Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material

Photocatalytic turnover of CO_2 under visible light by [$Re(CO)_3$(1-(1,10) phenanthroline-5-(4-nitro-naphthalimide))Cl] in tandem with the sacrificial donor BIH

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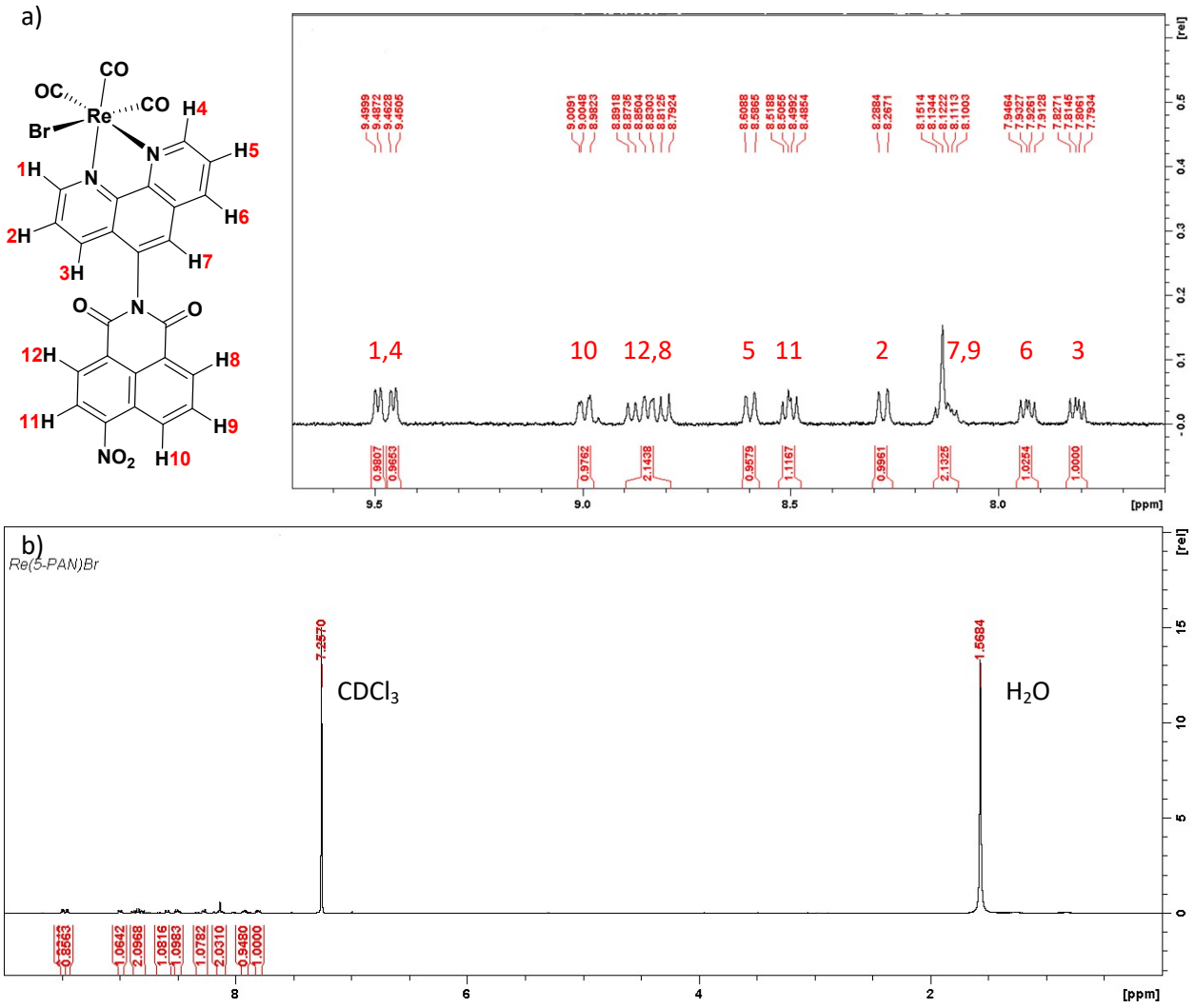
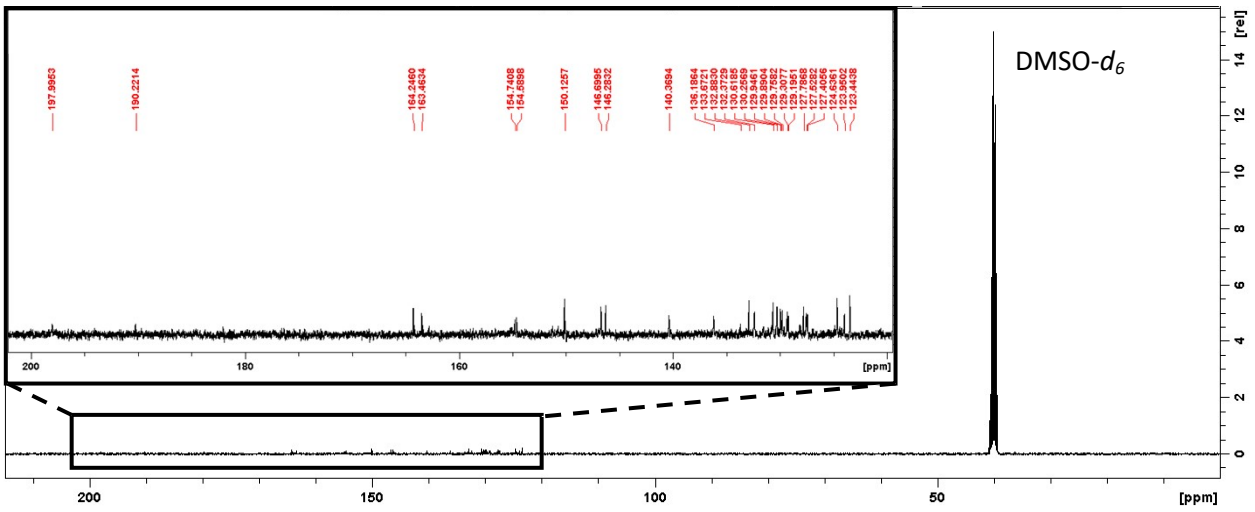
Supplementary Material—Table of Contents

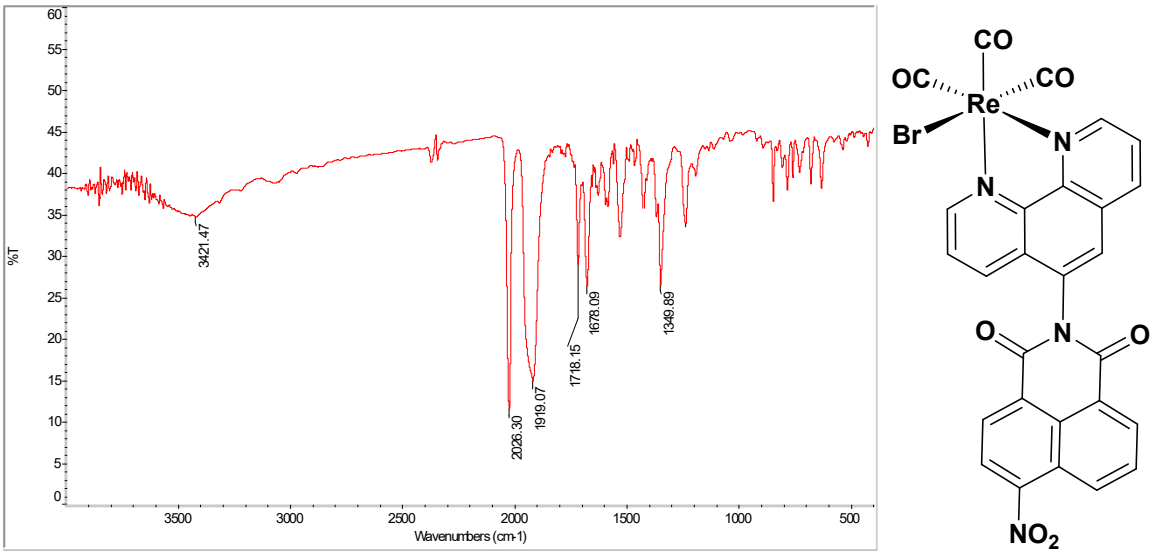
PAGE



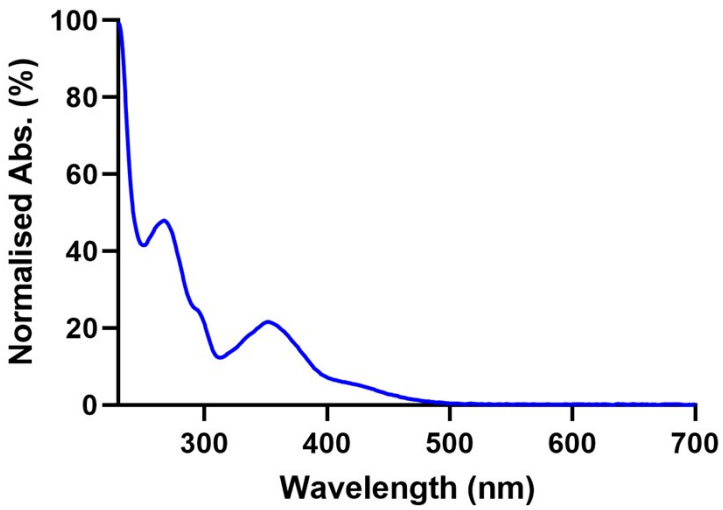
S1. ^{1}H NMR of **2** in $CDCl_3$ (a) with zoomed-in aromatic region (400 MHz, chloroform-d) and image of **2** with assigned peaks and (b) from 0-10 ppm. δ 9.49-9.48 (d, 1H, J=5.1 Hz), 9.46-9.45 (d, 1H, J=4.9 Hz), 9.00-8.98 (dd, 1H, J=9.1, 1.7 Hz), 8.89-8.79 (2H, overlapped), 8.60-8.58 (d, 1H, J=8.9 Hz), 8.50-8.48 (dd, 1H, J=7.9, 5.4 Hz), 8.28-8.26 (d, 1H, J=8.5 Hz), 8.15-8.10 (2H, overlapped), 7.94-7.91 (dd, 1H, J=8.0, 5.4 Hz), 7.82-7.79 (dd, 1H, J=8.4, 5.1 Hz). The appropriate integration of 12 was observed.



