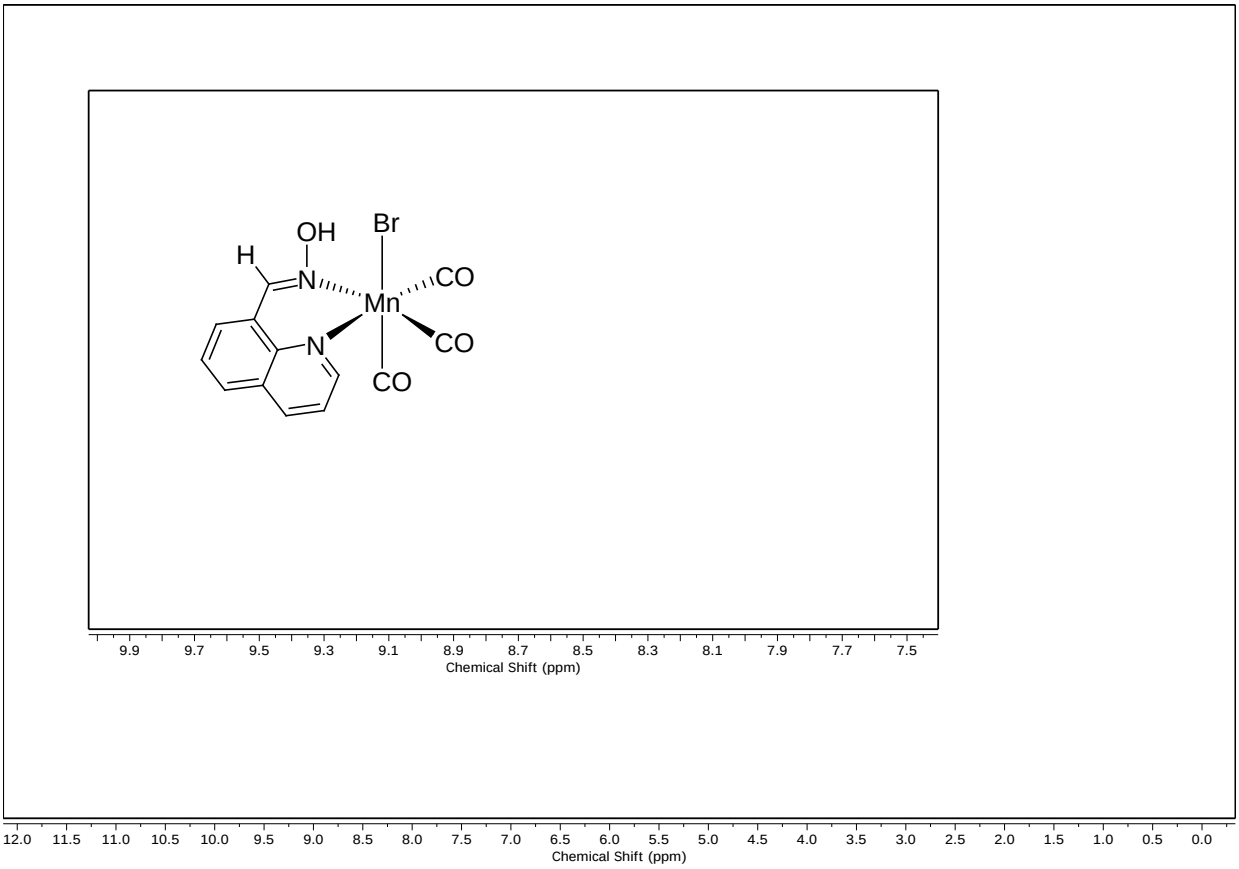


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of Compound **Mn-6**. δ 9.78 (s, 1H), 8.83 (s, 1H), 8.59 (s, 1H), 8.38 (s, 1H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.88 (s, 1H), 7.77 (s, 1H), 7.64 (s, 1H).

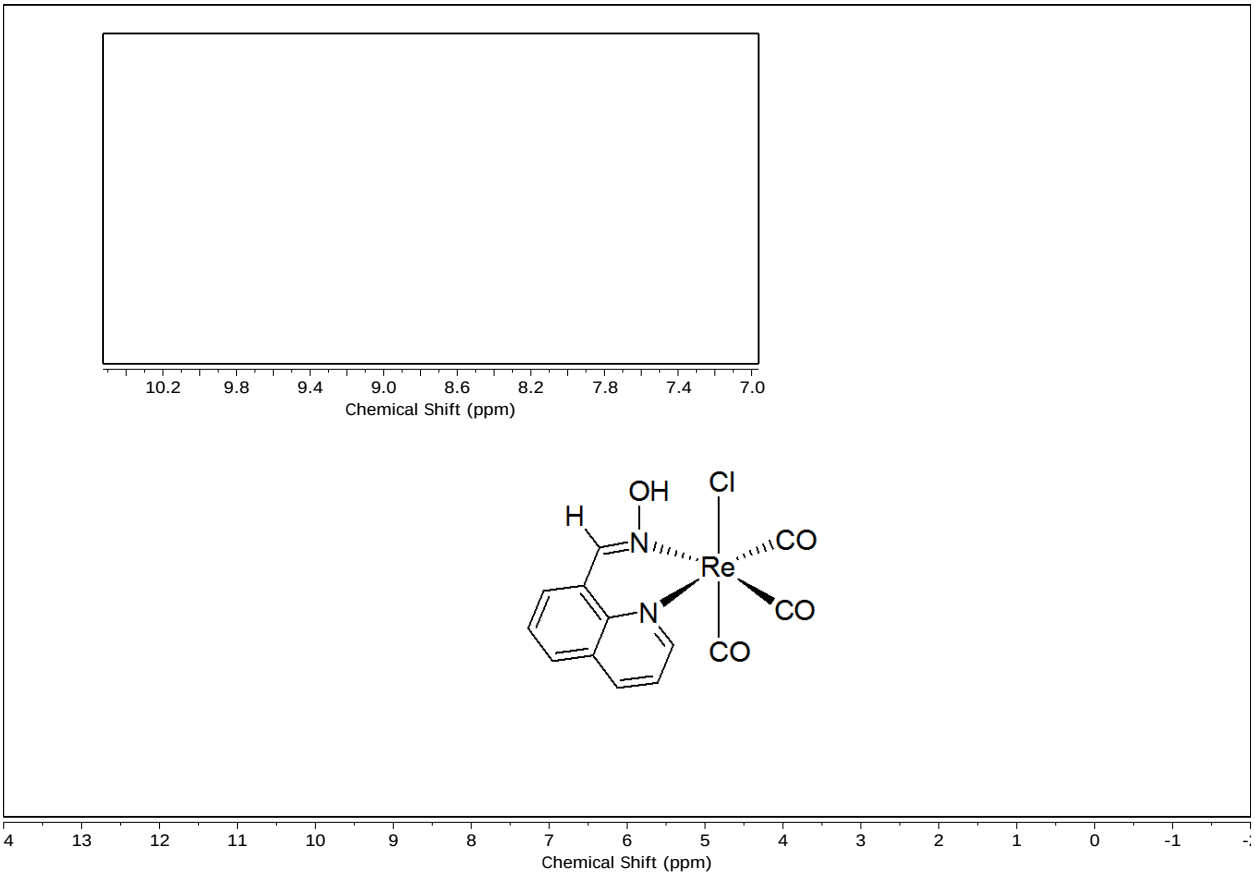


Figure S12. ^{1}H NMR (500 MHz, CD_3CN) spectrum of Compound **Re-6**. δ 9.67 (dd, *J* = 5.2, 1.7 Hz, 1H), 9.43 (s, 1H), 8.71 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.70 (d, *J* = 0.6 Hz, 1H), 8.31 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.10 (ddd, *J* = 7.3, 1.6, 0.6 Hz, 1H), 7.86 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.69 (dd, *J* = 8.3, 5.3 Hz, 1H).

^{19}F NMR spectroscopy

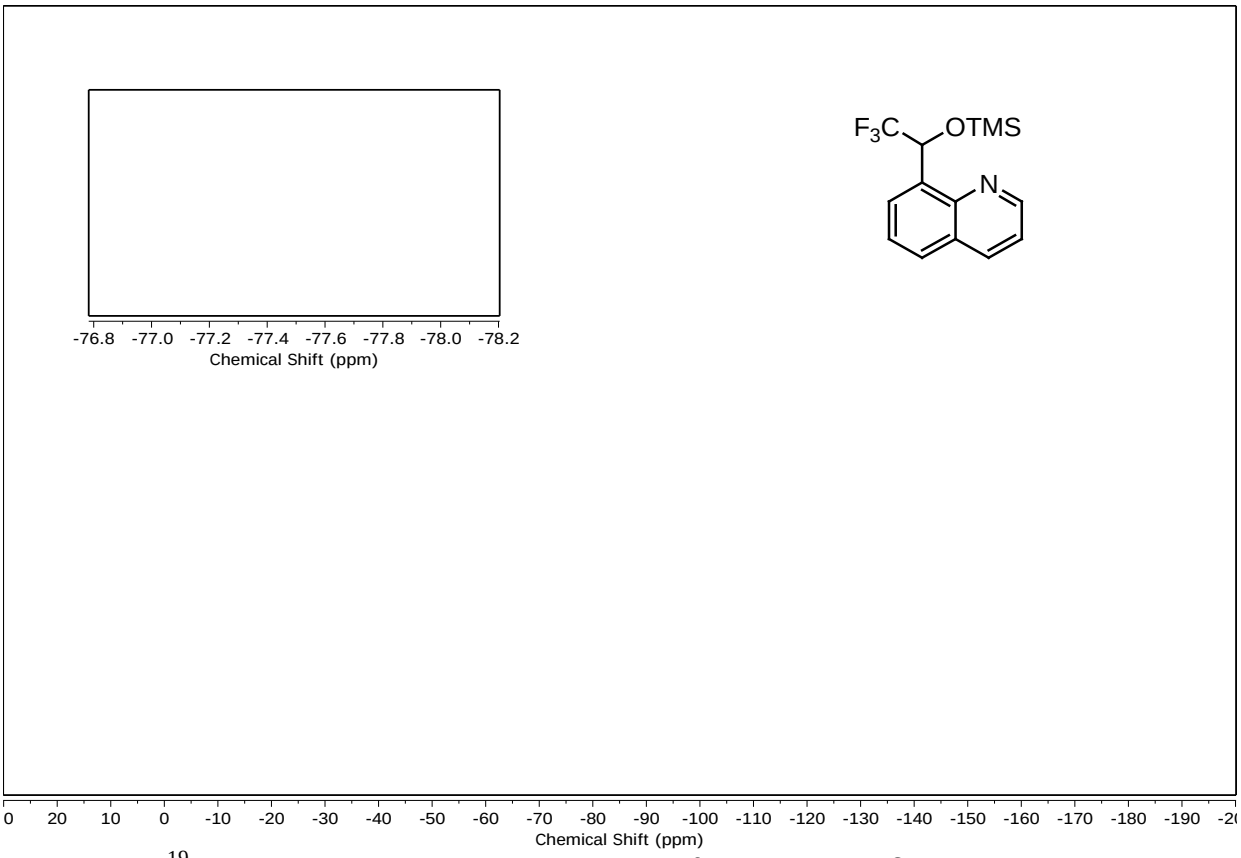


Figure S13. ^{19}F NMR (282 MHz, $CDCl_3$) spectrum of Compound **1**. δ -77.57 (d, *J* = 6.5 Hz).

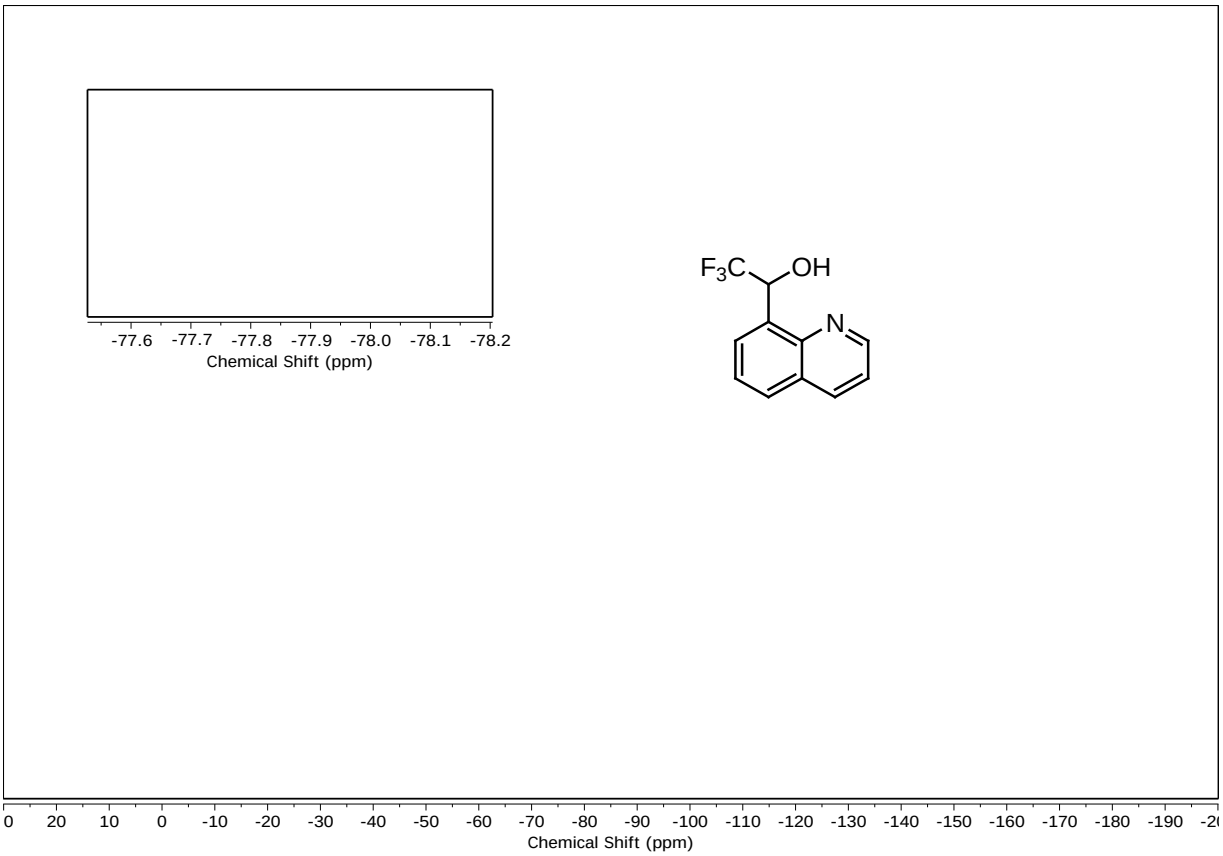


Figure S14. ^{19}F NMR (282 MHz, $CDCl_3$) spectrum of Compound **2**. δ -77.86 (d, *J* = 7.8 Hz).

