

SUPPORTING INFORMATION FOR

Aerobically stable and substitutionally labile α -diimine rhenium dicarbonyl complexes

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NMR spectra

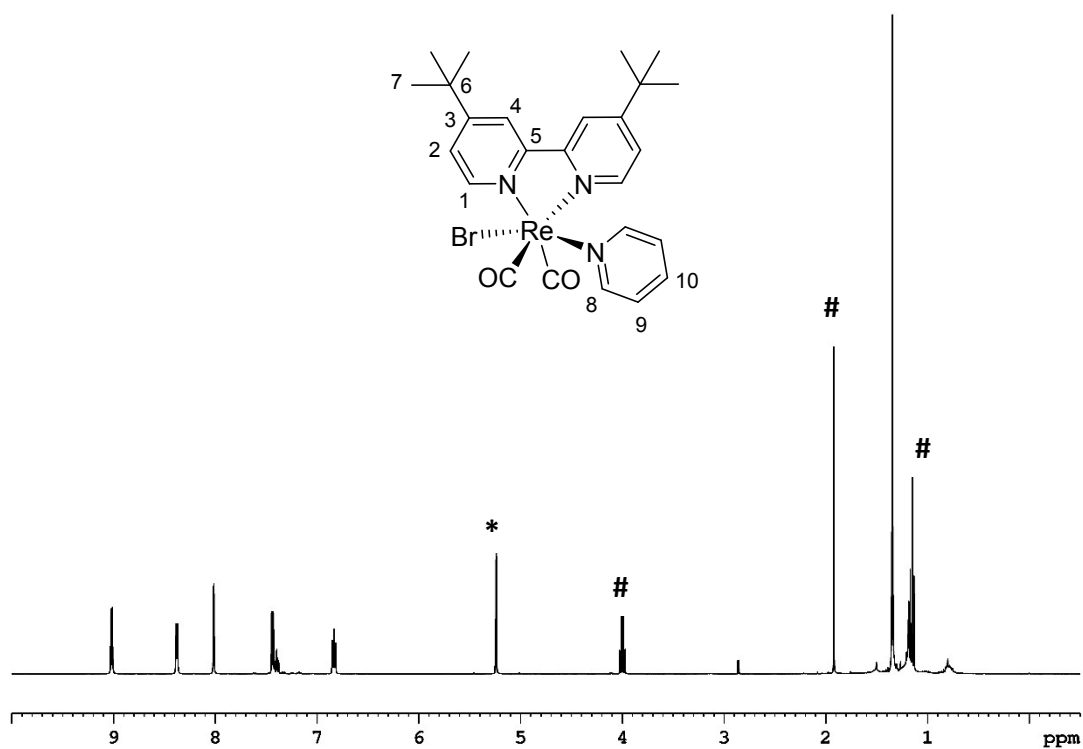


Figure S1. 400 MHz ^1H -NMR of **3** (in CD_2Cl_2 , * = solvent residual peak of DCM, # = solvent residual peaks of ethyl acetate). Numbers correspond to the main text.