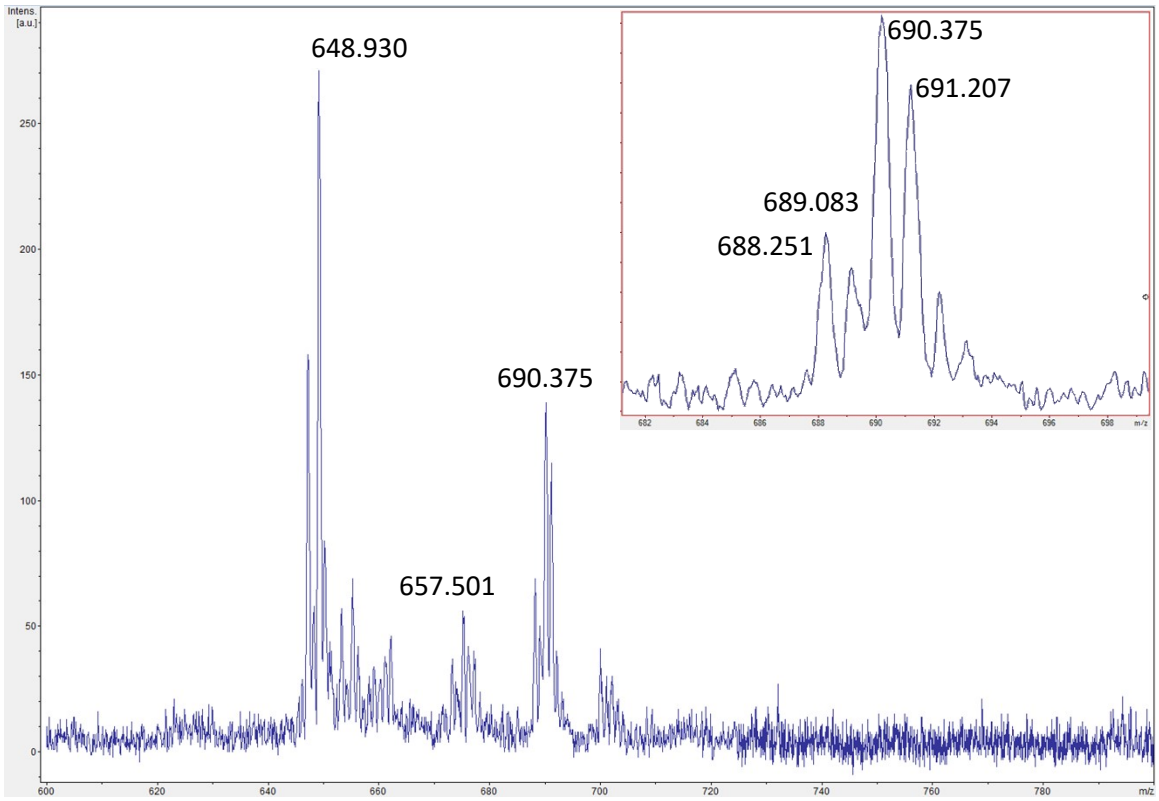
S2. ^{13}C NMR spectrum of **2**, acquired in DMSO-d_6 exhibiting the appropriate number of peaks. The carbon signals at 197 ppm and 180 ppm are assigned to the carbonyl carbons on the rhenium tricarbonyl core.



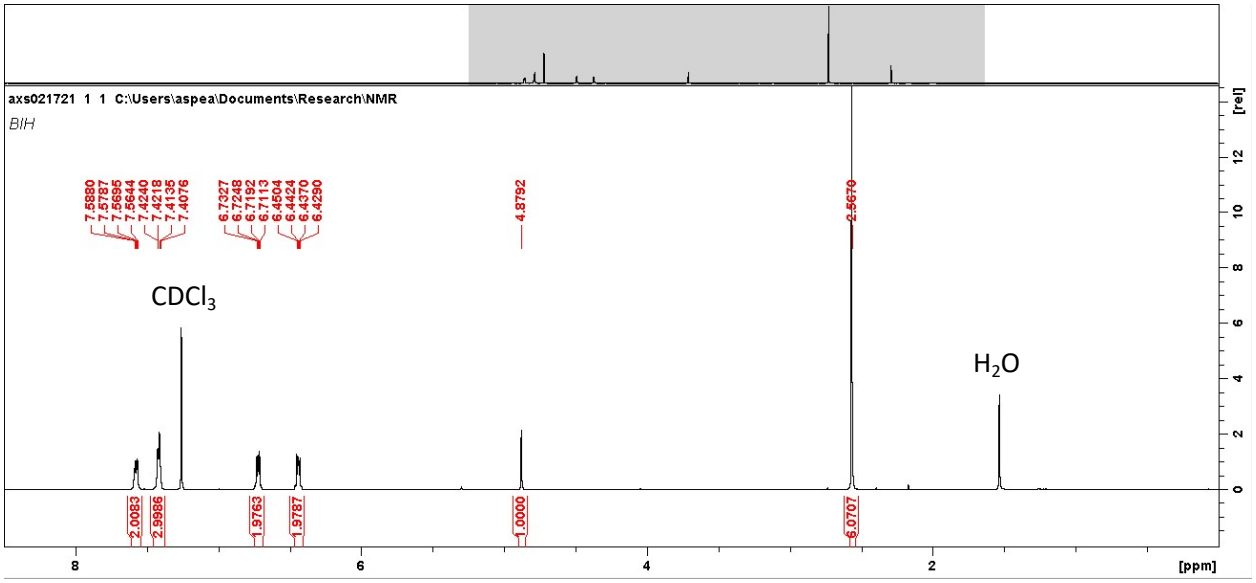
S3. FT-IR of **2** (KBr, cm^{-1}) C≡O: 2026.30; 1919.07, CO-N-CO: 1718.15, C=O: 1678.09, C-NO_2: 1349.89.



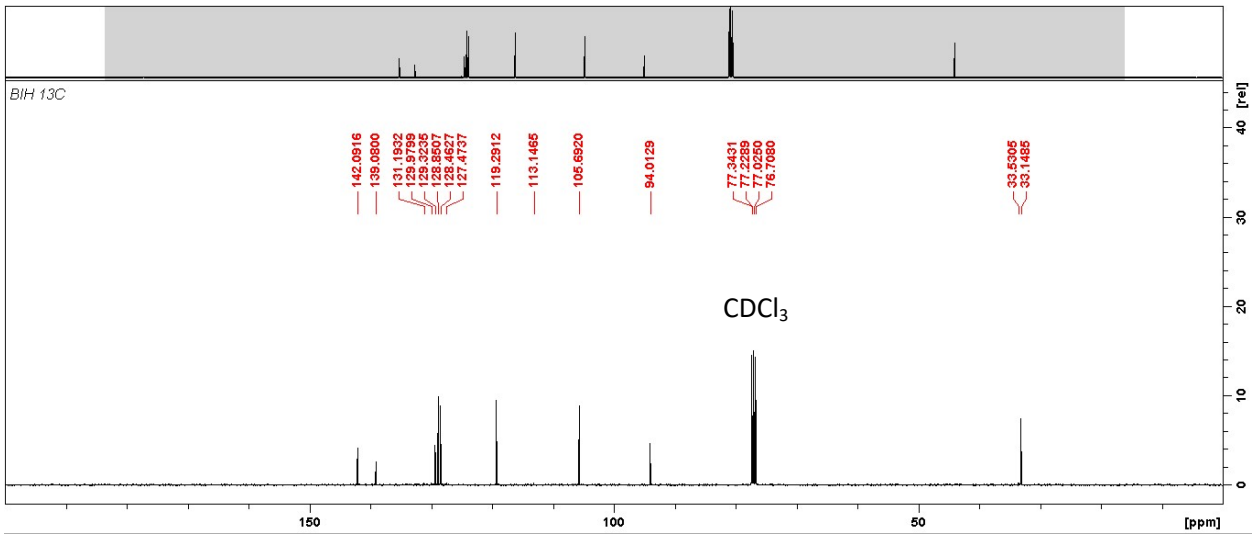
S4. Electronic absorption spectrum of **2** in MeOH/DCM (1:9 v:v).



S5. MALDI-TOF mass spectrum of **2** with insert of zoomed-in peaks of interest (650-700 m/z). The expected mass fragment of 690.375 m/z ([$Re(CO)_3$(**5-PAN**)]$^+$) was observed showing appropriate isotopic distribution as well as other fragments caused by ionization.