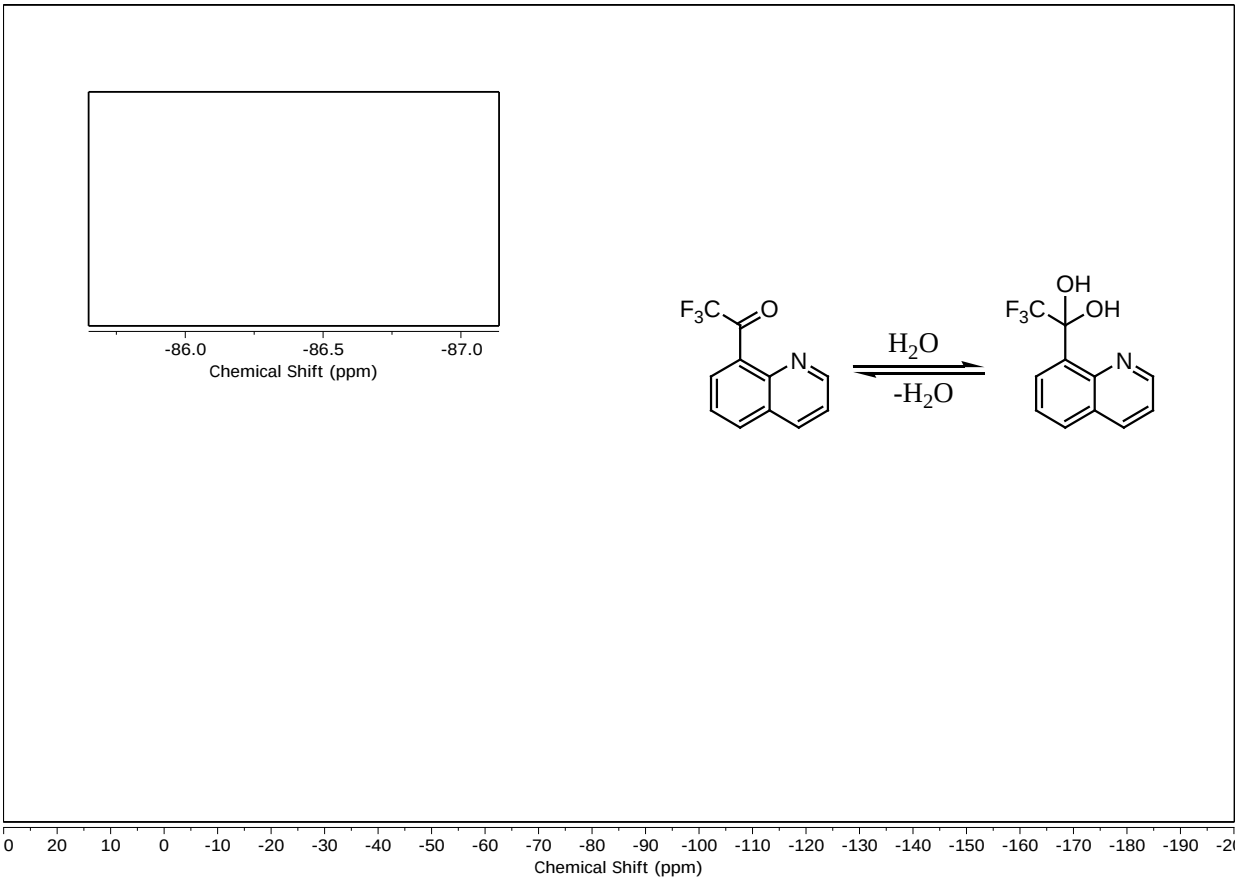


Figure S15. ^{19}F NMR (282 MHz, CD_3OD) spectrum of Compound **3**. δ -86.25.

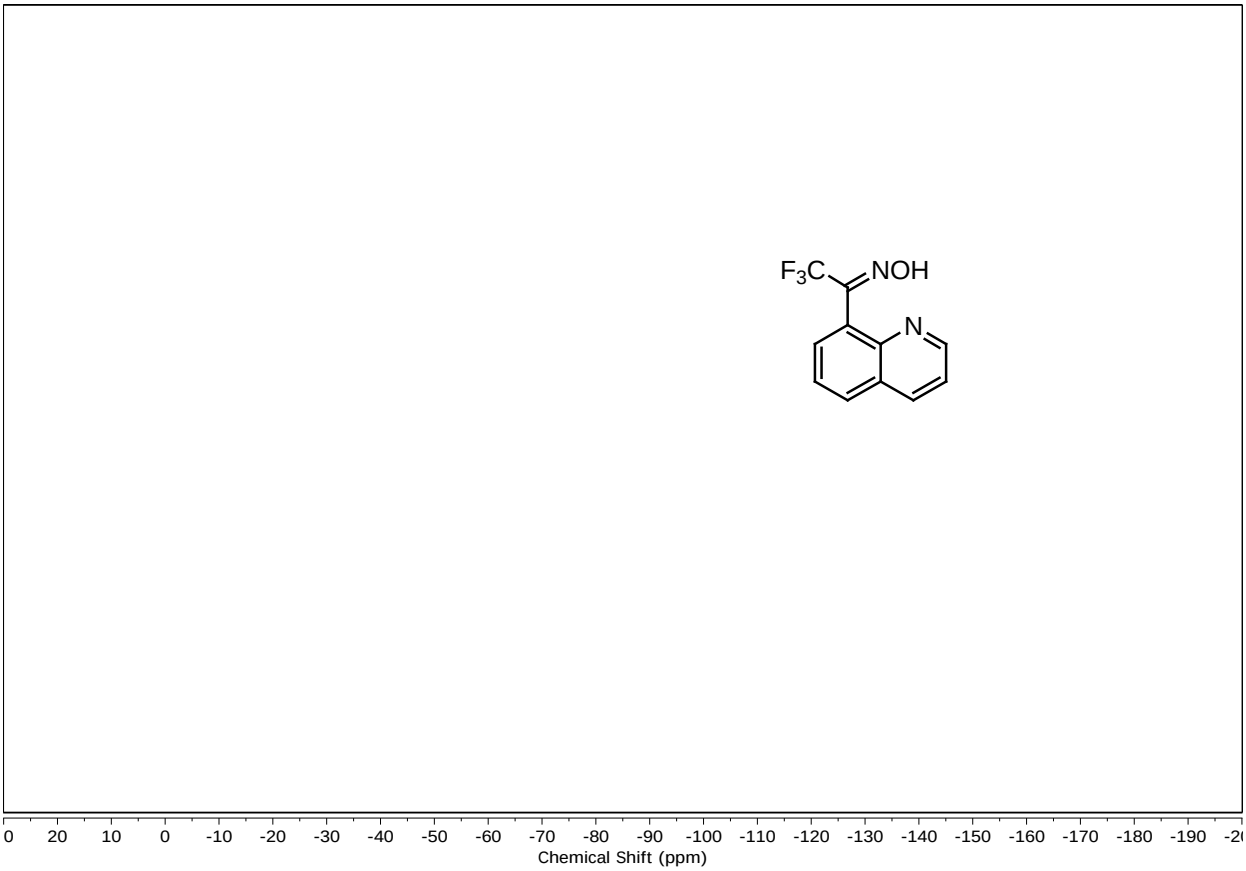


Figure S16. ^{19}F NMR (282 MHz, CD_3CN) spectrum of Compound **4**. δ -65.23 (33%), -67.57 (67%).

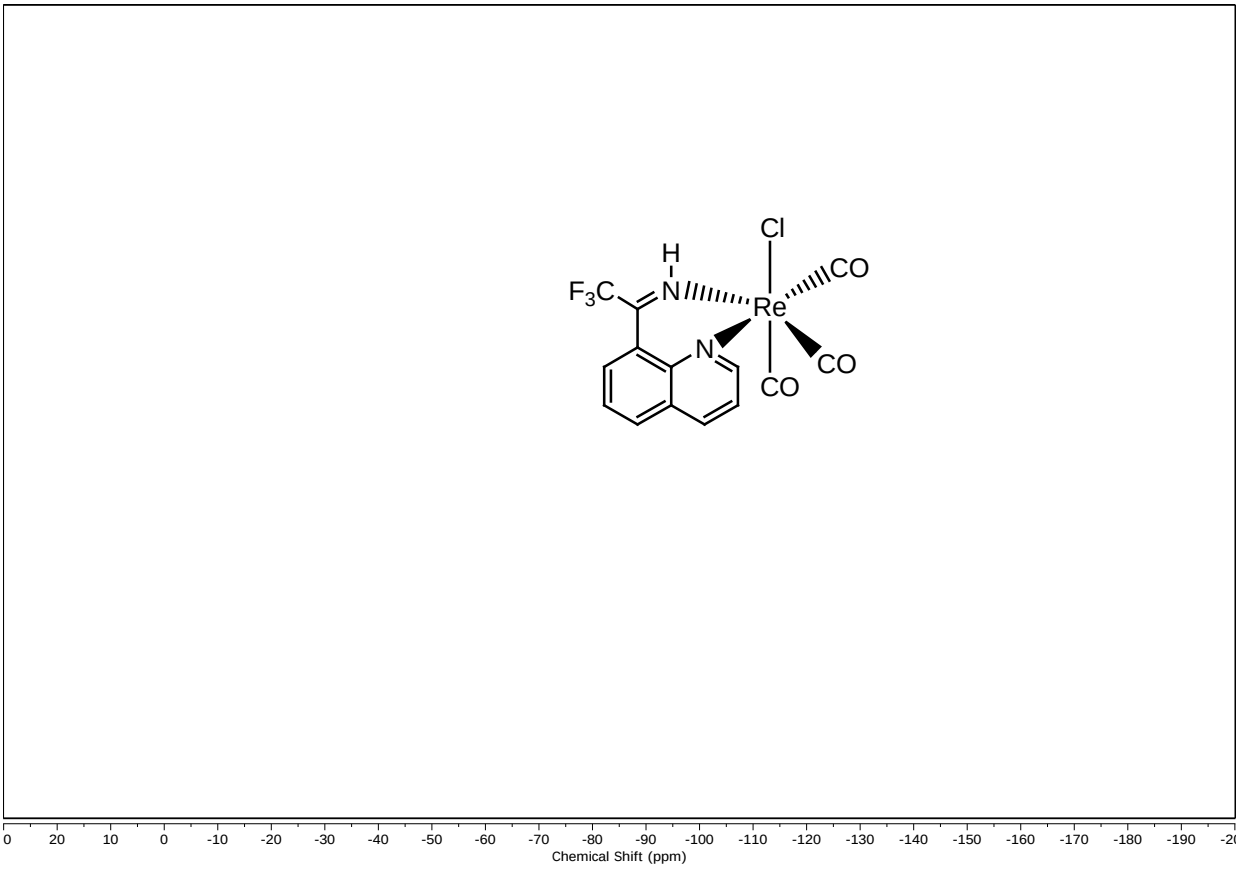


Figure S17. ^{19}F NMR (282 MHz, CD_3CN) spectrum of **Re-4im**. δ -65.56.

IR (ATR) Spectroscopy

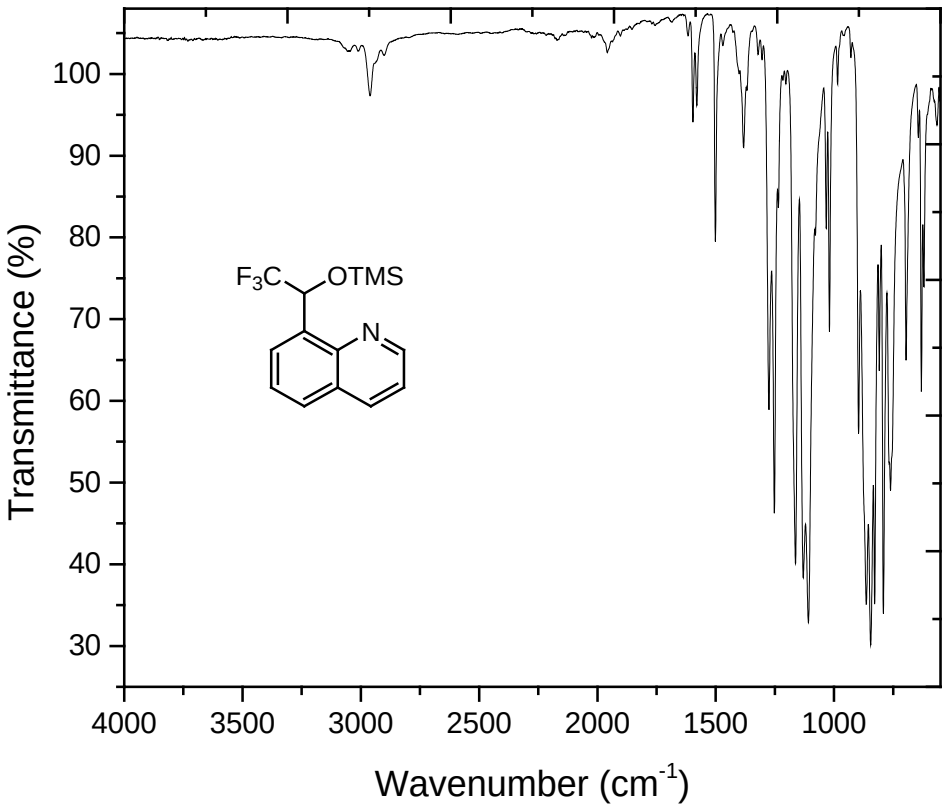


Figure S18. IR (ATR) spectrum of Compound **1**.