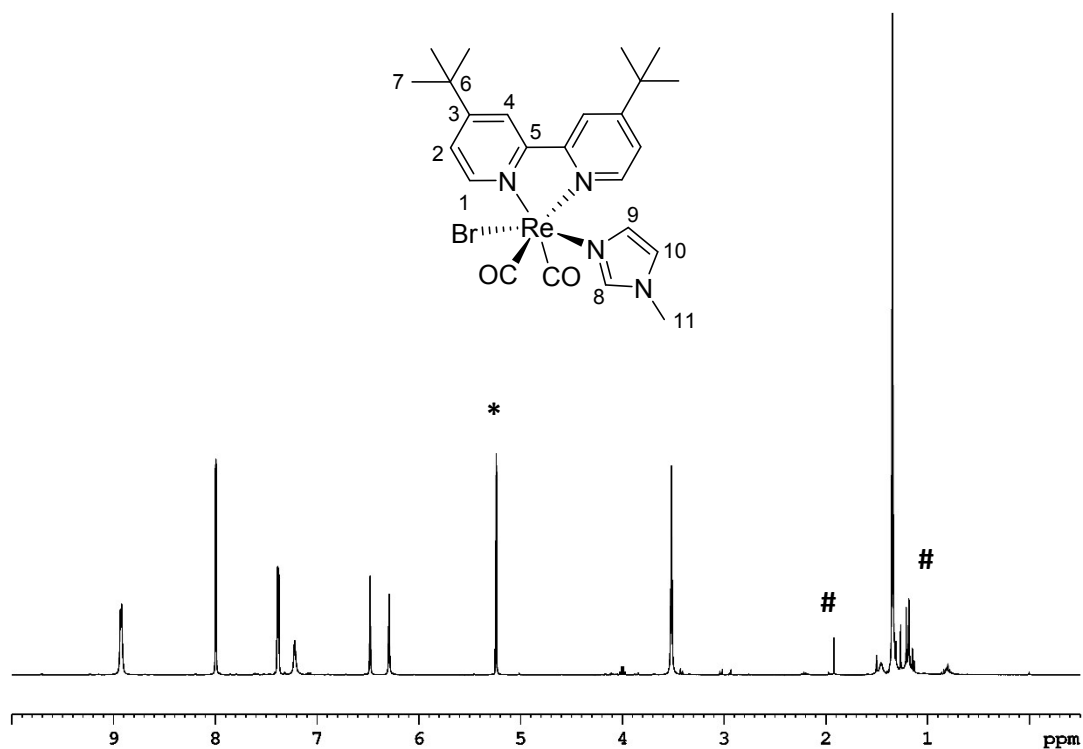


Figure S2. 400 MHz ^1H -NMR of **t-4** (in CD_2Cl_2 , * = solvent residual peak of DCM, # = solvent residual peaks of ethyl acetate). Numbers correspond to the main text.