S6. ^{1}H NMR of BIH (400 MHz, chloroform-d): δ 2.5670 (s, 6H), 4.88 (s, 1H), 6.43-6.45 (dd, J = 3.2, 5.4 Hz, 2H), 6.71-6.73 (dd, J = 3.2, 5.4 Hz, 2H), 7.41-7.42 (m, 3H), 7.56-7.59 (m, 2H).



S7. ^{13}C NMR of BIH (400 MHz, chloroform-d, D1=5). The peaks at 33.1485 and 33.5305 correspond to the methyl groups of BIH and the integration was set to 1 in subsequent NMR spectra in which the peaks were used as the internal reference.

Crystal Data Collection, Solution, and Refinement of [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br)

The following crystallographic work was done by William W. Brennessel at the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester, New York, United States.

Data collection

A crystal (0.149 x 0.05 x 0.041 mm^3) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections[1]. A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 0.07 and 0.30 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50º steps in *w* at different 2*q*, *k*, and *f* settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 29783 strong reflections from the actual data collection after integration.[1] See Table 1 for additional crystal and refinement information.

Structure solution and refinement

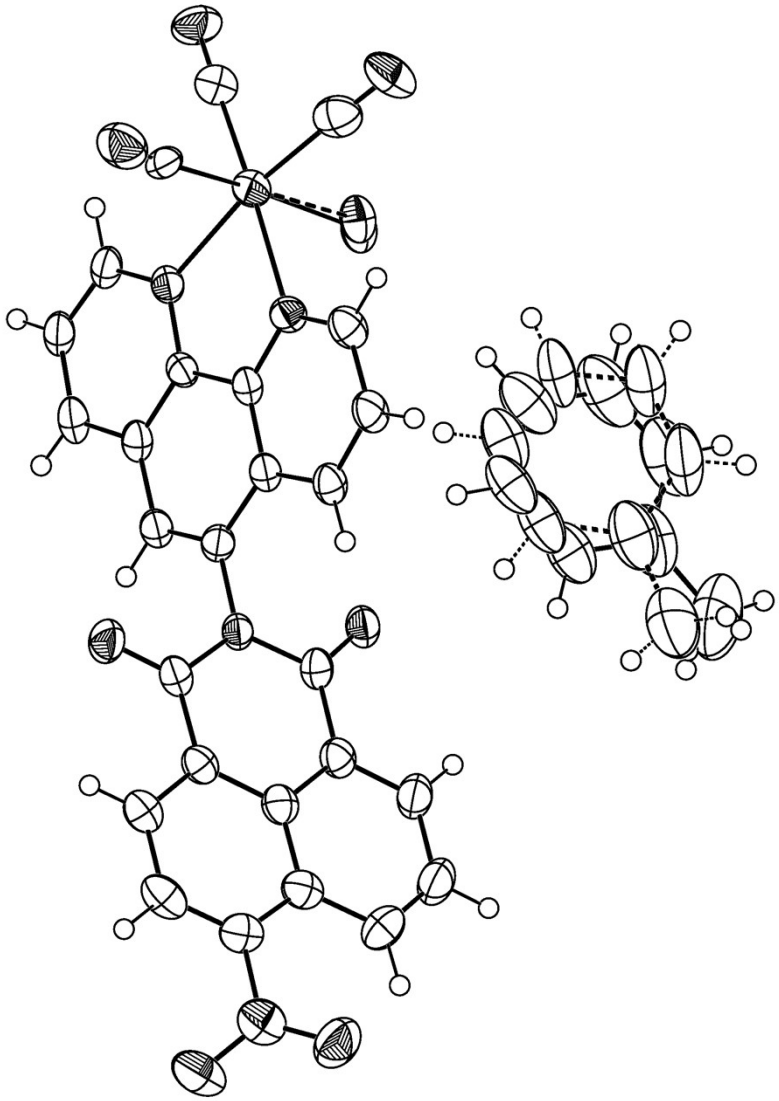
The structure was solved using SHELXT[2] and refined using SHELXL.[3] The space group *P*-1 was determined based on intensity statistics. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to *R*1 = 0.0488 (F^2, $I > 2s(I)$) and *wR*2 = 0.1249 (F^2, all data).

Structure description of [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br)

The asymmetric unit contains one Re complex and one toluene solvate molecule in general positions. The halido ligand site is modeled as a disorder of Br:Cl, 0.80:0.20. This disorder is due to combined batches of **1** and **2** having been made with the starting materials Re(CO)$_5$Cl[4] or Re(CO)$_5$Br. Carbonyl ligand C3-O3, which is *trans* to the halido ligand site, is likely disordered with the halido ligand site, based on the appearance of the ellipsoids and the short C-O distance; however, this disorder was unable to be modeled due to the very small mass of its minor component. The Re-Br and Re-Cl distances were restrained toward the average values obtained from the Cambridge Structural Database[5] for terminal ligands on six-coordinate Re centers. The toluene solvate molecule was modeled as disordered over two positions (0.52:0.48).

Structure manipulation and figure generation were performed using Olex2.[6] Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchison Hall, Department of Chemistry, University of Rochester. The instrument was purchased with funding from NSF MRI program grant CHE-1725028.



S8. ORTEP diagram of mixed [$Re(CO)_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br) and a toluene molecule disordered over two positions (0.52:0.48). Anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Table 1. Crystal data and structure refinement of [$Re(CO)_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br).

Empirical formula	C34 H20 Br0.80 Cl0.20 N4 O7 Re	
Formula weight	853.53	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 8.4778(2) Å	a = 107.983(2)°
	b = 13.3551(2) Å	b = 95.125(2)°
	c = 13.9955(3) Å	g = 96.9490(10)°
Volume	1482.59(5) $Å^3$	
Z	2	
Density (calculated)	1.912 Mg/m^3	
Absorption coefficient	9.949 mm^{-1}	
F(000)	829	
Crystal color, morphology	yellow, needle	
Crystal size	0.149 x 0.05 x 0.041 mm^3	
Theta range for data collection	3.350 to 77.951°	
Index ranges	-10 £ *h* £ 10, -16 £ *k* £ 16, -17 £ *l* £ 17	
Reflections collected	50161	
Independent reflections	6228 [*R*(int) = 0.0678]	
Observed reflections	5962	
Completeness to theta = 74.504°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.54834	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6228 / 202 / 494	
Goodness-of-fit on F^2	1.118	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0488, *wR*2 = 0.1235	
R indices (all data)	*R*1 = 0.0507, *wR*2 = 0.1249	
Largest diff. peak and hole	1.673 and -2.216 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [$Re(CO)_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Re1	3060(1)	2897(1)	6356(1)	36(1)
O1	3161(7)	5250(4)	7604(4)	58(1)
O2	257(6)	2321(5)	7419(4)	54(1)
O3	5449(7)	2675(5)	7973(5)	59(1)
O4	8985(6)	479(4)	3142(4)	48(1)
O5	5572(5)	2101(3)	1662(3)	37(1)
O6	13931(7)	456(4)	-528(5)	60(1)
O7	13365(7)	1984(5)	-563(5)	66(2)
N1	3090(6)	1315(4)	5288(4)	32(1)
N2	4876(6)	3144(4)	5412(4)	32(1)
N3	7322(5)	1354(4)	2444(4)	29(1)
N4	13160(7)	1206(5)	-271(5)	51(1)
C1	3126(8)	4373(6)	7151(6)	48(2)
C2	1306(9)	2533(6)	7040(5)	46(2)
C3	4730(9)	2747(5)	7434(5)	38(1)
C4	2190(7)	406(5)	5255(5)	35(1)
C5	2225(7)	-560(5)	4508(5)	38(1)
C6	3228(7)	-601(5)	3787(5)	38(1)
C7	4205(7)	338(4)	3799(5)	32(1)
C8	5296(7)	377(4)	3091(5)	32(1)
C9	6212(7)	1314(4)	3159(4)	31(1)
C10	6126(7)	2292(4)	3944(4)	30(1)
C11	7041(7)	3282(4)	4046(5)	34(1)
C12	6860(7)	4158(5)	4823(5)	39(1)
C13	5771(7)	4063(5)	5496(5)	39(1)
C14	5051(7)	2267(4)	4641(4)	29(1)
C15	4084(6)	1279(4)	4577(4)	29(1)
C16	8734(7)	913(4)	2510(5)	34(1)
C17	9848(7)	1003(4)	1785(5)	32(1)
C18	9476(7)	1474(4)	1032(5)	35(1)

C19	7986(7)	1861(5)	966(5)	35(1)
C20	6851(7)	1796(4)	1688(5)	33(1)
C21	11257(7)	598(5)	1819(5)	39(1)
C22	12326(7)	658(5)	1123(5)	43(2)
C23	11981(7)	1134(5)	425(5)	39(1)
C24	10542(7)	1553(5)	337(5)	38(1)
C25	10067(9)	2004(6)	-436(5)	47(2)
C26	8617(9)	2348(6)	-484(6)	49(2)
C27	7579(8)	2289(5)	222(5)	43(1)
Br1	987(4)	3007(2)	4910(2)	40(1)
Cl1	1110(40)	3110(30)	5080(20)	40(1)
C28	2370(40)	4851(19)	60(20)	132(10)
C29	2090(20)	4541(13)	1000(20)	82(5)
C30	790(30)	4805(18)	1540(20)	106(7)
C31	610(30)	4510(20)	2380(20)	96(5)
C32	1620(20)	3937(17)	2720(20)	73(5)
C33	2890(30)	3686(15)	2210(19)	63(5)
C34	3160(30)	3983(17)	1372(19)	67(4)
C28'	3540(30)	4781(18)	490(20)	121(10)
C29'	2710(20)	4621(12)	1328(19)	76(5)
C30'	1560(20)	5259(15)	1766(17)	89(6)
C31'	850(20)	5090(16)	2537(18)	81(5)
C32'	1150(20)	4285(12)	2882(19)	66(4)
C33'	2250(30)	3667(15)	2525(17)	65(5)
C34'	3020(30)	3816(17)	1758(19)	70(5)

Table 3. Bond lengths [Å] and angles [°] for [$Re(CO)_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br).