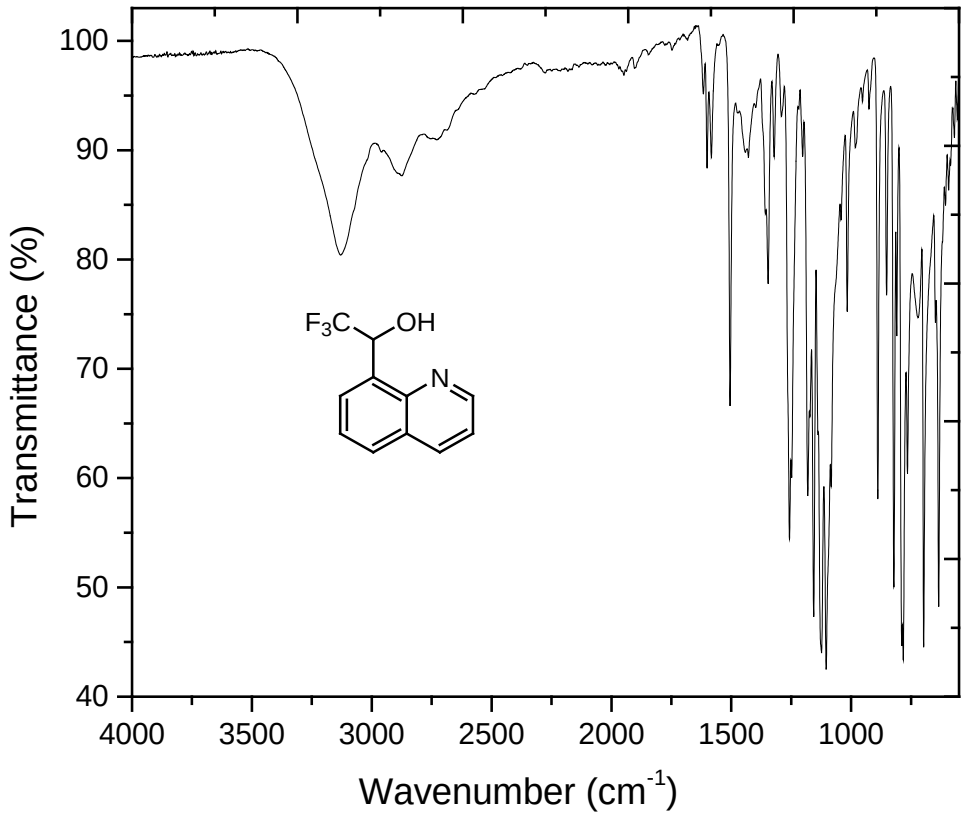


Figure S19. IR (ATR) spectrum of Compound **2**.

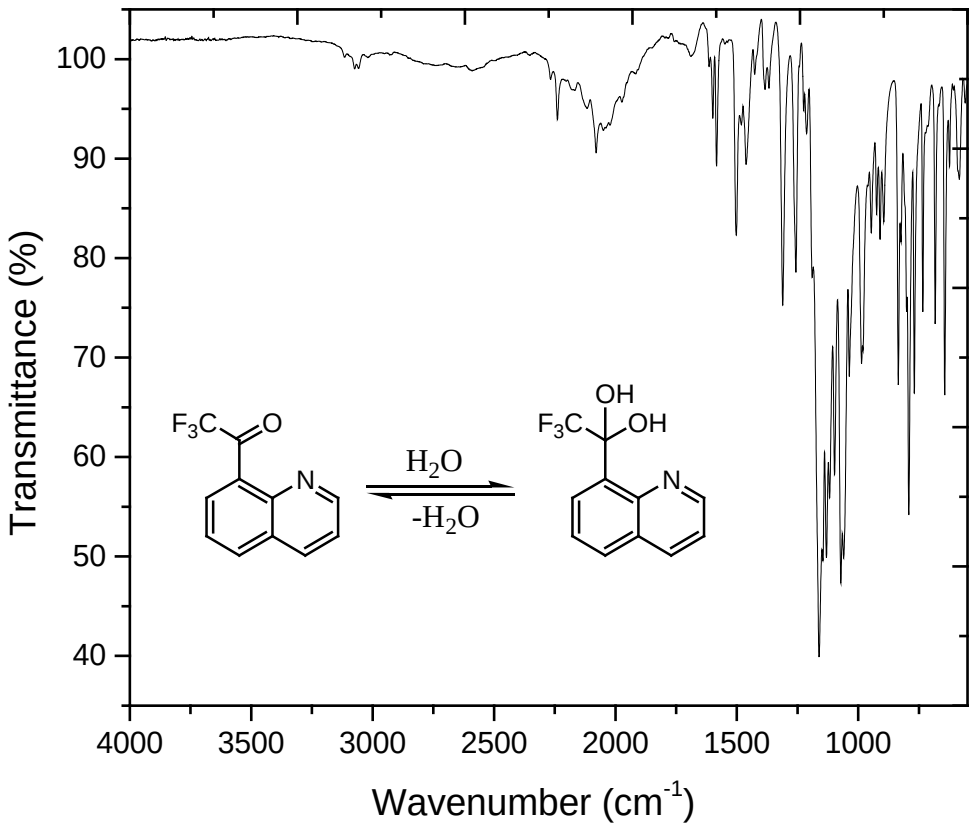


Figure S20. IR (ATR) spectrum of Compound **3**.

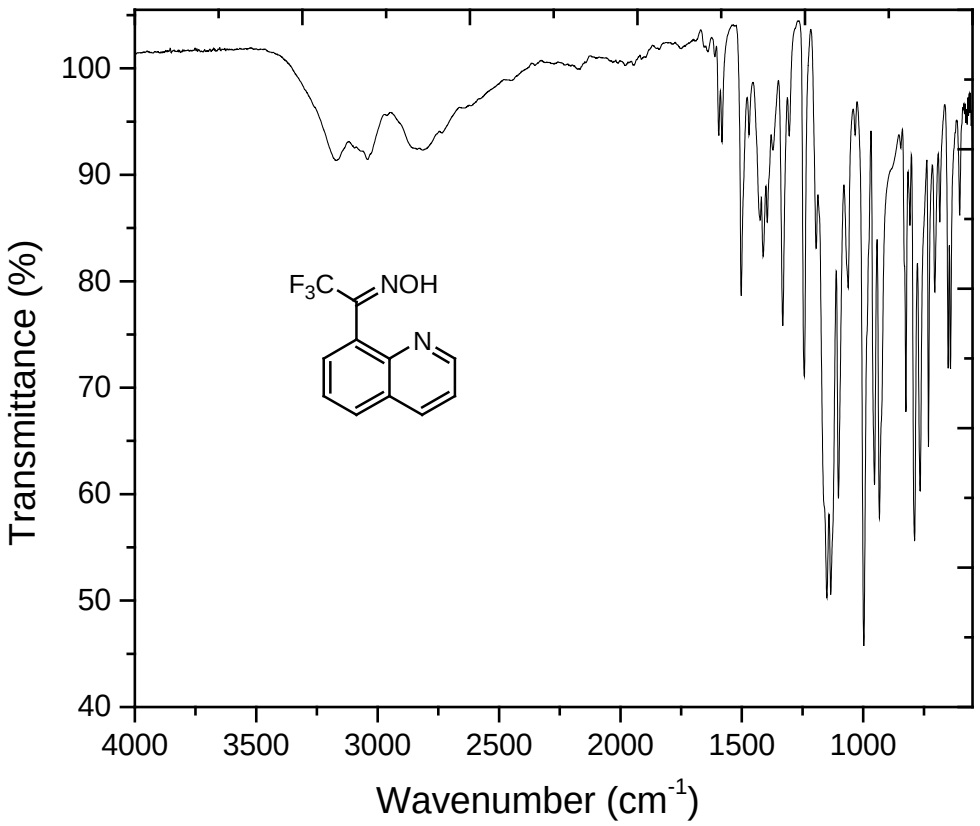


Figure S21. IR (ATR) spectrum of Compound **4**.

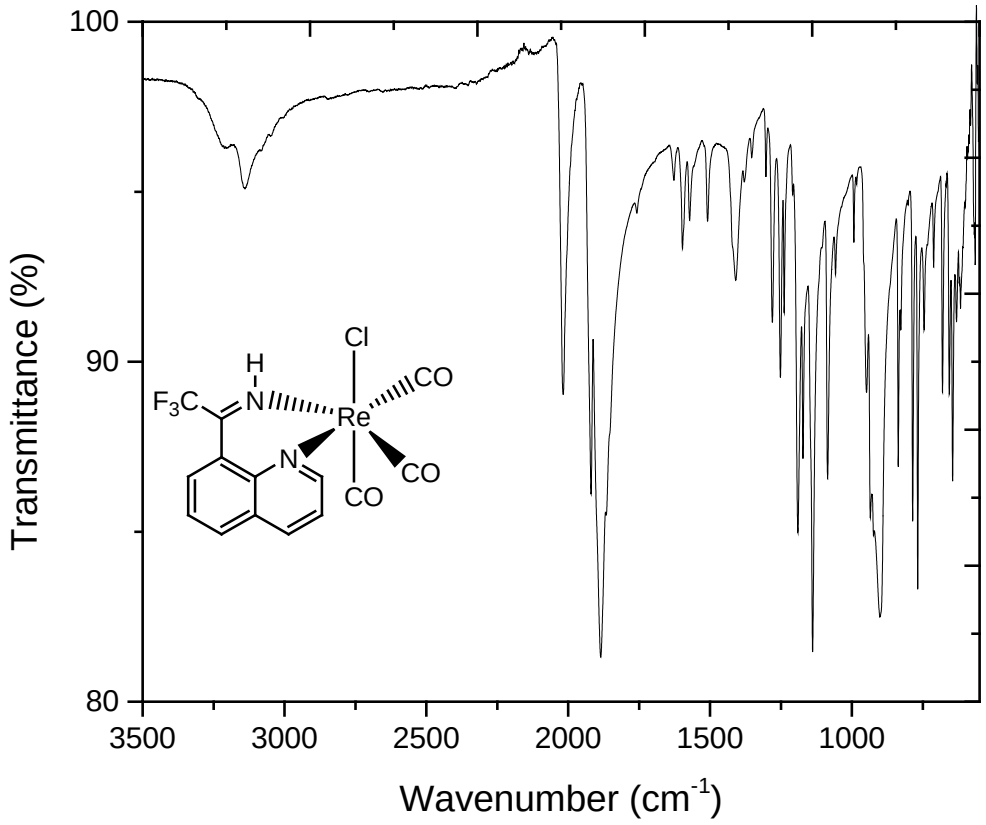


Figure S22. IR (ATR) spectrum of Compound **Re-4im**. ν/cm^{-1}: 3205 br, 3140 sh (ν_{N-H}).

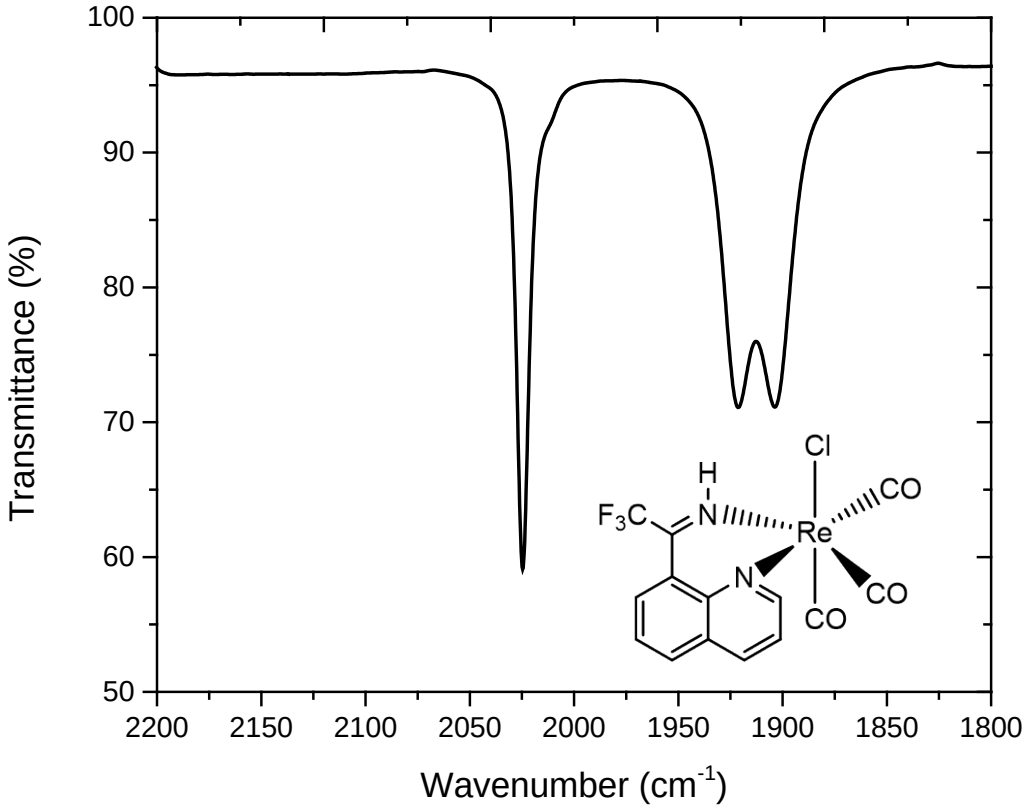


Figure S23. IR (MeCN) spectrum of Compound **Re-4im**. ν/cm^{-1}: [2025, 1922, 1904 ($\nu_{C\equiv O}$)].