Re(1)-N(1)	2.184(5)	C(10)-C(11)	1.409(7)
Re(1)-N(2)	2.175(5)	C(10)-C(14)	1.399(8)
Re(1)-C(1)	1.933(8)	C(11)-H(11)	0.9500
Re(1)-C(2)	1.932(7)	C(11)-C(12)	1.365(9)
Re(1)-C(3)	2.048(8)	C(12)-H(12)	0.9500
Re(1)-Br(1)	2.6107(18)	C(12)-C(13)	1.398(9)
Re(1)-Cl(1)	2.427(17)	C(13)-H(13)	0.9500
O(1)-C(1)	1.142(9)	C(14)-C(15)	1.439(7)
O(2)-C(2)	1.127(8)	C(16)-C(17)	1.468(8)
O(3)-C(3)	0.963(8)	C(17)-C(18)	1.415(9)
O(4)-C(16)	1.216(7)	C(17)-C(21)	1.372(8)
O(5)-C(20)	1.205(7)	C(18)-C(19)	1.428(9)
O(6)-N(4)	1.240(8)	C(18)-C(24)	1.404(9)
O(7)-N(4)	1.227(8)	C(19)-C(20)	1.470(8)
N(1)-C(4)	1.339(7)	C(19)-C(27)	1.373(9)
N(1)-C(15)	1.354(7)	C(21)-H(21)	0.9500
N(2)-C(13)	1.329(8)	C(21)-C(22)	1.401(9)
N(2)-C(14)	1.360(7)	C(22)-H(22)	0.9500
N(3)-C(9)	1.443(7)	C(22)-C(23)	1.350(10)
N(3)-C(16)	1.404(7)	C(23)-C(24)	1.413(9)
N(3)-C(20)	1.412(7)	C(24)-C(25)	1.442(10)
N(4)-C(23)	1.472(9)	C(25)-H(25)	0.9500
C(4)-H(4)	0.9500	C(25)-C(26)	1.367(10)
C(4)-C(5)	1.392(9)	C(26)-H(26)	0.9500
C(5)-H(5)	0.9500	C(26)-C(27)	1.394(10)
C(5)-C(6)	1.370(9)	C(27)-H(27)	0.9500
C(6)-H(6)	0.9500	C(28)-H(28A)	0.9800
C(6)-C(7)	1.411(8)	C(28)-H(28B)	0.9800
C(7)-C(8)	1.423(8)	C(28)-H(28C)	0.9800
C(7)-C(15)	1.407(8)	C(28)-C(29)	1.53(4)
C(8)-H(8)	0.9500	C(29)-C(30)	1.41(3)
C(8)-C(9)	1.362(8)	C(29)-C(34)	1.40(2)
C(9)-C(10)	1.439(8)	C(30)-H(30)	0.9500

C(30)-C(31)	1.37(3)	C(2)-Re(1)-C(3)	92.2(3)
C(31)-H(31)	0.9500	C(2)-Re(1)-Br(1)	89.3(2)
C(31)-C(32)	1.36(3)	C(2)-Re(1)-Cl(1)	88.6(10)
C(32)-H(32)	0.9500	C(3)-Re(1)-N(1)	94.5(2)
C(32)-C(33)	1.37(3)	C(3)-Re(1)-N(2)	92.2(2)
C(33)-H(33)	0.9500	C(3)-Re(1)-Br(1)	176.92(18)
C(33)-C(34)	1.38(3)	C(3)-Re(1)-Cl(1)	178.8(9)
C(34)-H(34)	0.9500	C(4)-N(1)-Re(1)	126.3(4)
C(28')-H(28D)	0.9800	C(4)-N(1)-C(15)	118.2(5)
C(28')-H(28E)	0.9800	C(15)-N(1)-Re(1)	115.4(4)
C(28')-H(28F)	0.9800	C(13)-N(2)-Re(1)	126.5(4)
C(28')-C(29')	1.48(4)	C(13)-N(2)-C(14)	117.9(5)
C(29')-C(30')	1.42(2)	C(14)-N(2)-Re(1)	115.6(4)
C(29')-C(34')	1.42(2)	C(16)-N(3)-C(9)	118.8(5)
C(30')-H(30')	0.9500	C(16)-N(3)-C(20)	124.8(5)
C(30')-C(31')	1.35(3)	C(20)-N(3)-C(9)	116.3(5)
C(31')-H(31')	0.9500	O(6)-N(4)-C(23)	116.7(6)
C(31')-C(32')	1.35(2)	O(7)-N(4)-O(6)	122.7(7)
C(32')-H(32')	0.9500	O(7)-N(4)-C(23)	120.6(6)
C(32')-C(33')	1.35(2)	O(1)-C(1)-Re(1)	178.7(7)
C(33')-H(33')	0.9500	O(2)-C(2)-Re(1)	178.2(7)
C(33')-C(34')	1.36(3)	O(3)-C(3)-Re(1)	175.5(7)
C(34')-H(34')	0.9500	N(1)-C(4)-H(4)	118.9
N(1)-Re(1)-Br(1)	82.57(14)	N(1)-C(4)-C(5)	122.3(6)
N(1)-Re(1)-Cl(1)	86.2(8)	C(5)-C(4)-H(4)	118.9
N(2)-Re(1)-N(1)	75.28(18)	C(4)-C(5)-H(5)	120.1
N(2)-Re(1)-Br(1)	86.00(16)	C(6)-C(5)-C(4)	119.8(5)
N(2)-Re(1)-Cl(1)	87.1(10)	C(6)-C(5)-H(5)	120.1
C(1)-Re(1)-N(1)	171.9(2)	C(5)-C(6)-H(6)	120.1
C(1)-Re(1)-N(2)	97.6(2)	C(5)-C(6)-C(7)	119.7(6)
C(1)-Re(1)-C(3)	89.6(3)	C(7)-C(6)-H(6)	120.1
C(1)-Re(1)-Br(1)	93.1(2)	C(6)-C(7)-C(8)	124.0(6)
C(1)-Re(1)-Cl(1)	89.5(8)	C(15)-C(7)-C(6)	116.7(5)
C(2)-Re(1)-N(1)	98.4(2)	C(15)-C(7)-C(8)	119.3(5)
C(2)-Re(1)-N(2)	172.6(2)	C(7)-C(8)-H(8)	119.7
C(2)-Re(1)-C(1)	88.3(3)	C(9)-C(8)-C(7)	120.6(5)

C(9)-C(8)-H(8)	119.7	N(3)-C(20)-C(19)	116.8(5)
C(8)-C(9)-N(3)	120.7(5)	C(17)-C(21)-H(21)	119.7
C(8)-C(9)-C(10)	121.8(5)	C(17)-C(21)-C(22)	120.6(6)
C(10)-C(9)-N(3)	117.5(5)	C(22)-C(21)-H(21)	119.7
C(11)-C(10)-C(9)	124.1(5)	C(21)-C(22)-H(22)	120.1
C(14)-C(10)-C(9)	118.2(5)	C(23)-C(22)-C(21)	119.7(6)
C(14)-C(10)-C(11)	117.7(5)	C(23)-C(22)-H(22)	120.1
C(10)-C(11)-H(11)	120.6	C(22)-C(23)-N(4)	117.9(6)
C(12)-C(11)-C(10)	118.9(6)	C(22)-C(23)-C(24)	122.7(6)
C(12)-C(11)-H(11)	120.6	C(24)-C(23)-N(4)	119.4(6)
C(11)-C(12)-H(12)	120.0	C(18)-C(24)-C(23)	116.7(6)
C(11)-C(12)-C(13)	119.9(5)	C(18)-C(24)-C(25)	118.3(6)
C(13)-C(12)-H(12)	120.0	C(23)-C(24)-C(25)	124.9(6)
N(2)-C(13)-C(12)	122.7(6)	C(24)-C(25)-H(25)	119.7
N(2)-C(13)-H(13)	118.7	C(26)-C(25)-C(24)	120.5(6)
C(12)-C(13)-H(13)	118.7	C(26)-C(25)-H(25)	119.7
N(2)-C(14)-C(10)	123.0(5)	C(25)-C(26)-H(26)	119.6
N(2)-C(14)-C(15)	116.7(5)	C(25)-C(26)-C(27)	120.9(6)
C(10)-C(14)-C(15)	120.3(5)	C(27)-C(26)-H(26)	119.6
N(1)-C(15)-C(7)	123.3(5)	C(19)-C(27)-C(26)	120.3(6)
N(1)-C(15)-C(14)	116.8(5)	C(19)-C(27)-H(27)	119.9
C(7)-C(15)-C(14)	119.8(5)	C(26)-C(27)-H(27)	119.9
O(4)-C(16)-N(3)	120.2(5)	H(28A)-C(28)-H(28B)	109.5
O(4)-C(16)-C(17)	123.0(5)	H(28A)-C(28)-H(28C)	109.5
N(3)-C(16)-C(17)	116.7(5)	H(28B)-C(28)-H(28C)	109.5
C(18)-C(17)-C(16)	121.2(5)	C(29)-C(28)-H(28A)	109.5
C(21)-C(17)-C(16)	119.5(6)	C(29)-C(28)-H(28B)	109.5
C(21)-C(17)-C(18)	119.2(6)	C(29)-C(28)-H(28C)	109.5
C(17)-C(18)-C(19)	119.7(6)	C(30)-C(29)-C(28)	123(2)
C(24)-C(18)-C(17)	121.0(6)	C(34)-C(29)-C(28)	120(2)
C(24)-C(18)-C(19)	119.3(6)	C(34)-C(29)-C(30)	117(3)
C(18)-C(19)-C(20)	120.6(5)	C(29)-C(30)-H(30)	120.1
C(27)-C(19)-C(18)	120.6(6)	C(31)-C(30)-C(29)	120(2)
C(27)-C(19)-C(20)	118.8(6)	C(31)-C(30)-H(30)	120.1
O(5)-C(20)-N(3)	119.8(5)	C(30)-C(31)-H(31)	118.4
O(5)-C(20)-C(19)	123.4(5)	C(32)-C(31)-C(30)	123(2)

C(32)-C(31)-H(31)	118.4	C(30')-C(29')-C(34')	116(2)
C(31)-C(32)-H(32)	121.3	C(34')-C(29')-C(28')	121.6(17)
C(31)-C(32)-C(33)	117(3)	C(29')-C(30')-H(30')	119.7
C(33)-C(32)-H(32)	121.3	C(31')-C(30')-C(29')	120.7(17)
C(32)-C(33)-H(33)	118.9	C(31')-C(30')-H(30')	119.7
C(32)-C(33)-C(34)	122(2)	C(30')-C(31')-H(31')	119.6
C(34)-C(33)-H(33)	118.9	C(32')-C(31')-C(30')	120.7(18)
C(29)-C(34)-H(34)	119.8	C(32')-C(31')-H(31')	119.6
C(33)-C(34)-C(29)	120(2)	C(31')-C(32')-H(32')	119.1
C(33)-C(34)-H(34)	119.8	C(31')-C(32')-C(33')	122(2)
H(28D)-C(28')-H(28E)	109.5	C(33')-C(32')-H(32')	119.1
H(28D)-C(28')-H(28F)	109.5	C(32')-C(33')-H(33')	120.3
H(28E)-C(28')-H(28F)	109.5	C(32')-C(33')-C(34')	119.5(19)
C(29')-C(28')-H(28D)	109.5	C(34')-C(33')-H(33')	120.3
C(29')-C(28')-H(28E)	109.5	C(29')-C(34')-H(34')	119.3
C(29')-C(28')-H(28F)	109.5	C(33')-C(34')-C(29')	121.4(19)
C(30')-C(29')-C(28')	122.7(17)	C(33')-C(34')-H(34')	119.3

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Re(CO)_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	34(1)	38(1)	40(1)	14(1)	10(1)	11(1)
O1	59(3)	42(3)	65(3)	-1(2)	16(3)	14(2)
O2	45(3)	70(3)	58(3)	30(3)	26(2)	12(2)
O3	47(3)	63(3)	69(4)	20(3)	18(3)	18(3)
O4	46(3)	58(3)	59(3)	37(2)	17(2)	23(2)
O5	36(2)	34(2)	46(2)	18(2)	6(2)	10(2)
O6	53(3)	46(3)	74(4)	3(3)	23(3)	8(2)
O7	60(3)	80(4)	82(4)	52(4)	27(3)	16(3)
N1	33(2)	29(2)	38(3)	14(2)	8(2)	9(2)
N2	29(2)	31(2)	38(3)	12(2)	9(2)	4(2)
N3	29(2)	28(2)	36(2)	15(2)	7(2)	8(2)
N4	43(3)	49(3)	56(4)	11(3)	7(3)	5(3)
C1	36(3)	64(5)	47(4)	19(3)	8(3)	11(3)
C2	52(4)	47(4)	44(4)	16(3)	14(3)	16(3)
C3	60(4)	32(3)	26(3)	11(2)	16(3)	9(3)
C4	28(3)	36(3)	52(3)	28(3)	9(2)	8(2)
C5	32(3)	35(3)	58(4)	28(3)	10(3)	9(2)
C6	35(3)	27(3)	56(4)	19(3)	4(3)	7(2)
C7	28(3)	29(3)	42(3)	17(2)	2(2)	7(2)
C8	33(3)	28(3)	37(3)	13(2)	5(2)	8(2)
C9	30(3)	31(3)	35(3)	15(2)	6(2)	6(2)
C10	30(3)	26(2)	37(3)	13(2)	4(2)	6(2)
C11	30(3)	27(3)	46(3)	14(2)	5(2)	3(2)
C12	39(3)	24(3)	52(4)	11(3)	11(3)	1(2)
C13	36(3)	29(3)	48(3)	8(3)	6(3)	3(2)
C14	30(3)	25(2)	36(3)	12(2)	4(2)	8(2)
C15	29(3)	26(2)	34(3)	11(2)	8(2)	9(2)
C16	33(3)	27(3)	42(3)	12(2)	5(2)	8(2)
C17	29(3)	28(3)	38(3)	8(2)	3(2)	4(2)

C18	39(3)	25(3)	38(3)	7(2)	4(2)	1(2)
C19	35(3)	28(3)	41(3)	11(2)	6(2)	3(2)
C20	35(3)	26(3)	40(3)	14(2)	4(2)	4(2)
C21	35(3)	35(3)	46(3)	10(3)	5(3)	9(2)
C22	27(3)	35(3)	57(4)	4(3)	5(3)	4(2)
C23	35(3)	36(3)	40(3)	7(3)	7(3)	-2(2)
C24	36(3)	33(3)	40(3)	7(2)	8(3)	1(2)
C25	48(4)	49(4)	48(4)	24(3)	11(3)	0(3)
C26	53(4)	49(4)	56(4)	33(3)	12(3)	9(3)
C27	45(3)	41(3)	53(4)	27(3)	10(3)	10(3)
Br1	36(1)	35(1)	50(1)	17(1)	-2(1)	7(1)
Cl1	36(1)	35(1)	50(1)	17(1)	-2(1)	7(1)
C28	180(30)	82(16)	150(20)	67(16)	5(18)	8(19)
C29	74(12)	52(9)	103(13)	13(9)	-23(9)	4(9)
C30	83(14)	73(15)	160(17)	35(14)	2(12)	26(11)
C31	53(9)	72(12)	156(13)	25(11)	10(9)	18(9)
C32	51(11)	44(11)	102(11)	-2(9)	2(8)	3(7)
C33	55(10)	40(8)	77(12)	-5(7)	-8(8)	12(7)
C34	58(8)	39(8)	86(12)	3(7)	-6(8)	4(6)
C28'	150(30)	74(14)	160(20)	50(15)	53(18)	43(16)
C29'	64(10)	45(8)	108(12)	17(8)	-9(8)	4(7)
C30'	75(13)	62(12)	157(16)	66(12)	23(11)	25(9)
C31'	43(8)	62(10)	160(14)	65(11)	16(9)	13(8)
C32'	43(9)	36(8)	119(11)	31(8)	-4(7)	5(6)
C33'	53(12)	39(7)	86(11)	5(8)	-19(7)	6(7)
C34'	67(9)	36(8)	93(14)	2(8)	-7(9)	12(7)

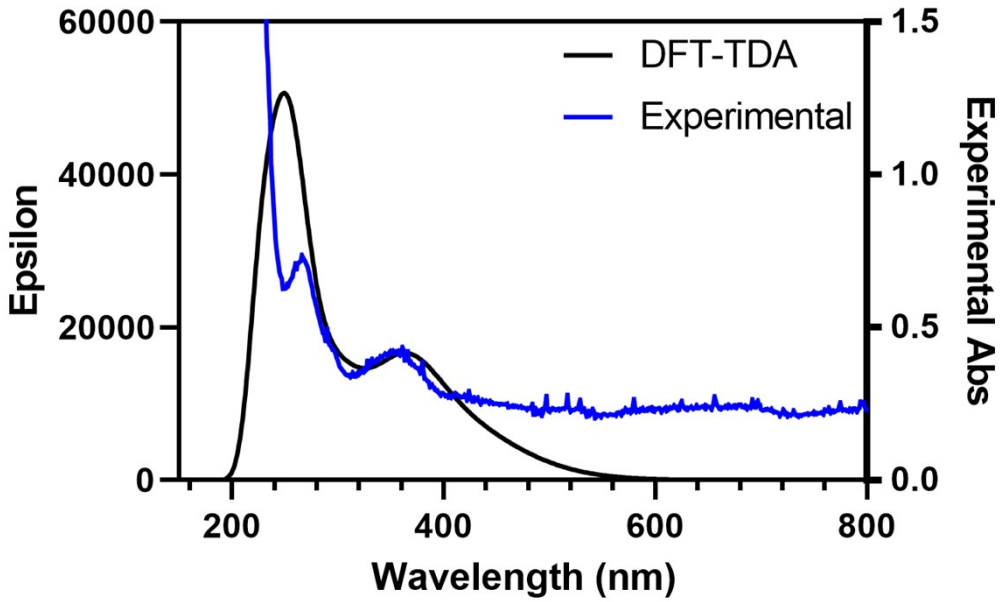
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br).