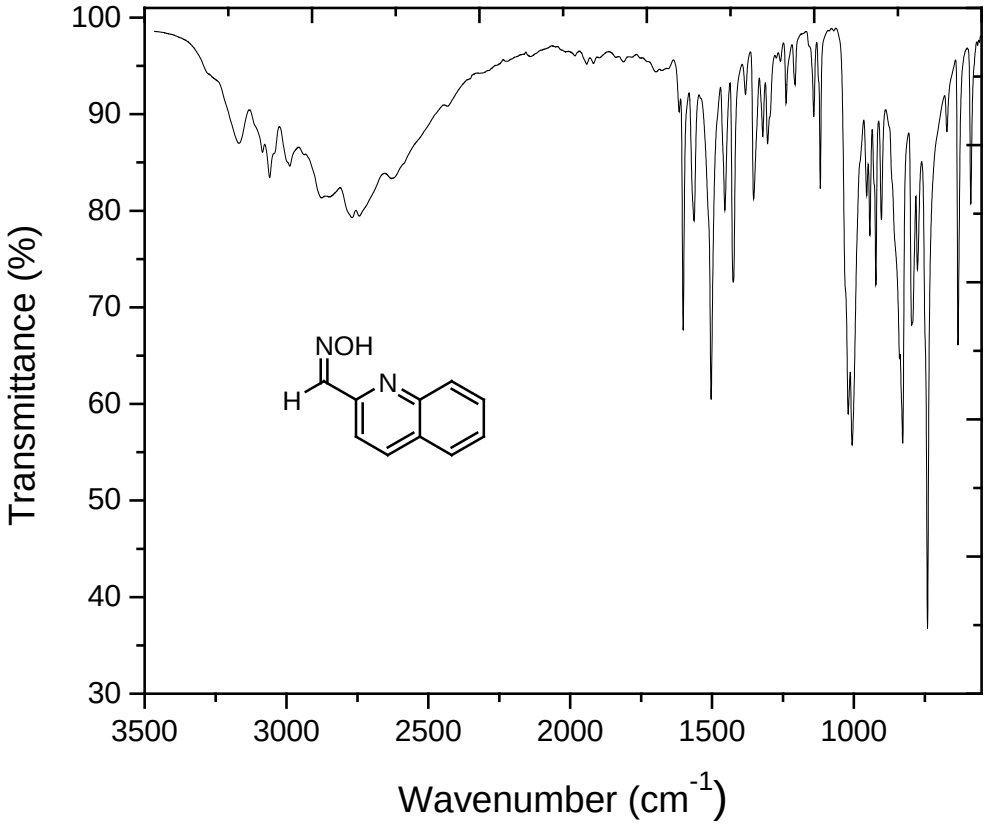


Figure S24. IR (ATR) spectrum of compound **5**. ν/cm^{-1}: 3168 ($\nu_{O\text{-}H}$).

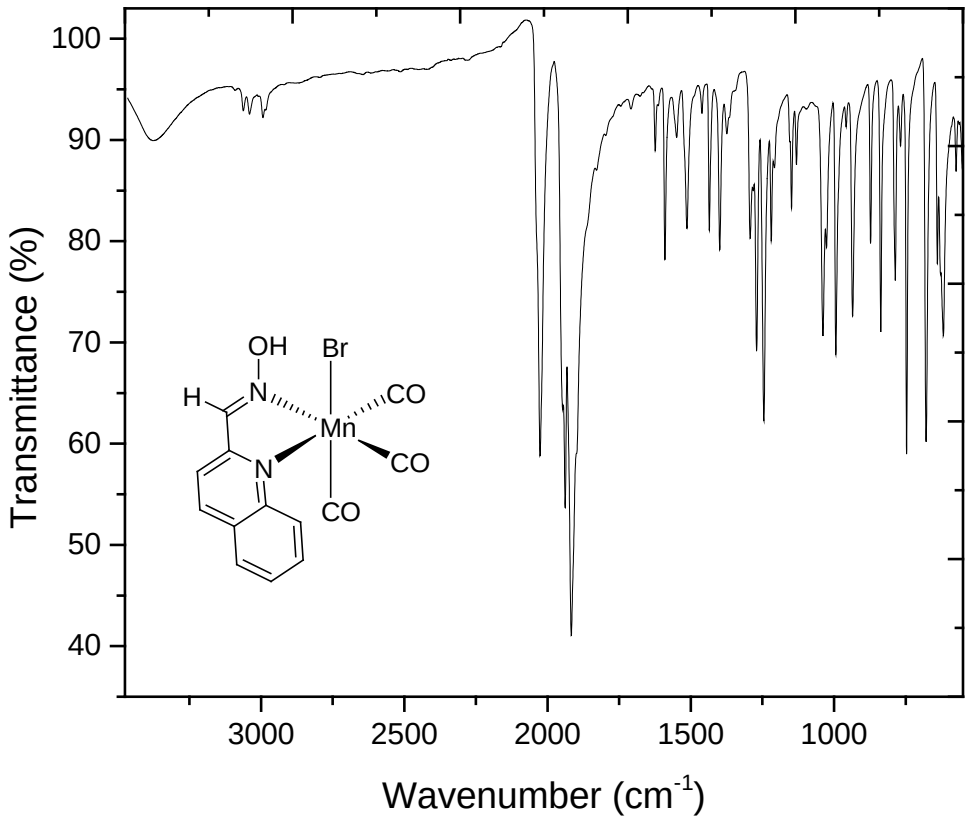


Figure S25. IR (ATR) spectrum of **Mn-5**. ν/cm^{-1}: 3376 ($\nu_{O\text{-}H}$).

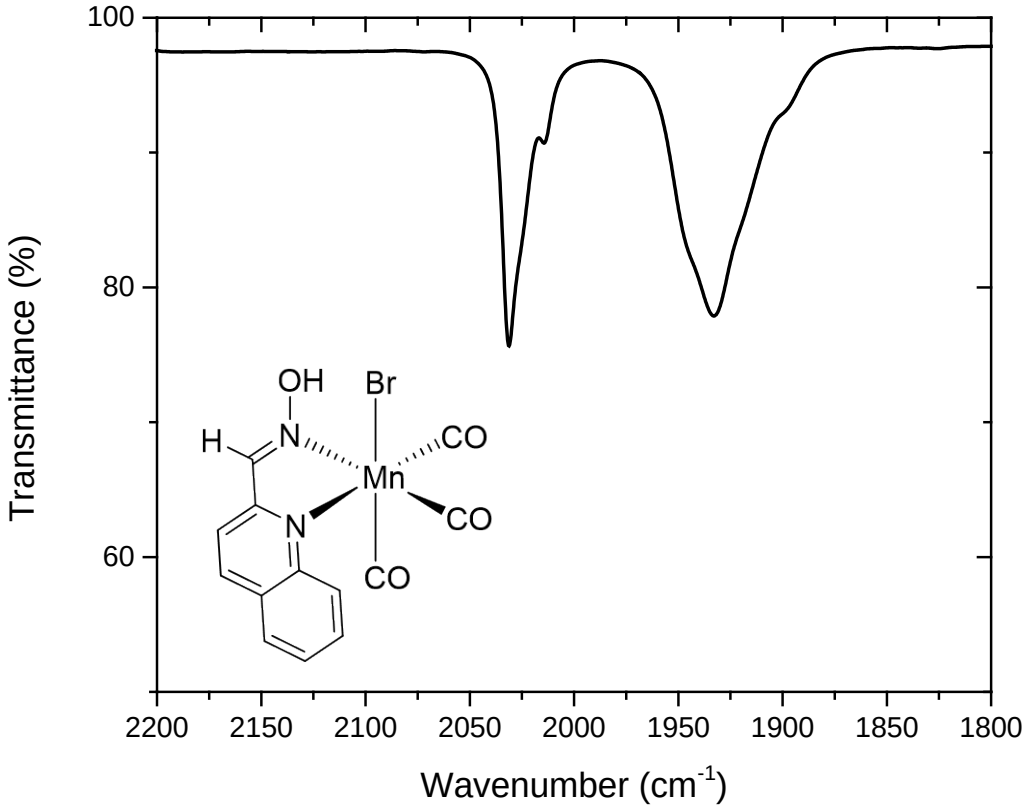


Figure S26. IR (MeCN) spectrum of Compound **Mn-5**. ν/cm^{-1}: [2031, 1933, 1899 ($\nu_{C\equiv O}$)].

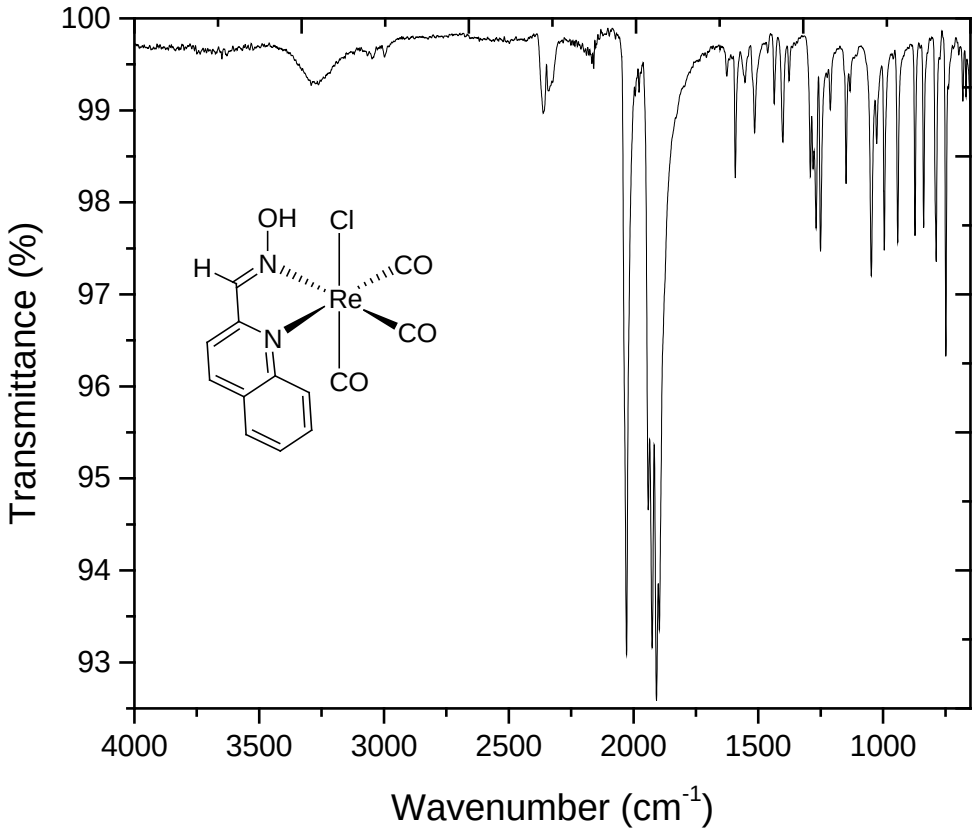


Figure S27. IR (ATR) spectrum of **Re-5**. ν/cm^{-1}: 3280 ($\nu_{O\text{-}H}$).

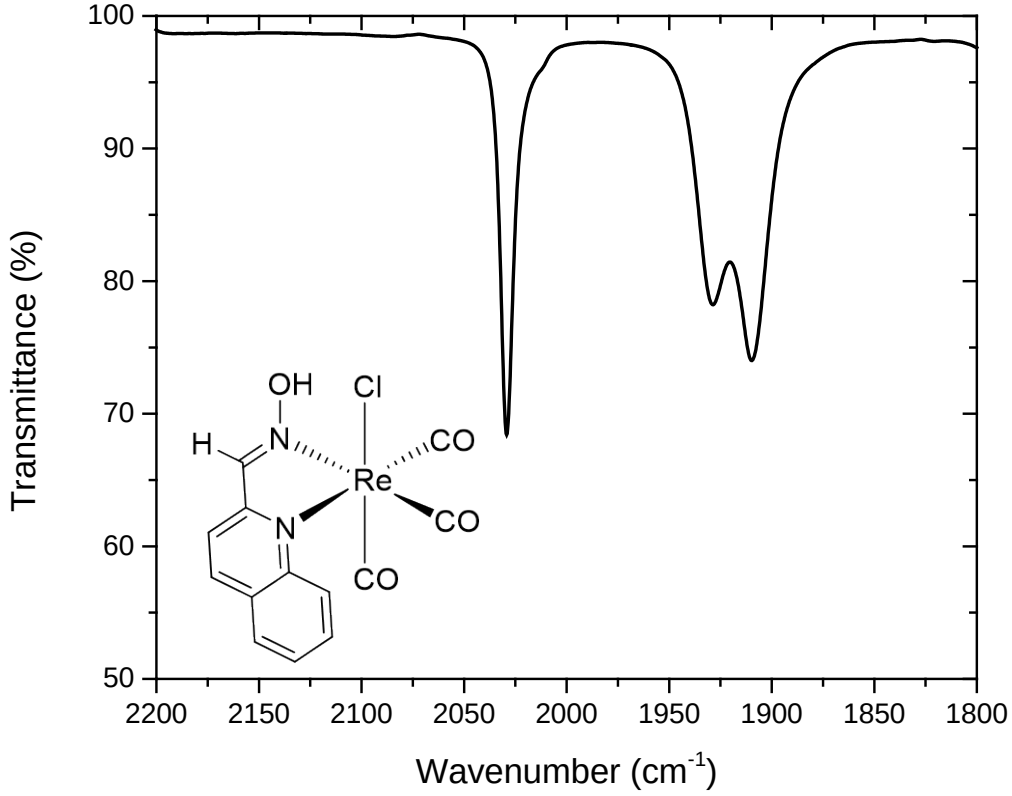


Figure S28. IR (MeCN) spectrum of Compound **Re-5**. ν/cm^{-1}: [2029, 1930, 1910 ($\nu_{C\equiv O}$)].