	x	y	z	U(eq)
H4	1504	420	5758	42
H5	1556	-1188	4500	45
H6	3266	-1259	3280	46
H8	5387	-256	2566	39
H11	7771	3339	3582	41
H12	7472	4831	4907	46
H13	5667	4681	6035	47
H21	11510	276	2319	47
H22	13290	364	1143	51
H25	10768	2063	-916	56
H26	8312	2630	-1006	58
H27	6586	2547	188	52
H28A	1428	5124	-164	198
H28B	2544	4224	-488	198
H28C	3314	5404	217	198
H30	36	5186	1315	127
H31	-255	4715	2745	115
H32	1446	3721	3298	87
H33	3620	3292	2439	76
H34	4072	3810	1045	80
H28D	2810	4477	-152	181
H28E	4488	4427	439	181
H28F	3864	5546	615	181
H30'	1304	5810	1512	107
H31'	121	5543	2840	97
H32'	565	4149	3390	79
H33'	2488	3132	2809	78
H34'	3788	3373	1502	85

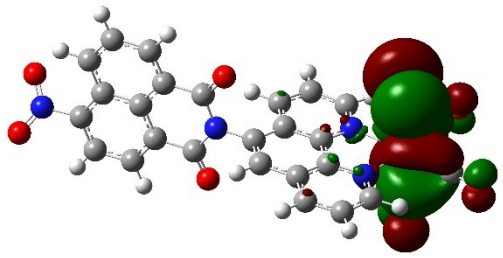
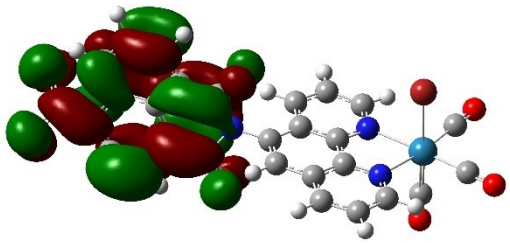
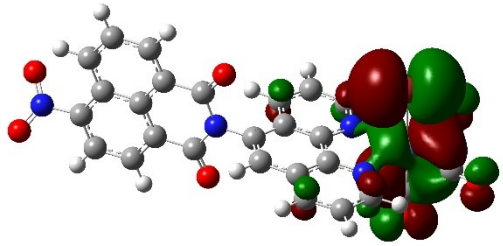
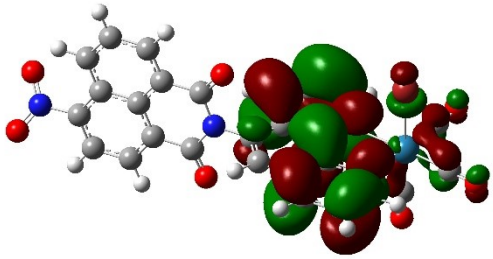
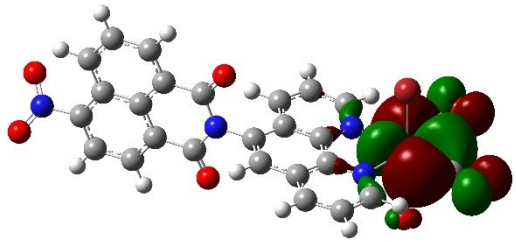
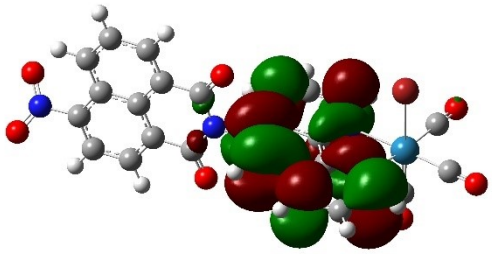
Table 6. Torsion angles [°] for [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br).

Re1-N1-C4-C5	176.3(4)	C8-C9-C10-C14	-0.8(8)
Re1-N1-C15-C7	-177.0(4)	C9-N3-C16-O4	2.2(8)
Re1-N1-C15-C14	3.0(6)	C9-N3-C16-C17	-178.2(5)
Re1-N2-C13-C12	-176.8(5)	C9-N3-C20-O5	-0.9(8)
Re1-N2-C14-C10	177.9(4)	C9-N3-C20-C19	178.9(5)
Re1-N2-C14-C15	-3.2(6)	C9-C10-C11-C12	-179.8(6)
O4-C16-C17-C18	177.2(6)	C9-C10-C14-N2	179.9(5)
O4-C16-C17-C21	-1.1(9)	C9-C10-C14-C15	1.0(8)
O6-N4-C23-C22	33.9(9)	C10-C11-C12-C13	-0.5(9)
O6-N4-C23-C24	-145.7(6)	C10-C14-C15-N1	179.1(5)
O7-N4-C23-C22	-145.3(7)	C10-C14-C15-C7	-1.0(8)
O7-N4-C23-C24	35.1(9)	C11-C10-C14-N2	-1.1(8)
N1-C4-C5-C6	1.2(9)	C11-C10-C14-C15	-179.9(5)
N2-C14-C15-N1	0.1(8)	C11-C12-C13-N2	-0.4(10)
N2-C14-C15-C7	-179.9(5)	C13-N2-C14-C10	0.2(9)
N3-C9-C10-C11	0.8(8)	C13-N2-C14-C15	179.1(5)
N3-C9-C10-C14	179.8(5)	C14-N2-C13-C12	0.5(9)
N3-C16-C17-C18	-2.4(8)	C14-C10-C11-C12	1.2(9)
N3-C16-C17-C21	179.3(5)	C15-N1-C4-C5	-1.2(9)
N4-C23-C24-C18	-179.1(5)	C15-C7-C8-C9	-0.3(8)
N4-C23-C24-C25	4.0(9)	C16-N3-C9-C8	-72.7(7)
C4-N1-C15-C7	0.8(8)	C16-N3-C9-C10	106.8(6)
C4-N1-C15-C14	-179.2(5)	C16-N3-C20-O5	175.9(5)
C4-C5-C6-C7	-0.7(9)	C16-N3-C20-C19	-4.4(8)
C5-C6-C7-C8	179.3(6)	C16-C17-C18-C19	-0.7(8)
C5-C6-C7-C15	0.3(8)	C16-C17-C18-C24	-179.7(5)
C6-C7-C8-C9	-179.3(6)	C16-C17-C21-C22	178.9(5)
C6-C7-C15-N1	-0.3(8)	C17-C18-C19-C20	1.4(8)
C6-C7-C15-C14	179.7(5)	C17-C18-C19-C27	-177.9(6)
C7-C8-C9-N3	179.8(5)	C17-C18-C24-C23	0.5(8)
C7-C8-C9-C10	0.4(9)	C17-C18-C24-C25	177.6(6)
C8-C7-C15-N1	-179.5(5)	C17-C21-C22-C23	1.2(9)
C8-C7-C15-C14	0.5(8)	C18-C17-C21-C22	0.5(9)
C8-C9-C10-C11	-179.8(6)	C18-C19-C20-O5	-179.3(6)