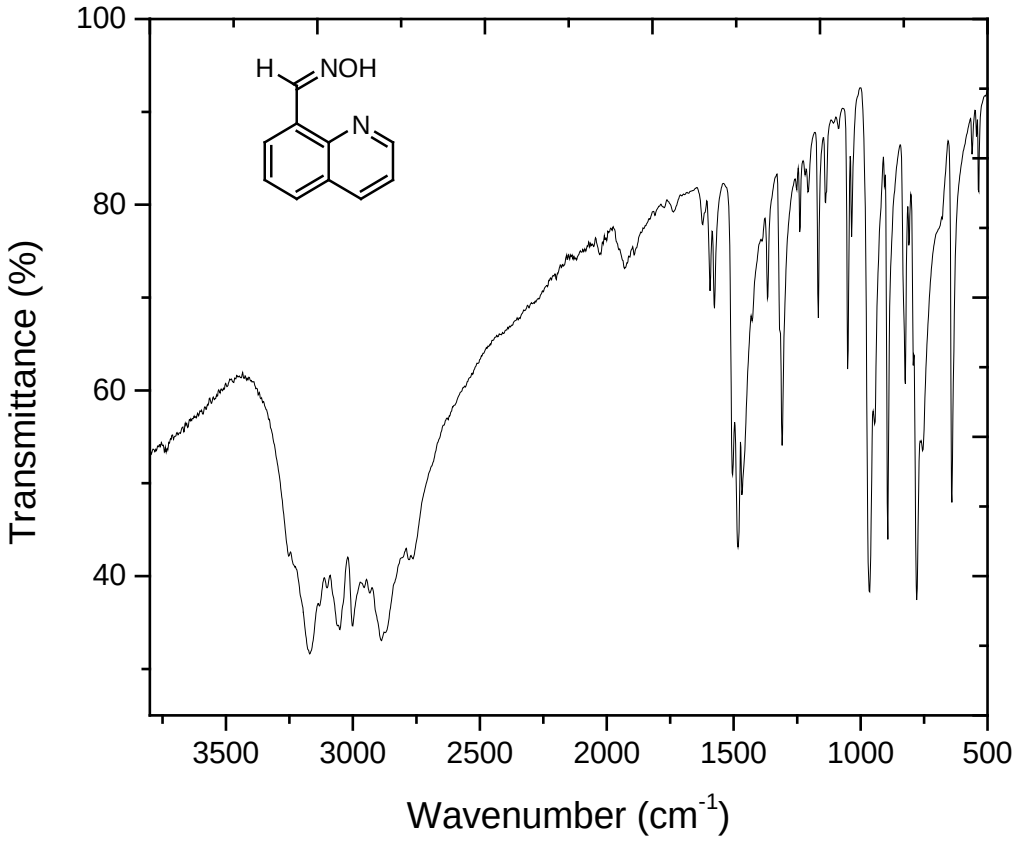


Figure S29. IR (ATR) spectrum of compound **6**. ν/cm^{-1}: 3170 ($\nu_{O\text{-}H}$).

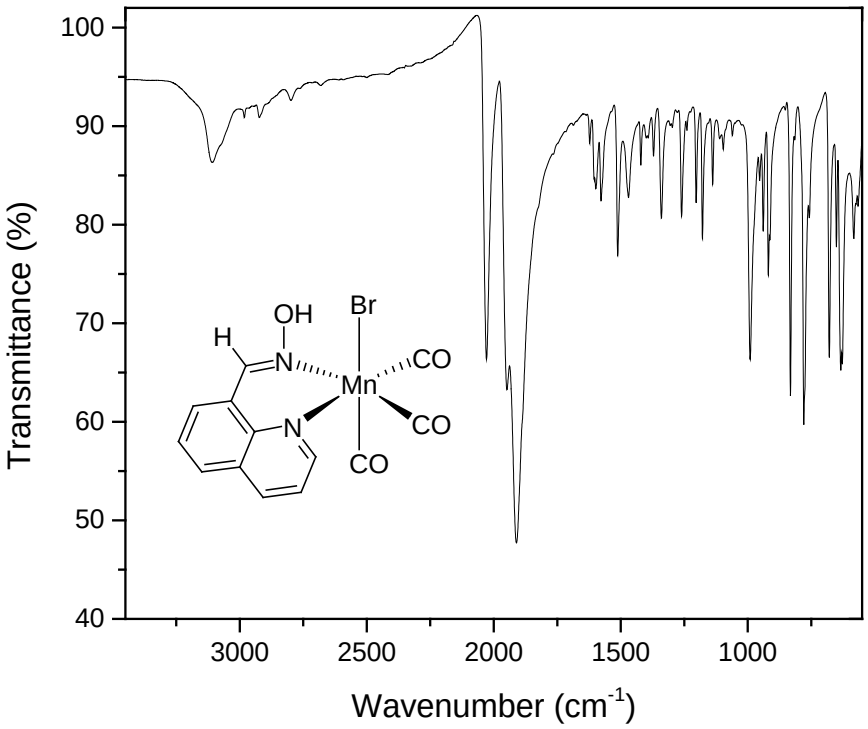


Figure S30. IR (ATR) spectrum of **Mn-6**. ν/cm^{-1}: 3107 ($\nu_{O\text{-}H}$).

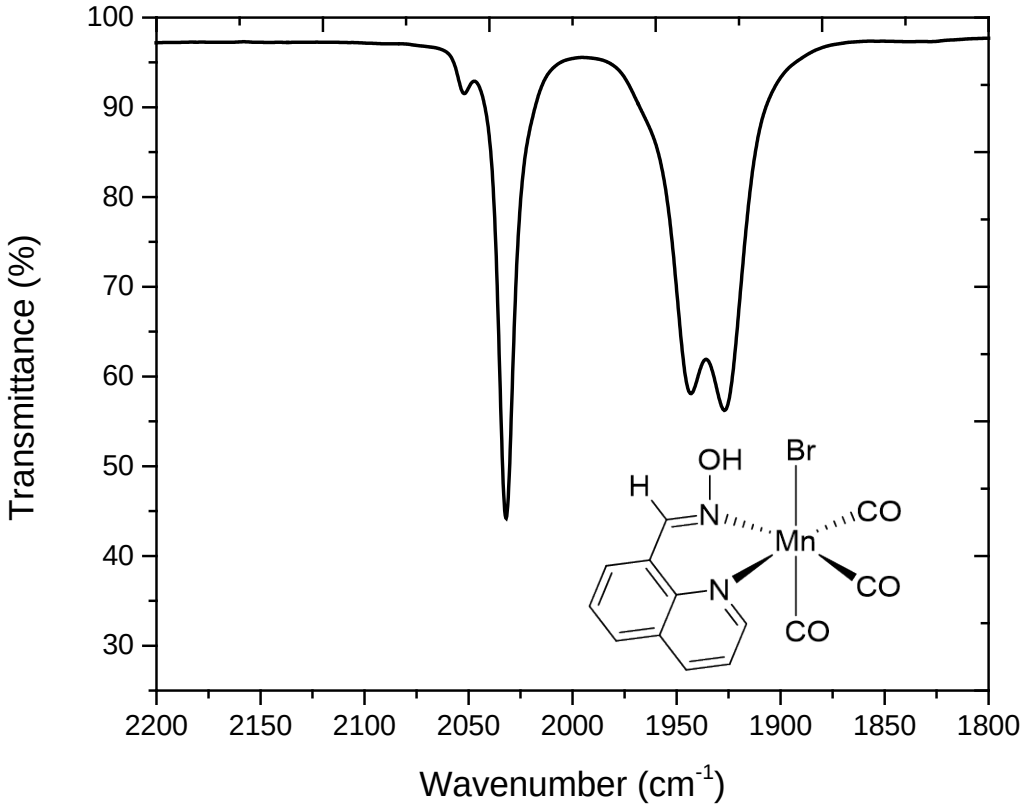


Figure S31. IR (MeCN) spectrum of Compound **Mn-6**. ν/cm^{-1}: [2032, 1943, 1927 ($\nu_{C\equiv O}$)].

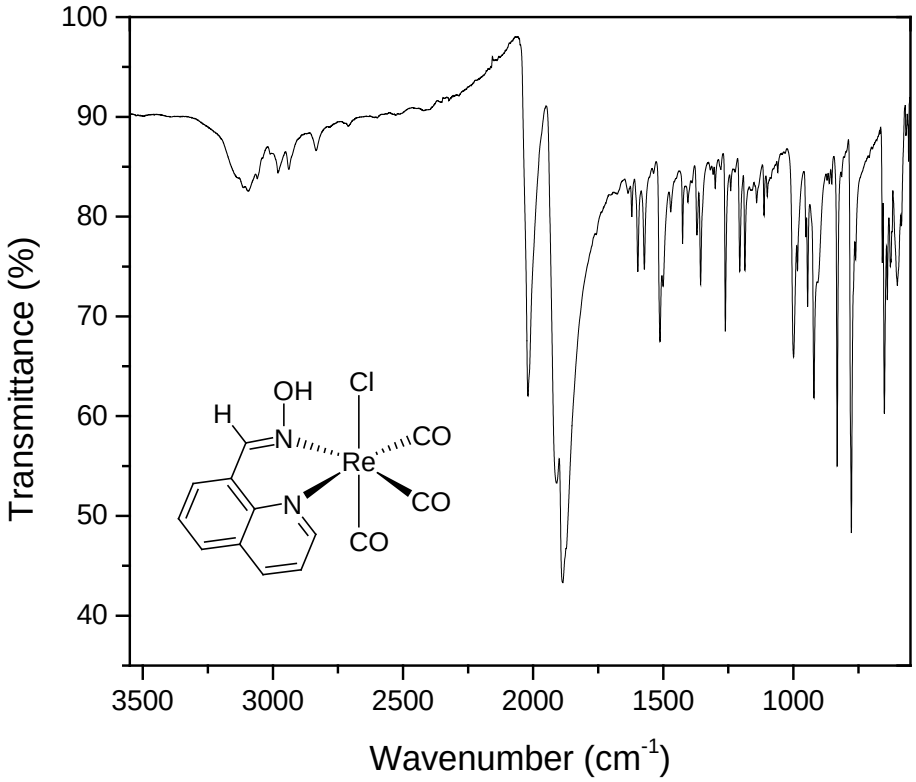


Figure S32. IR (ATR) spectrum of **Re-6**. ν/cm^{-1}: 3095 ($\nu_{O\text{-}H}$).

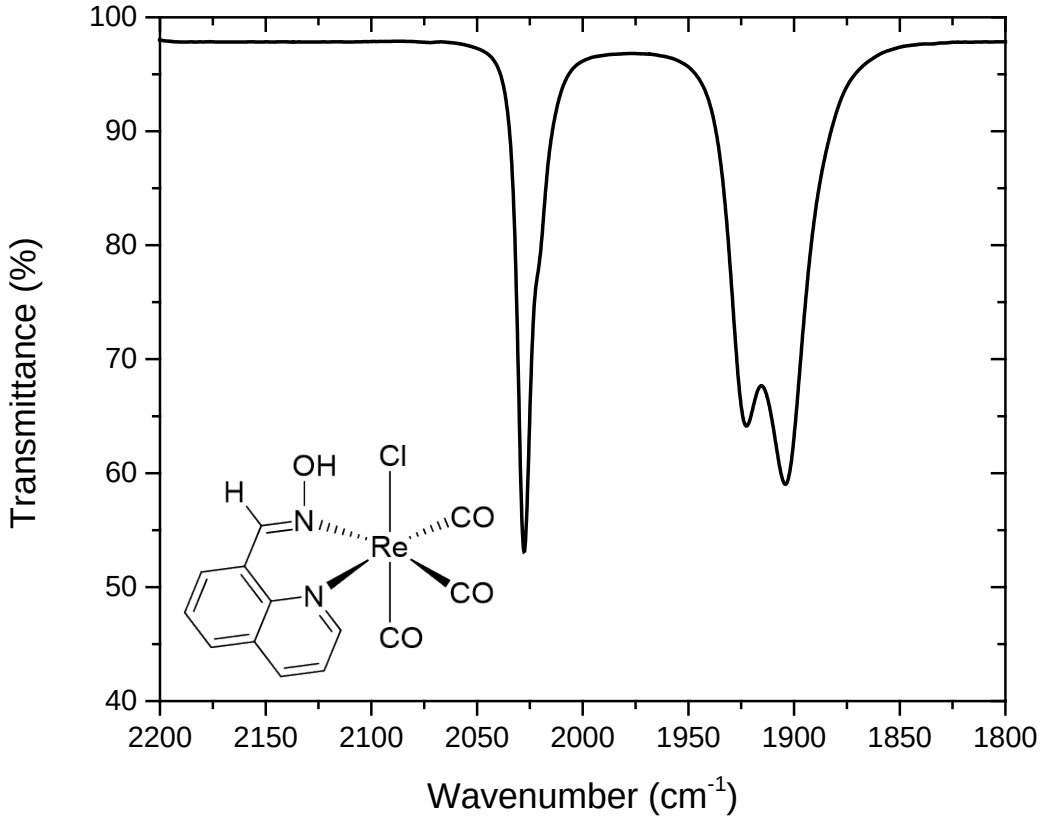


Figure S33. IR (MeCN) spectrum of Compound **Re-6**. ν/cm^{-1}: [2028, 1923, 1904 ($\nu_{C\equiv O}$)].

Electrochemistry

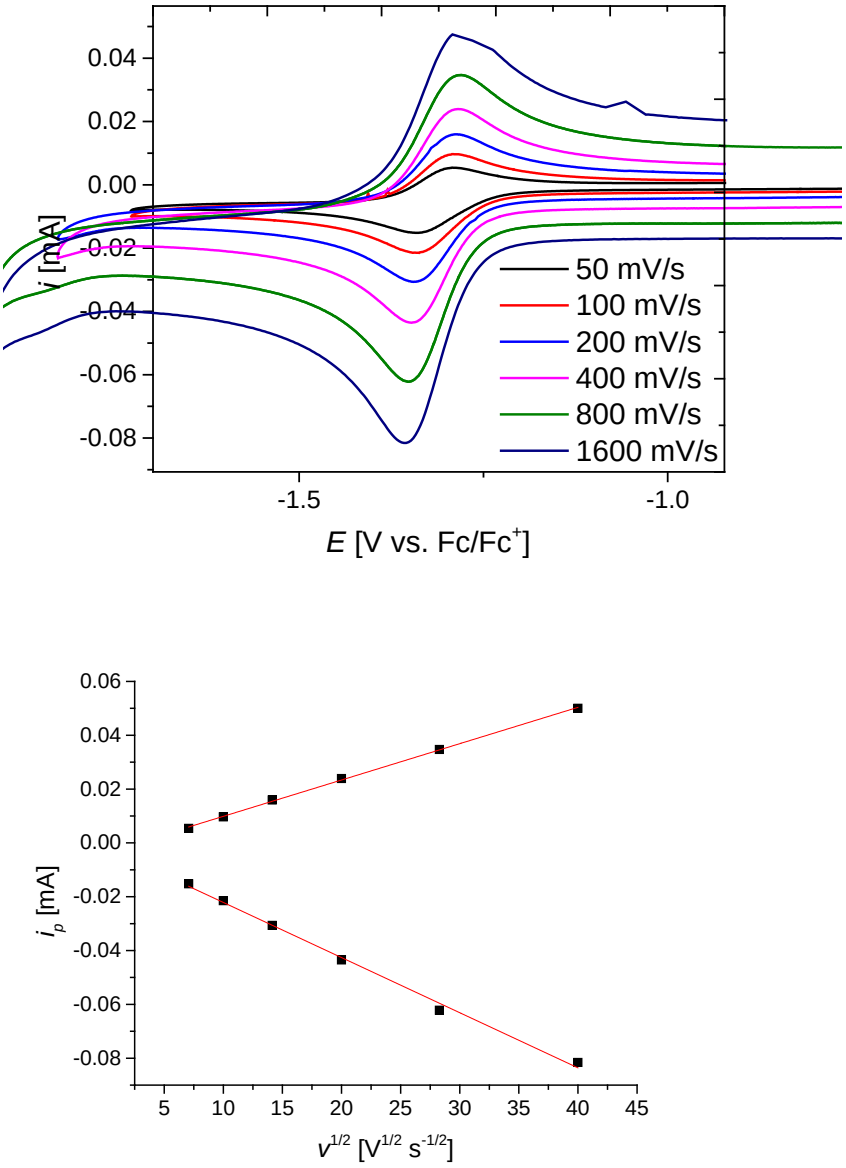


Figure S34. Cyclic voltammograms of **Re-4im** at different scan rates (top), with a graph of i_p vs. $\nu^{1/2}$ (bottom) under N_2. Calculated lines of best fit are shown in red. Experiments performed in acetonitrile containing 100 mM $TBAPF_6$ as supporting electrolyte.

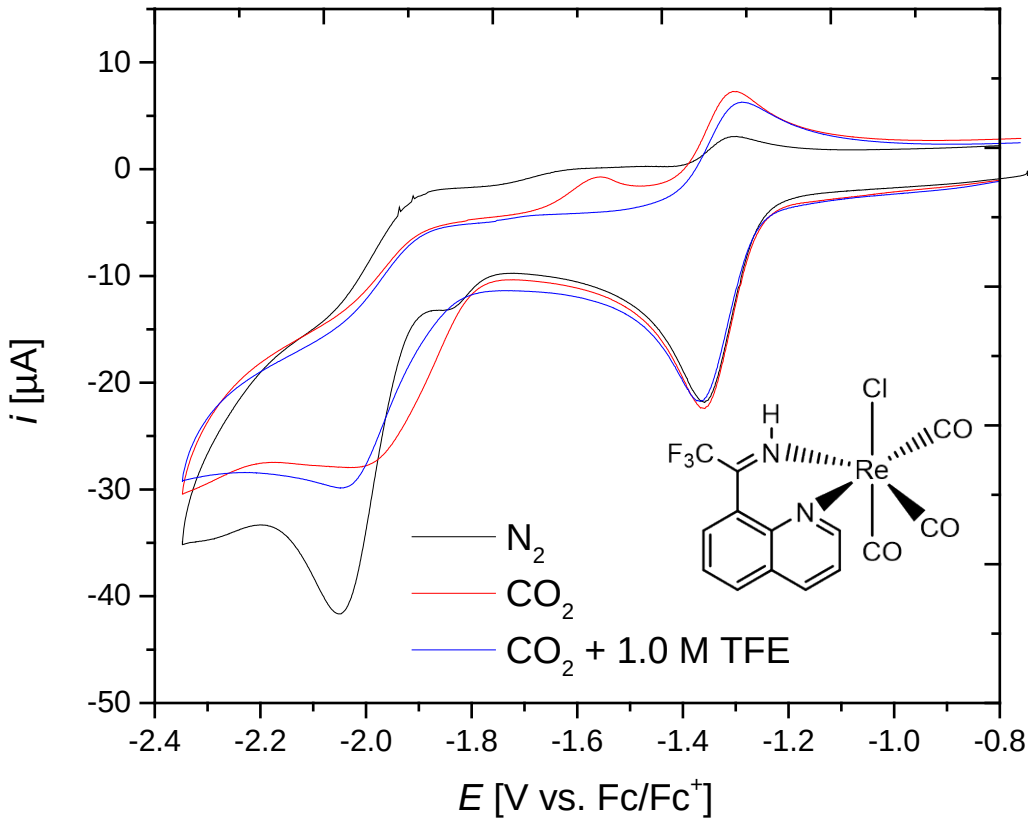


Figure S35. Cyclic voltammograms of **Re-4im**. Experiment performed at 100 mV/s in acetonitrile containing 100 mM $TBAPF_6$ as supporting electrolyte under N_2 (black), CO_2 (red), and under CO_2 with added TFE (blue).

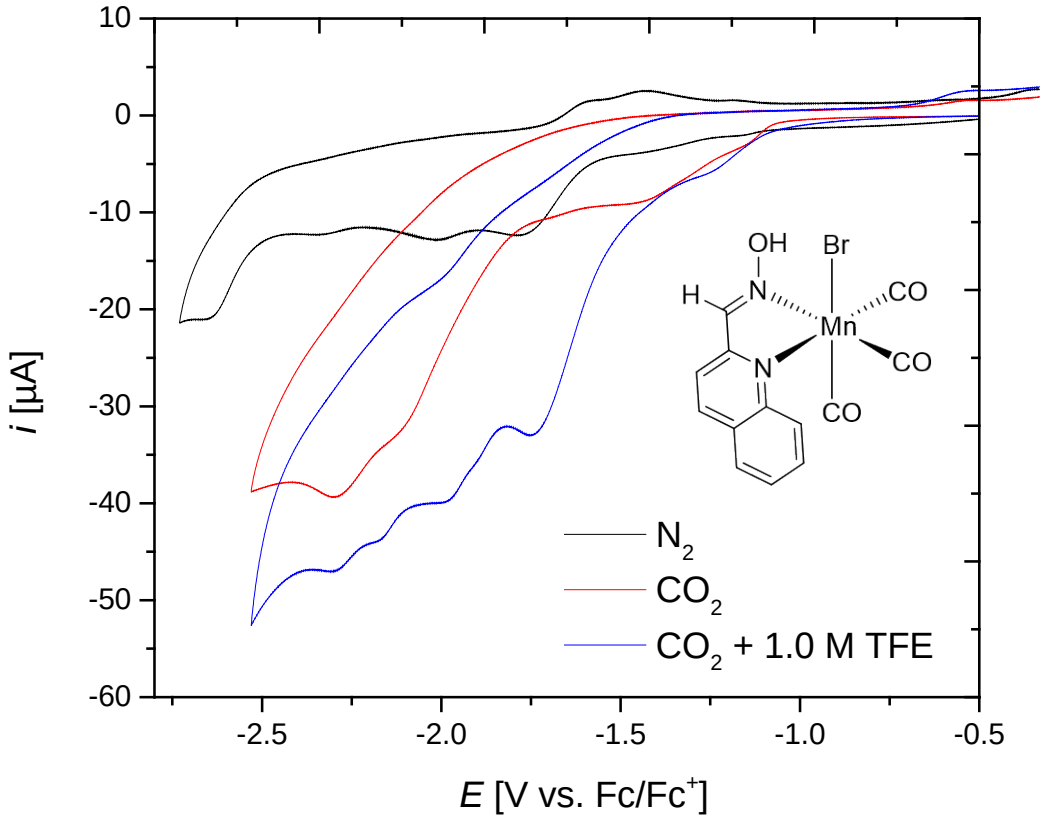


Figure S36. Cyclic voltammograms of **Mn-5**. Experiment performed at 100 mV/s in acetonitrile containing 100 mM $TBAPF_6$ as supporting electrolyte under N_2 (black), CO_2 (red), and under CO_2 with added TFE (blue).

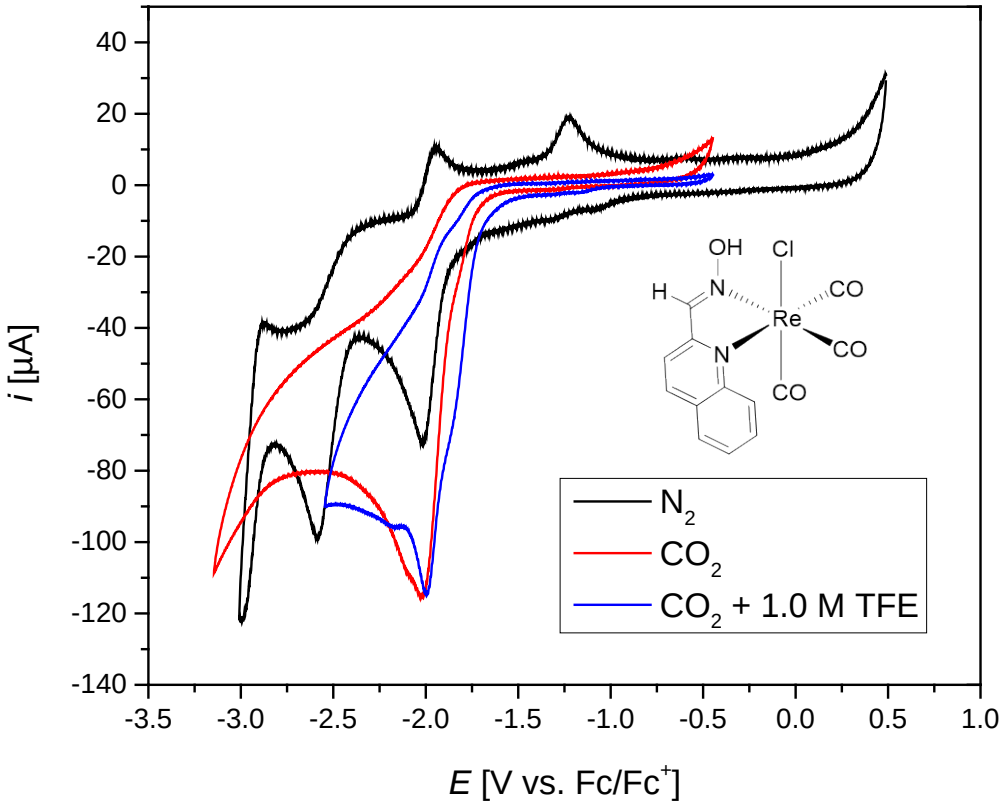


Figure S37. Cyclic voltammograms of **Re-5**. Experiment performed at 500 mV/s in acetonitrile containing 100 mM $TBAPF_6$ as supporting electrolyte under N_2 (black), CO_2 (red), and under CO_2 with added TFE (blue).

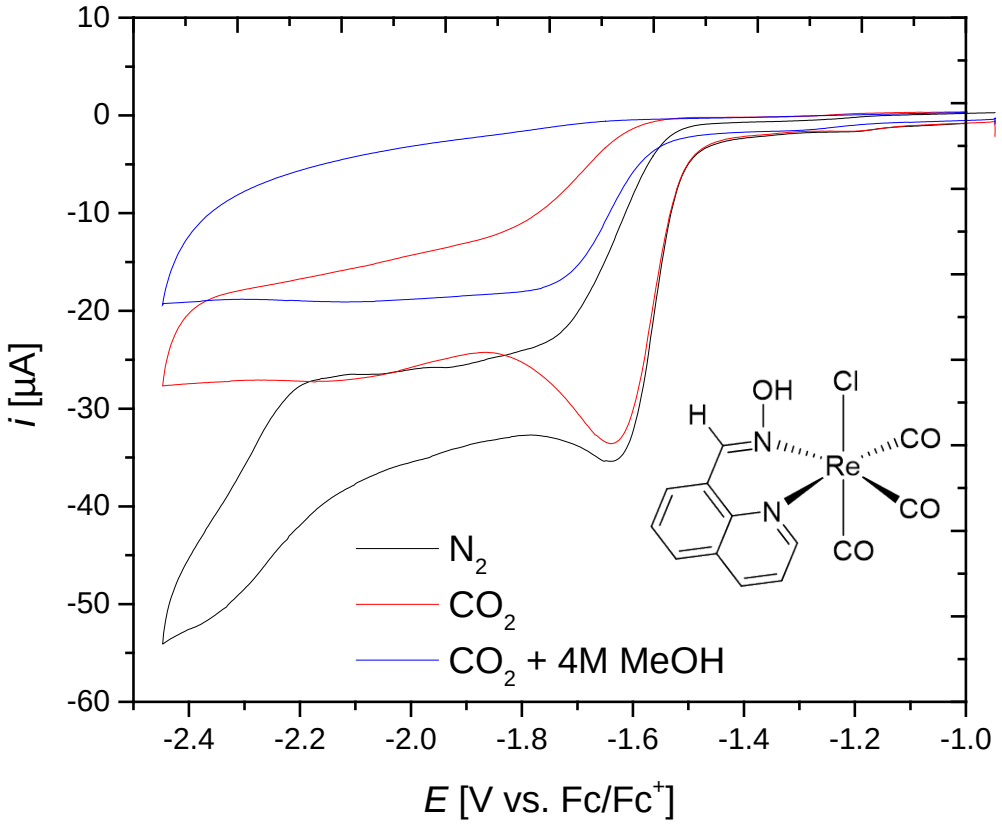


Figure S38. Cyclic voltammograms of **Re-6**. Experiment performed at 100 mV/s in acetonitrile containing 100 mM $TBAPF_6$ as supporting electrolyte under N_2 (black), CO_2 (red), and under CO_2 with added methanol (blue).