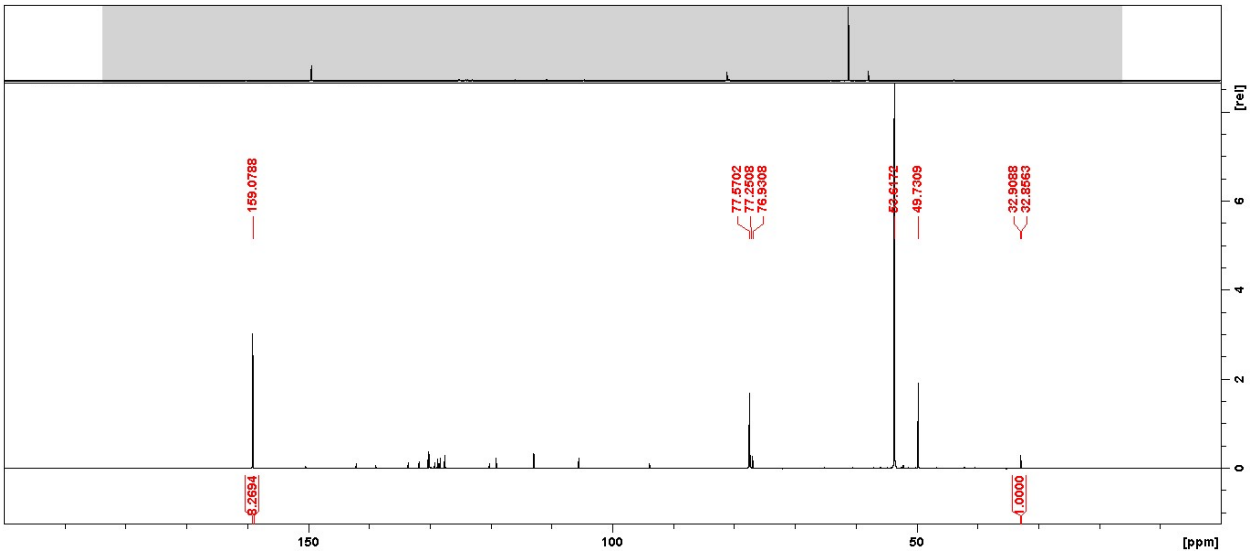
C18-C19-C20-N3	0.9(8)
C18-C19-C27-C26	0.3(10)
C18-C24-C25-C26	0.2(10)
C19-C18-C24-C23	-178.5(5)
C19-C18-C24-C25	-1.4(9)
C20-N3-C9-C8	104.3(6)
C20-N3-C9-C10	-76.3(6)
C20-N3-C16-O4	-174.5(6)
C20-N3-C16-C17	5.1(8)
C20-C19-C27-C26	-179.0(6)
C21-C17-C18-C19	177.6(6)
C21-C17-C18-C24	-1.4(8)
C21-C22-C23-N4	178.2(6)
C21-C22-C23-C24	-2.2(9)
C22-C23-C24-C18	1.3(9)
C22-C23-C24-C25	-175.6(6)
C23-C24-C25-C26	177.1(7)
C24-C18-C19-C20	-179.5(5)
C24-C18-C19-C27	1.2(9)
C24-C25-C26-C27	1.2(11)
C25-C26-C27-C19	-1.5(11)
C27-C19-C20-O5	0.0(9)
C27-C19-C20-N3	-179.7(5)
C28-C29-C30-C31	-179.5(10)
C28-C29-C34-C33	-178.8(12)
C29-C30-C31-C32	-2(2)
C30-C29-C34-C33	2.0(19)
C30-C31-C32-C33	2(3)
C31-C32-C33-C34	-1(3)
C32-C33-C34-C29	-2(3)
C34-C29-C30-C31	-0.4(14)
C28'-C29'-C30'-C31'	-179.5(10)
C28'-C29'-C34'-C33'	-179.6(12)
C29'-C30'-C31'-C32'	-3(2)
C30'-C29'-C34'-C33'	1.0(18)
C30'-C31'-C32'-C33'	5(3)
C31'-C32'-C33'-C34'	-4(3)
C32'-C33'-C34'-C29'	1(2)
C34'-C29'-C30'-C31'	-0.1(14)



S9. Overlay of DFT-TDA (black) and experimental absorbance spectrum (blue) of **1**.

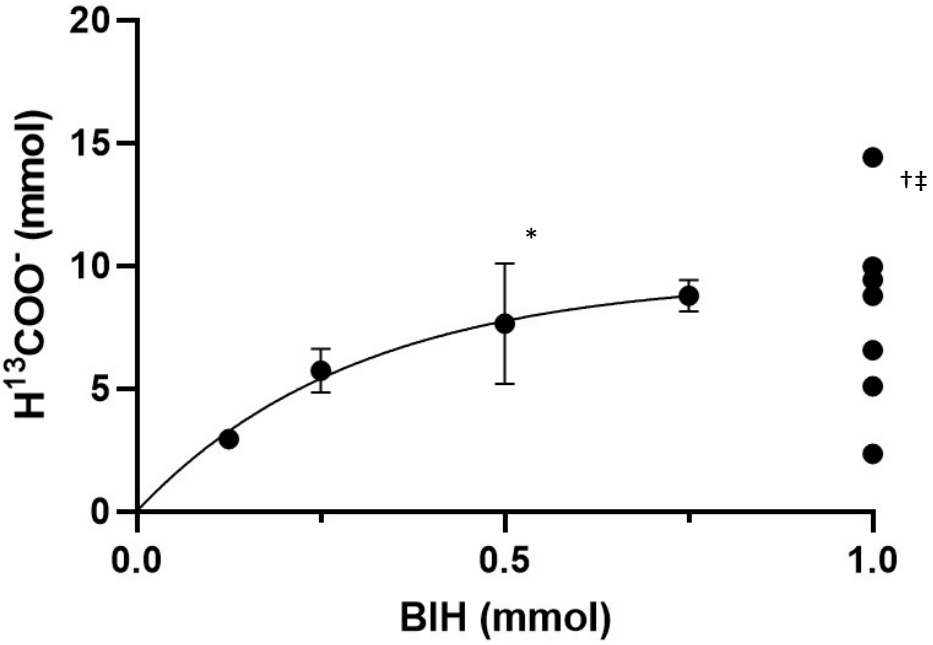
 HOMO	 LUMO
 HOMO-1	 LUMO+1
 HOMO-2	 LUMO+2

S10. Orbital density plots of **1.**



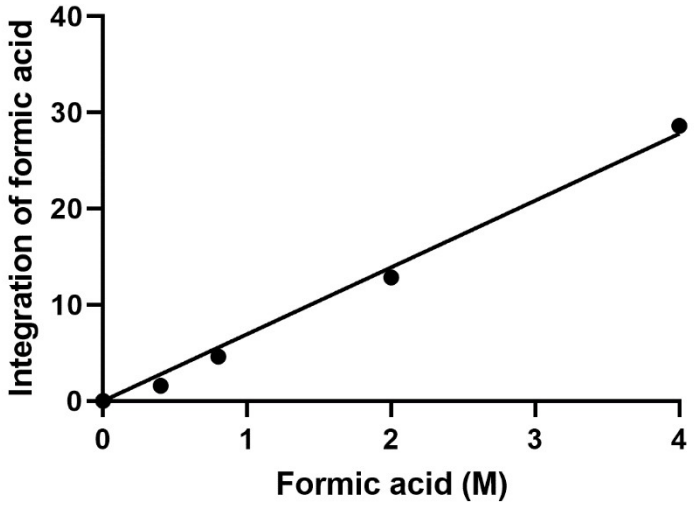
S11. ^{13}C NMR for **1** and 0.15 M (0.75 mmol) BIH. The BIH methyl peaks are 32.86 and 32.91 ppm. Methanol peak is at 49.73 ppm. DCM peak is at 53.61 ppm. $CDCl_3$ peaks are at 76.93, 77.25, and 77.57 ppm. $H^{13}COO^-$ peak is at 159.08 ppm. The remaining peaks between 90-150 ppm are attributed to BIH.

a)

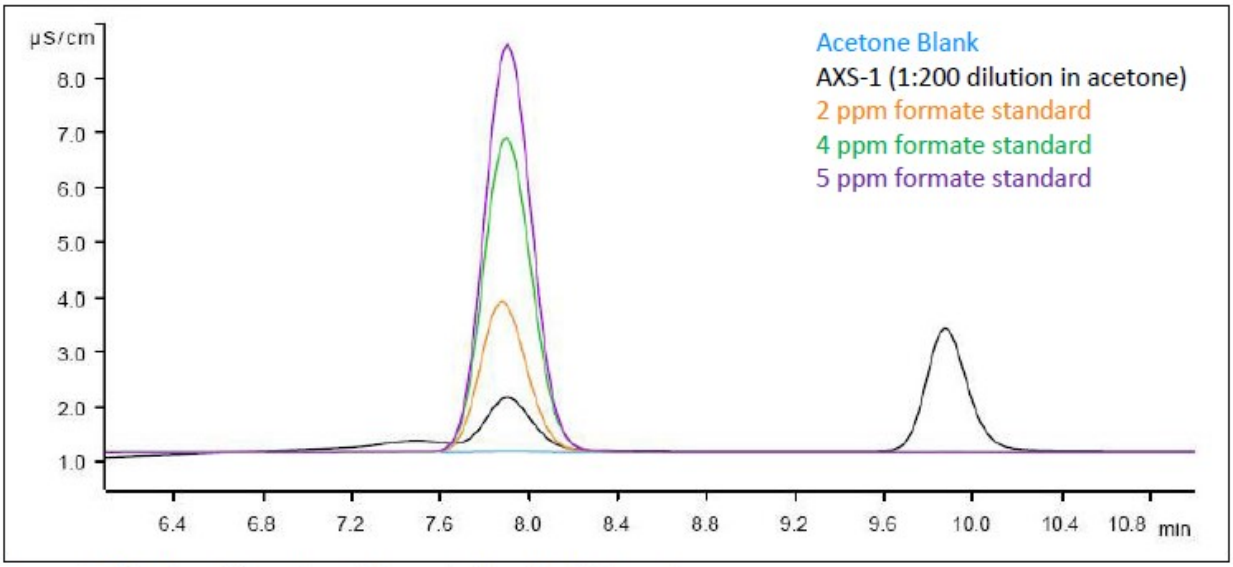


b)