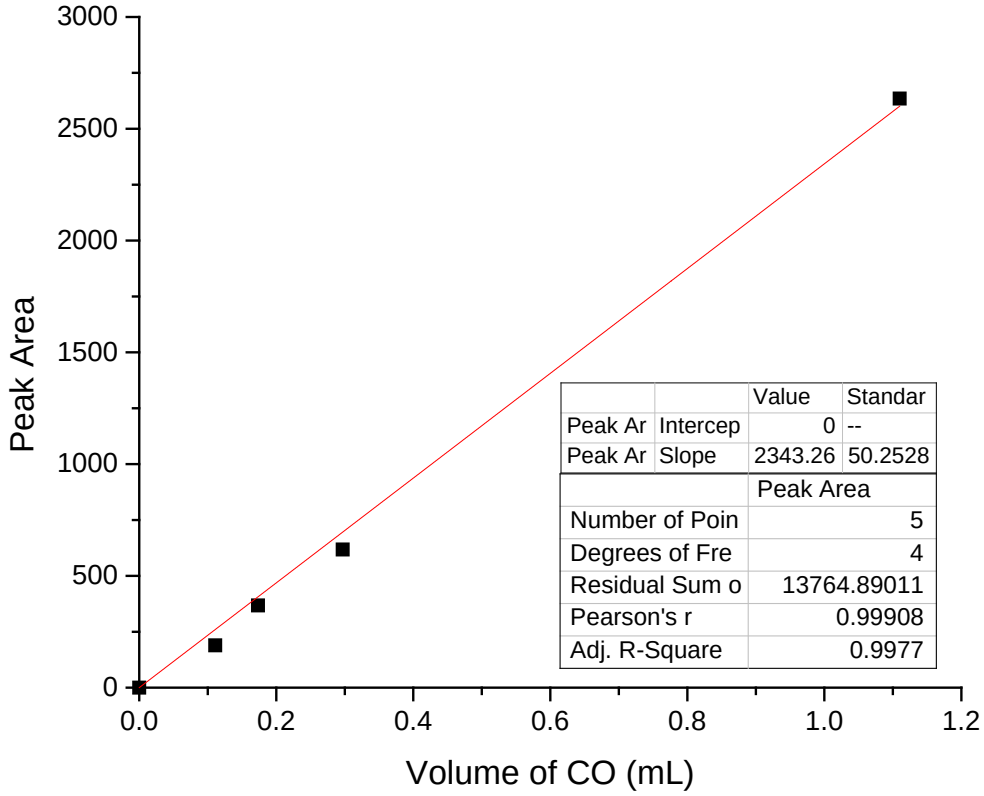


Figure S39. GC Calibration Curve.

Table S2. Bulk Electrolysis Data Summary.

Experimental Charge Passed	0.179 C
Theoretical CO from Charge Passed	9.28 x 10^{-7} mol
Theoretical CO from complete decomposition of complex in solution	6 x 10^{-5} mol
Experimental CO Produced	7.20 x 10^{-6} mol
Faradaic Efficiency	776%

Calculation of Theoretical CO from Charge Passed if FE = 100%:

$$\frac{0.179\ C}{[2\ electrons\ per\ CO\ formed] * 96485 \frac{C}{mol\ CO}} = 9.28 * 10^{-7}\ mol\ CO$$

Calculation of Theoretical CO from Complete Decomposition of Complex:

$$\frac{3\ moles\ of\ CO}{1\ mole\ of\ complex} * \frac{1\ mole\ of\ complex}{391.059\ g\ complex} * 0.008\ g\ complex = 6 * 10^{-5}\ mol\ C$$

Calculation of Experimental CO Produced:

From Calibration Curve:

$$Peak\ Area = 414.4 = 2343.26 * [Volume\ of\ CO\ in\ mL]$$
$$[Volume\ of\ CO\ in\ mL] = 0.177\ mL$$

Conversion from mL to moles:

$$[Volume\ of\ CO\ in\ mL] * \frac{1.14\ g\ CO}{1000\ mL\ CO} * \frac{1\ mol\ CO}{28.01\ g\ CO} = 7.198 * 10^{-6}\ mol\ CO$$

Calculation of Faradaic Efficiency:

$$\frac{Moles\ of\ CO\ measured}{Moles\ of\ CO\ formed\ if\ all\ charge\ passed\ went\ towards\ forming\ CO} = \frac{Charge\ passed\ to\ form\ CO\ measured\ with\ 2\ electrons\ for\ each\ CO}{Charge\ experimentally\ passed}$$
$$= 776\%$$

Table S3. DFT-calculated orbital energies and compositions for Mn(I) and Re(I) quinoline oximes/imines.

Orbital Energies				Orbital Composition			
Complex	$\Delta E_{HOMO-LUMO}$ (eV)	Orbital	E (eV)	M	quinoline	halide	CO
		LUMO+1	-2.29	3.0	89.9	0.1	3.6
		LUMO	-3.29	3.3	88.2	1.0	4.1
Re-4im	2.88	HOMO	-6.17	35.7	8.3	28.9	25.3
		HOMO-1	-6.20	36.6	4.9	31.2	25.2
		HOMO-2	-6.75	53.0	7.6	3.4	34.9
		LUMO+1	-1.72	2.1	92.9	0.1	2.1
		LUMO	-2.83	1.4	93.5	1.2	1.4
Mn-6	3.30	HOMO	-6.13	26.4	1.4	61.4	9.6
		HOMO-1	-6.14	27.5	5.4	56.7	8.7
		HOMO-2	-6.76	26.3	32.3	27.0	11.0
		LUMO+1	-1.95	2.8	90	0.1	4.0
		LUMO	-3.00	1.7	92.6	0.7	2.5
Re-6	3.19	HOMO	-6.19	33.5	10.3	29.8	24.5
		HOMO-1	-6.20	36.8	2.5	33.5	26.1
		HOMO-2	-6.84	47.4	12.5	6.0	31.5
		LUMO+1	-1.73	0.7	95.4	0.5	1.0
		LUMO	-2.96	3.0	89.8	2.8	2.5
Mn-5	3.29	HOMO	-6.25	28.8	1.1	58.2	10.4
		HOMO-1	-6.32	27.2	4.2	58.5	8.4
		HOMO-2	-7.05	30.3	25.0	30.0	12.8
		LUMO+1	-1.89	0.7	95.8	0.1	1.0
		LUMO	-3.19	3.7	87.2	1.4	4.9
Re-5	3.06	HOMO	-6.25	37.4	2.7	31.9	26.6
		HOMO-1	-6.38	33.5	7.2	34.8	22.5
		HOMO-2	-7.07	55.9	4.6	0.8	36.8

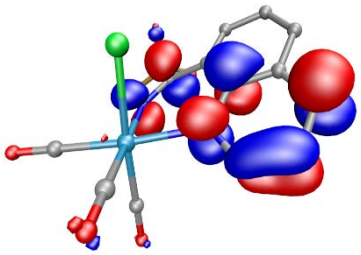
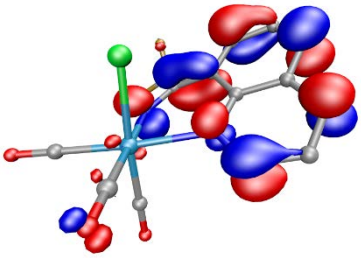
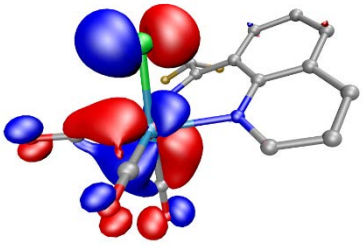
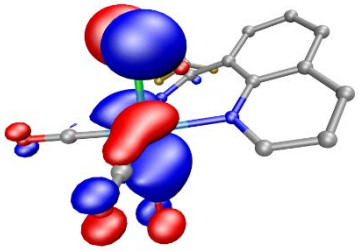
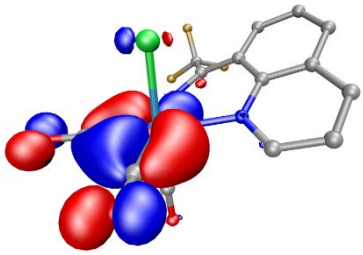
	Re-4im
LUMO+1	
LUMO	
HOMO	
HOMO-1	
HOMO-2	

Figure S40. DFT-calculated orbitals for **Re-4im**.

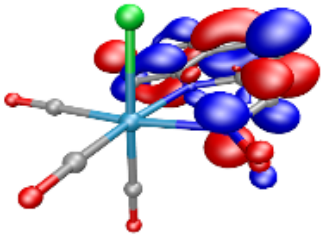
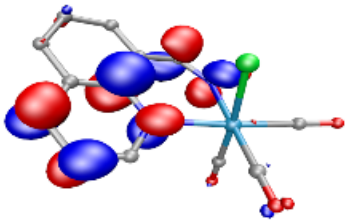
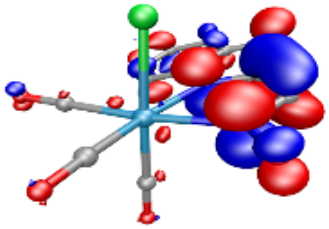
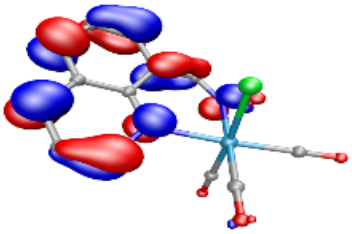
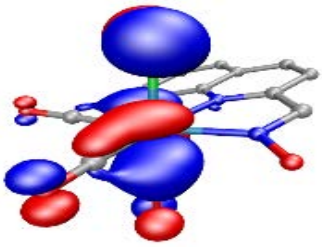
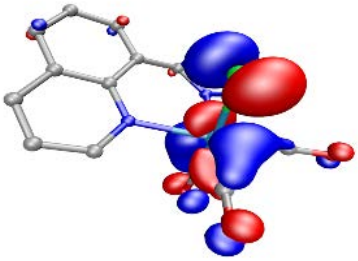
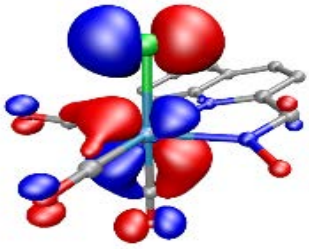
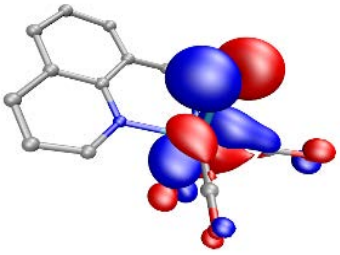
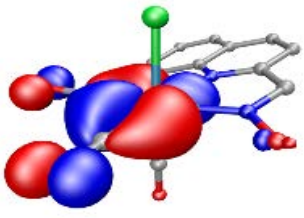
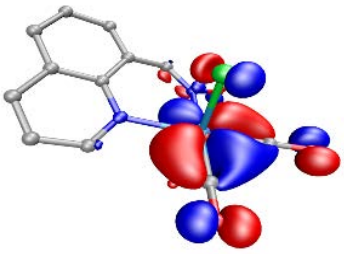
	Re-5	Re-6
LUMO+1		
LUMO		
HOMO		
HOMO-1		
HOMO-2		

Figure S41. DFT-calculated orbitals for **Re-5** and **Re-6**.