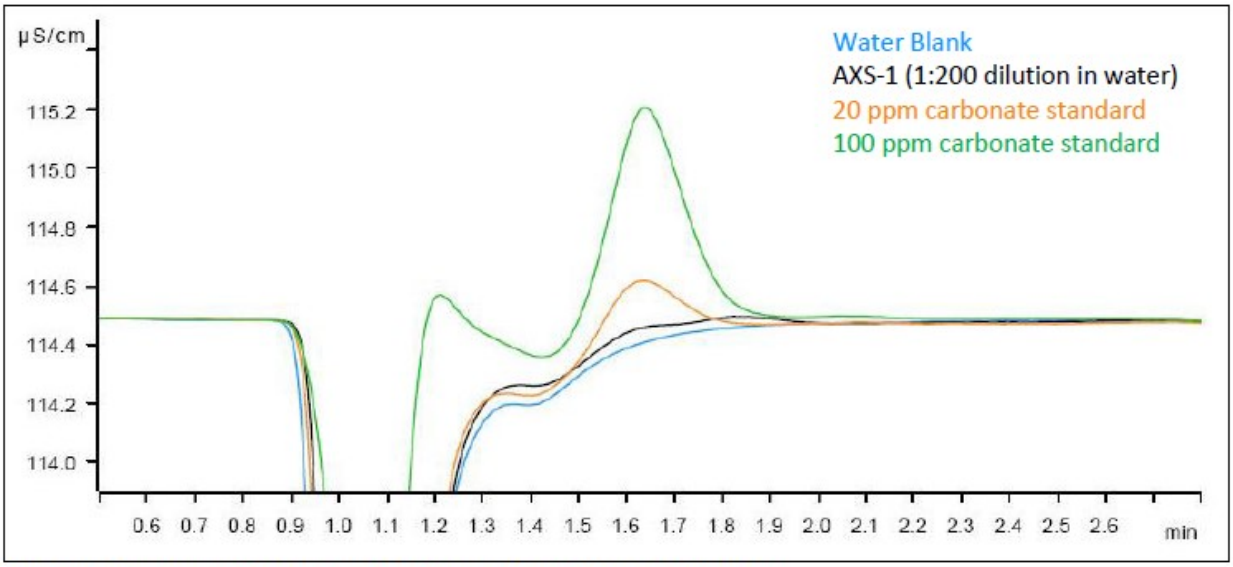
S12. (a) CO_2RR procedure without Pre-mixing BIH. At higher concentrations of BIH (1 mmol and above) the solubility limit of BIH in CH_3OH/DCM (1:9 v:v) is met, which varies the amount of BIH available to react and the amount of $H^{13}COO^-$ produced. Pre-mixing BIH in the solvent for 10 min before adding **1** and $^{13}CO_2$ mitigates the variability. (b) Images of the reaction mixture at 0.5 mmol BIH* and 1.0 mmol BIH without pre-mixing† show clear and cloudy solutions, respectively. Pre-mixing the BIH (1.0 mmol), then adding **1,** results in a transparent solution‡.



S13. Calibration curve of the ^{13}C NMR integration of $H^{13}COO^-$ supplemented with an internal standard of 0.1 M BIH at a D1 relaxation time of 5 s. The linear regression is y=6.946x. The R^2 = 0.9927.

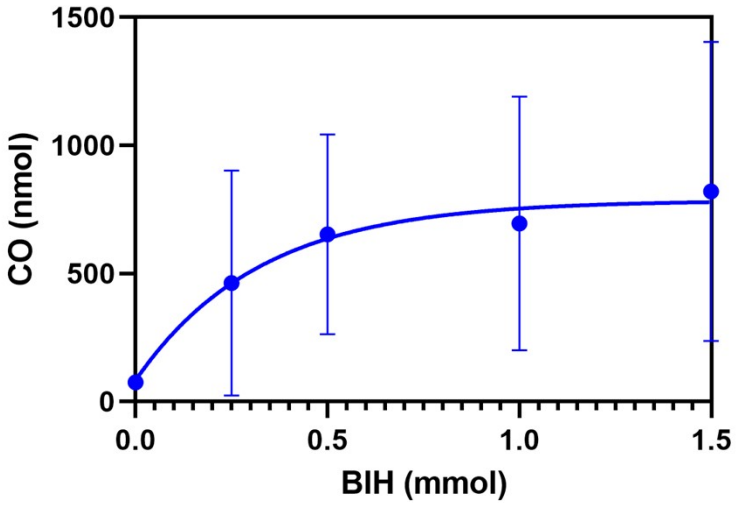


A Overlay of Sample and Formate Standard Chromatograms

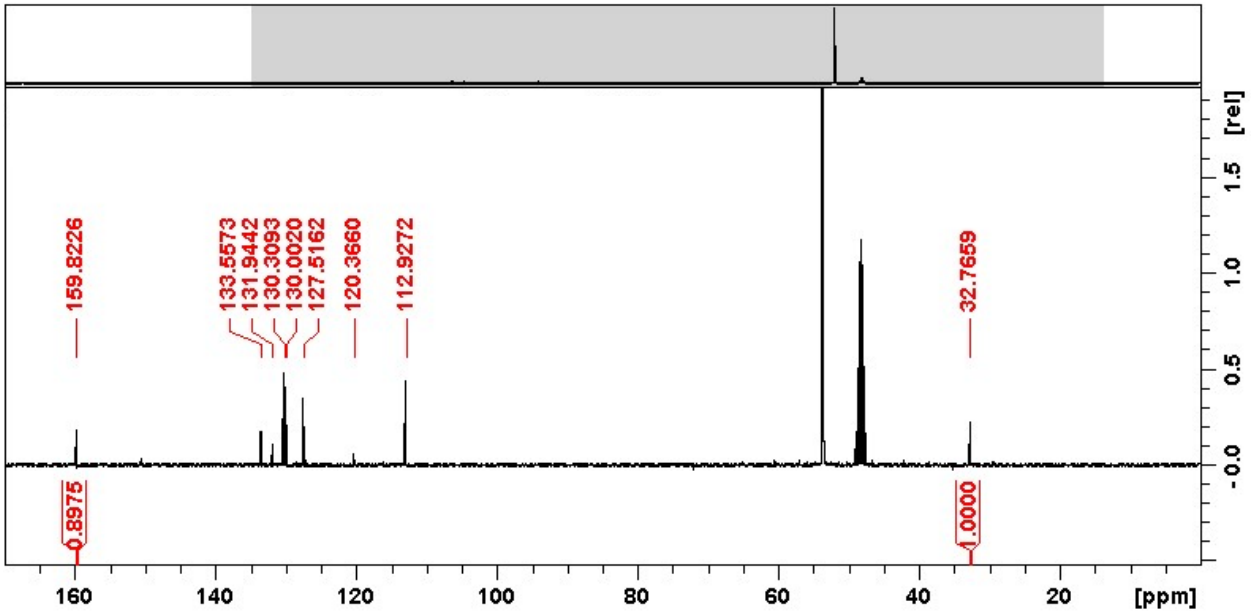


B Overlay of Sample and Carbonate Standard Chromatograms

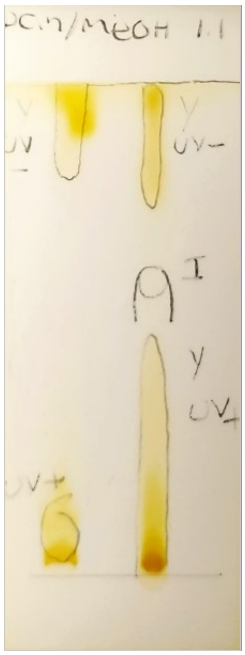
S14. Ion chromatography of a reaction solution containing **1** and BIH after irradiation. Formate was detected while carbonate was not. The peak eluting just before 10 min in **A** is likely chloride.



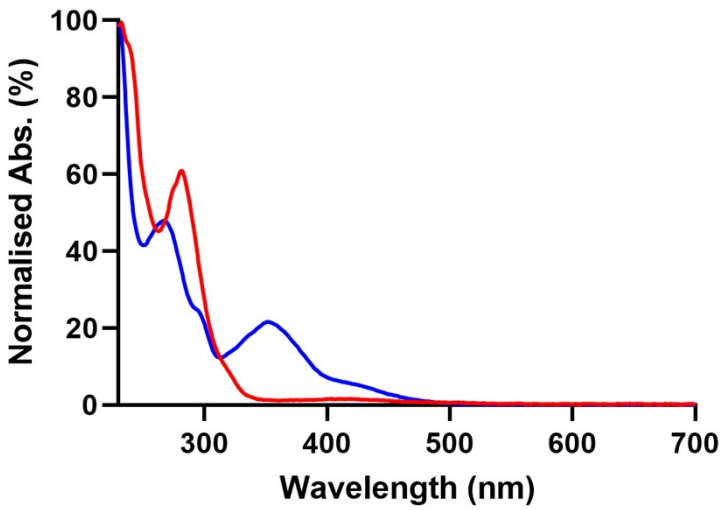
S15. A plot of CO (nmol) vs BIH (mmol) upon blue light irradiation of **1** for 30 min. CO amounts were determined by GC analysis of the headspace of a vial containing the reaction mixture.



S16. ^{13}C NMR of **1** and 0.1 M BIH in CD_3OD/DCM (1:9 v:v) after irradiation with blue light for 1.5 hours. The integration of the formate peak at ~160 ppm is greatly diminished from 10.6 (average value for experiments using 0.1 M BIH) to 0.9. The peaks between 112-133 ppm and ~32 ppm are attributed to BIH. The remaining peaks are solvent related.



S17. TLC of reaction solution before and after irradiation. DCM/MeOH (1:1, v:v) was used as the mobile phase. The Rf values are listed; **1** = 0.90, BIH = 0.04, BI^+ = 0.59. Spots were determined by UV and iodine vapor.



S18. Electronic absorption spectra of **2** in MeOH/DCM (1:9 v:v) (blue) and the reaction solution containing **2** and 0.3 M BIH after irradiation with blue light (450-460 nm) in MeOH/DCM (1:9 v:v) (red). The MLCT band at 352 nm is bleached and the LC band is red shifted 268 nm to 281 nm.

4. References

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