Table S4. Calculated and Experimental Bond Lengths for **Mn-5** and **Mn-6.**

		Mn-5 Bond Lengths (Å)		**Mn-6** Bond Lengths (Å)	
Atom 1	Atom 2	Exp.	Calc.	Exp.	Calc.
Mn1	Br1	2.52253	2.5097	2.5391	2.5093
Mn1	N1	2.02218	1.9956	2.0261	2.0105
Mn1	N2	2.1001	2.1373	2.0882	2.1331
Mn1	C11	1.7991	1.7873	1.8182	1.7875
Mn1	C12	1.8181	1.7905	1.8062	1.8097
Mn1	C13	1.8171	1.813	1.7922	1.7878
N1	O1	0.842	0.9646	1.3952	1.3704
N1	C1	1.3741	1.3526	1.2743	1.2728
O1	H1O	1.2812	1.277	0.852	0.9639
C1	H1	0.950	1.0844	0.950	1.0871
C1	C2	1.4532	1.4386	1.4493	1.4404
C2	C3	1.4082	1.4069	1.3823	1.3818
C2	C10	1.3421	1.3308	1.4312	1.4253
C3	H3	0.9498	1.0828	0.950	1.0842
C3	C4	1.3642	1.3599	1.3963	1.3970
C4	H4	0.950	1.0844	0.949	1.0829
C4	C5	1.4101	1.4067	1.363	1.3649
C5	H5	1.4172	1.4098	0.949	1.0843
C5	C6	1.4242	1.4261	1.414	1.4113
C6	C7	0.949	1.0849	1.413	1.4067
C6	C10	1.3671	1.3658	1.420	1.4240
C7	H7	0.950	1.0829	0.950	1.0842
C7	C8	1.4102	1.4059	1.357	1.3624
C8	H8	0.950	1.0832	0.950	1.0818
C8	C9	1.3722	1.3681	1.389	1.3975
C9	H9	0.949	1.0785	0.950	1.0813
C9	N2	1.4151	1.4091	1.334	1.3213
N2	C10	1.3772	1.3658	1.377	1.3646
C11	O11	1.1502	1.1445	1.137	1.1438
C12	O12	1.1452	1.1438	1.142	1.1404
C13	O13	1.1471	1.1392	1.148	1.1452

Table S5. Calculated and Experimental Bond Angles for **Mn-5** and **Mn-6.**

			Mn-5 Bond Angles (°)		**Mn-6** Bond Angles (°)	
Atom 1	Atom 2	Atom 3	Exp.	Calc.	Exp.	Calc.
Br1	Mn1	N1	87.063	87.2	88.655	87.9
Br1	Mn1	N2	86.413	87.5	87.744	87.72
Br1	Mn1	C12	175.8	174	85.057	87.23
Br1	Mn1	C13	85.844	87.8	87.347	83.69
Br1	Mn1	C14	85.144	81.3	176.717	177
N1	Mn1	N2	77.364	77	85.806	87.07
N1	Mn1	C12	95.995	98.3	95.288	93
N1	Mn1	C13	96.665	93.2	175.718	171.5
N1	Mn1	C14	171.58	168	94.368	94.09
N2	Mn1	C12	97.065	92.3	172.698	174.9
N2	Mn1	C13	170.45	169	92.538	94
N2	Mn1	C14	98.925	101	93.808	90.15
C12	Mn1	C13	90.936	93.3	85.889	85.18
C12	Mn1	C14	91.976	93.2	93.31	94.89
C13	Mn1	C14	85.986	87.8	89.699	94.38
H1O	O1	N1	1061	105	121.51	120.3
Mn1	N1	O1	128.95	128	127.71	129
Mn1	N1	C1	117.19	118	110.52	110.6
O1	N1	C1	113.31	114	106.2	104.6
N1	C1	H1	122.2	121	117.5	117
N1	C1	C2	115.51	116	124.92	125.9
H1	C1	C2	122.2	123	117.5	117.1
C1	C2	C3	120.81	120	117.22	115
C1	C2	N2	115.11	116	124.02	125.4
C3	C2	N2	124.11	124	118.72	119.3
C2	C3	H3	120.7	119	118.7	118.2
C2	C3	C4	118.61	119	122.62	122.6
H3	C3	C4	120.7	122	118.7	119.2
C3	C4	H4	120.2	121	120.3	119.7
C3	C4	C5	119.51	119	119.52	119.2
H4	C4	C5	120.2	119	120.3	121.1
C4	C5	C6	121.91	121	119.8	121.1
C4	C5	C10	118.71	119	120.42	120.5
C6	C5	C10	119.41	120	119.8	118.4
C5	C6	H6	119.7	119	121.12	120.4
C5	C6	C7	120.51	121	120.42	120.7

H6	C6	C7	119.7	121	118.52	118.9
C6	C7	H7	120	120	120.3	119.3
C6	C7	C8	119.91	119	119.32	119.1
H7	C7	C8	120	120	120.4	121.6
C7	C8	H8	119.5	120	120.7	122.3
C7	C8	C9	121.01	121	118.72	118.4
H8	C8	C9	119.5	119	120.7	119.3
C8	C9	H9	119.8	120	117.5	118.7
C8	C9	C10	120.31	121	125.02	124.8
H9	C9	C10	119.9	119	117.5	116.5
C5	C10	C9	118.51	118	117.81	116.1
C5	C10	N2	121.11	121	123.61	125.7
C9	C10	N2	120.31	121	116.82	117.9
Mn1	N2	C2	111.8	111	118.12	117.6
Mn1	N2	C10	129.76	131	120.82	121.6
C2	N2	C10	117.41	118	121.12	120.8
Mn1	C12	O2	176.31	177	174.52	178.6
Mn1	C13	O3	175.61	178	178.42	176.6
Mn1	C14	O4	175.71	176	176.42	178

Table S6. Calculated and Experimental Bond Lengths for **Re-5** and **Re-6.**

		Re-5 Bond Lengths (Å)		**Re-6** Bond Lengths (Å)	
Atom 1	Atom 2	Exp.	Calc.	Exp.	Calc.
Cl1	Re1	2.47796	2.444	2.48285	2.447
Re1	N1	2.1581	2.127	2.1452	2.139
Re1	N2	2.2142	2.249	2.2171	2.243
Re1	C12	1.9033	1.911	1.9052	1.907
Re1	C13	1.9253	1.902	1.9201	1.905
Re1	C14	1.9282	1.928	1.9252	1.921
O1	H1O	0.852	0.966	0.842	0.966
O1	N1	1.3743	1.353	1.3942	1.370
N1	C1	1.2813	1.278	1.2822	1.275
C1	H1	0.950	1.084	0.950	1.087
C1	C2	1.4583	1.441	1.4542	1.445
C2	C3	1.4073	1.406	1.3362	1.322
C2	N2	1.3412	1.333	1.3802	1.366
C3	H3	0.950	1.082	0.950	1.081
C3	C4	1.3703	1.361	1.4012	1.395
C4	H4	0.949	1.084	0.950	1.082
C4	C5	1.4093	1.407	1.3663	1.363
C5	C6	1.4193	1.409	0.950	1.084
C5	C10	1.4273	1.424	1.4123	1.406
C6	H6	0.950	1.084	1.4223	1.411
C6	C7	1.3633	1.366	1.4242	1.423
C7	H7	0.950	1.083	0.950	1.084
C7	C8	1.4044	1.406	1.3633	1.364
C8	H8	0.950	1.084	0.951	1.083
C8	C9	1.3753	1.368	1.4092	1.397
C9	H9	0.950	1.079	0.950	1.084
C9	C10	1.4053	1.408	1.3882	1.382
C10	N2	1.3813	1.366	1.4312	1.428
C12	O2	1.1603	1.151	1.1562	1.153
C13	O3	1.1483	1.150	1.1492	1.149
C14	O4	1.1483	1.144	1.1513	1.146

Table S7. Calculated and Experimental Bond Angles for **Re-5** and **Re-6.**

			Re-5 Bond Angles (°)		**Re-6** Bond Angles (°)	
Atom 1	Atom 2	Atom 3	Exp.	Calc.	Exp.	Calc.
Cl1	Re1	N1	83.635	83.72	85.624	87.063
Cl1	Re1	N2	82.955	82.62	83.234	86.413
Cl1	Re1	C12	178.83	176.9	178.89	175.8
Cl1	Re1	C13	89.427	93.85	89.955	85.844
Cl1	Re1	C14	89.457	89.52	90.825	85.144
N1	Re1	N2	73.547	73.44	83.055	77.364
N1	Re1	C12	96.929	96.06	93.706	95.995
N1	Re1	C13	98.798	95.78	94.567	96.665
N1	Re1	C14	171.29	173.1	176.05	171.58
N2	Re1	C12	98.219	94.31	95.816	97.065
N2	Re1	C13	169.69	168.9	172.93	170.45
N2	Re1	C14	100.42	104.1	94.856	98.925
C12	Re1	C13	89.51	89.29	90.987	90.936
C12	Re1	C14	90.11	90.6	89.847	91.976
C13	Re1	C14	86.41	86.27	87.147	85.986
H1O	O1	N1	1102	104.7	1072	1061
Re1	N1	O1	128.11	126.1	121.41	128.95
Re1	N1	C1	117.71	119	127.51	117.19
O1	N1	C1	113.62	114.5	110.81	113.31
N1	C1	H1	121.8	121.1	117.2	122.2
N1	C1	C2	116.32	116.7	125.62	115.51
H1	C1	C2	121.8	122.2	117.2	122.2
C1	C2	C3	119.92	119.5	116.51	120.81
C1	C2	N2	116.02	116.9	124.11	115.11
C3	C2	N2	124.12	123.6	117.81	124.11
C2	C3	H3	120.7	119.1	117.7	120.7
C2	C3	C4	118.52	119.1	124.62	118.61
H3	C3	C4	120.8	121.8	117.7	120.7
C3	C4	H4	120.2	121.1	120.8	120.2
C3	C4	C5	119.72	119.3	118.32	119.51
H4	C4	C5	120.2	119.5	120.8	120.2
C4	C5	C6	122.22	121.7	120.4	121.91
C4	C5	C10	118.72	118.6	119.32	118.71
C6	C5	C10	119.12	119.7	120.3	119.41
C5	C6	H6	119.6	118.5	120.52	119.7
C5	C6	C7	120.72	120.7	119.22	120.51
H6	C6	C7	119.7	120.9	120.22	119.7

C6	C7	H7	120.1	120.4	119.8	120
C6	C7	C8	119.82	119.7	120.52	119.91
H7	C7	C8	120.1	119.9	119.7	120
C7	C8	H8	119.5	119.7	120.3	119.5
C7	C8	C9	121.22	121	119.52	121.01
H8	C8	C9	119.4	119.3	120.2	119.5
C8	C9	H9	119.8	120.4	118.8	119.8
C8	C9	C10	120.32	120.7	122.32	120.31
H9	C9	C10	119.9	118.9	118.9	119.9
C5	C10	C9	118.72	118.2	115.11	118.51
C5	C10	N2	120.82	121.2	125.82	121.11
C9	C10	N2	120.42	120.6	118.82	120.31
Re1	N2	C2	113.01	112.5	120.22	111.8
Re1	N2	C10	128.11	129.1	121.42	129.76
C2	N2	C10	117.72	118.1	118.42	117.41
Re1	C12	O2	177.22	179.1	178.72	176.31
Re1	C13	O3	177.42	177.7	177.02	175.61
Re1	C14	O4	178.32	177.8	179.52	175.71

Table S8. Calculated and Experimental Bond Lengths for **Re-4im.**

		Re-4im Bond Lengths (Å)	
Atom 1	Atom 2	Exp.	Calc.
Cl1	Re1	2.47666	2.451
Re1	N1	2.1232	2.101
Re1	N2	2.2162	2.236
Re1	C12	1.9152	1.907
Re1	C13	1.9112	1.907
Re1	C14	1.9232	1.928
N1	H1N	0.872	1.015
N1	C1	1.2812	1.277
C1	C11	1.5393	1.535
C1	C9	1.4692	1.461
C11	F1	1.3393	1.336
C11	F2	1.3343	1.333
C11	F3	1.3352	1.336
C2	H2	0.949	1.082
C2	C3	1.4022	1.394
C2	N2	1.3382	1.323
C3	H3	0.950	1.082
C3	C4	1.3612	1.362
C4	H4	0.950	1.084
C4	C5	1.4123	1.406
C5	C6	1.4132	1.410
C5	C10	1.4282	1.424
C6	H6	0.950	1.084
C6	C7	1.3593	1.362
C7	H7	0.950	1.083
C7	C8	1.4002	1.397
C8	H8	0.950	1.080
C8	C9	1.3872	1.384
C9	C10	1.4443	1.436
C10	N2	1.3832	1.365
C12	O2	1.1483	1.153
C13	O3	1.1572	1.147
C14	O4	1.1533	1.146

Table S9. Calculated and Experimental Bond Angles for **Re-4im.**

			Re-4im Bond Angles (°)	
Atom 1	Atom 2	Atom 3	Exp.	Calc.
Cl1	Re1	N1	85.015	84.8
Cl1	Re1	N2	83.994	82.3
Cl1	Re1	C12	174.56	176
Cl1	Re1	C13	94.806	94
Cl1	Re1	C14	91.676	91.3
N1	Re1	N2	82.966	82.1
N1	Re1	C12	94.758	93.8
N1	Re1	C13	92.708	94.3
N1	Re1	C14	176.45	176
N2	Re1	C12	90.587	94.2
N2	Re1	C13	175.59	175
N2	Re1	C14	97.977	96
C12	Re1	C13	90.649	89.4
C12	Re1	C14	88.689	90
C13	Re1	C14	86.318	87.4
Re1	N1	H1N	1151	116
Re1	N1	C1	131.51	131
H1N	N1	C1	1131	113
N1	C1	C11	116.02	116
N1	C1	C9	125.52	125
C11	C1	C9	118.52	119
C1	C11	F1	111.32	112
C1	C11	F2	112.52	112
C1	C11	F3	110.92	111
F1	C11	F2	107.92	108
F1	C11	F3	107.22	107
F2	C11	F3	106.82	107
H2	C2	C3	117.7	120
H2	C2	N2	117.7	116
C3	C2	N2	124.62	125
C2	C3	H3	121	120
C2	C3	C4	118.12	118
H3	C3	C4	121	122
C3	C4	H4	120.1	122
C3	C4	C5	119.82	119
H4	C4	C5	120.1	119
C4	C5	C6	119.92	120

C4	C5	C10	119.52	119
C6	C5	C10	120.62	121
C5	C6	H6	119.6	119
C5	C6	C7	120.92	120
H6	C6	C7	119.6	121
C6	C7	H7	120.4	121
C6	C7	C8	119.12	119
H7	C7	C8	120.5	120
C7	C8	H8	118.5	117
C7	C8	C9	123.12	123
H8	C8	C9	118.4	120
C1	C9	C8	117.82	118
C1	C9	C10	123.62	123
C8	C9	C10	118.32	118
C5	C10	C9	117.62	118
C5	C10	N2	119.52	120
C9	C10	N2	122.92	123
Re1	N2	C2	114.21	115
Re1	N2	C10	127.11	125
C2	N2	C10	118.32	119
Re1	C12	O2	176.72	179
Re1	C13	O3	179.52	179
Re1	C14	O4	178.02	180

Re-4im Elemental Analysis.

Anal. Found: C, 27.74; H, 1.53; N, 5.38. Calcd: C, 31.73; H, 1.33; N, 5.29.