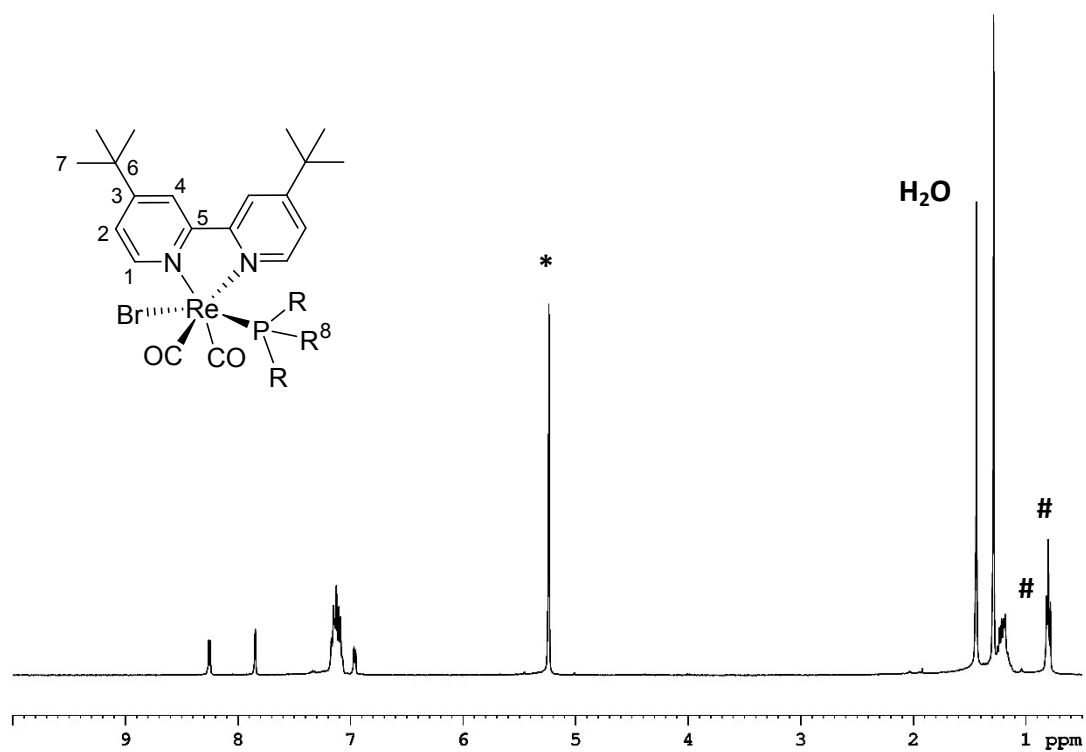


Figure S3. 400 MHz ¹H-NMR of **5** (in CD₂Cl₂, * = solvent residual peak of DCM, # = solvent residual peaks of pentane), R = Phen. Numbers correspond to the main text.

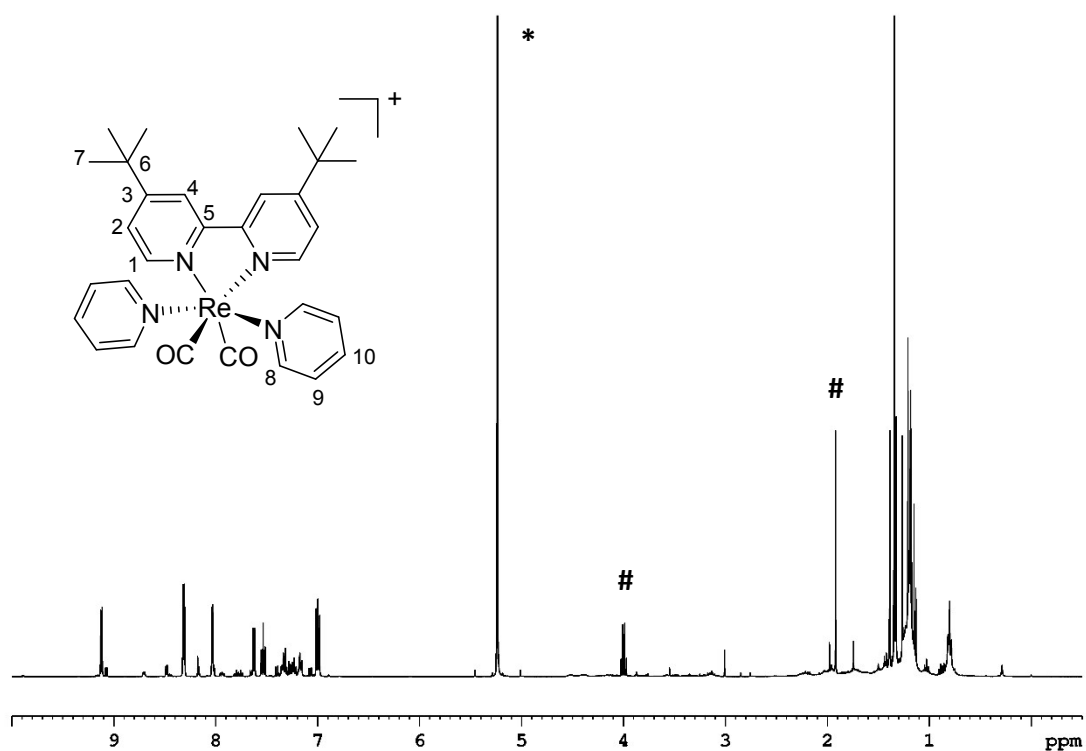


Figure S4. 400 MHz $^1\text{H-NMR}$ of **6** (in CD_2Cl_2 , * = solvent residual peak of DCM, # = solvent residual peaks of ethyl acetate). Numbers correspond to the main text.

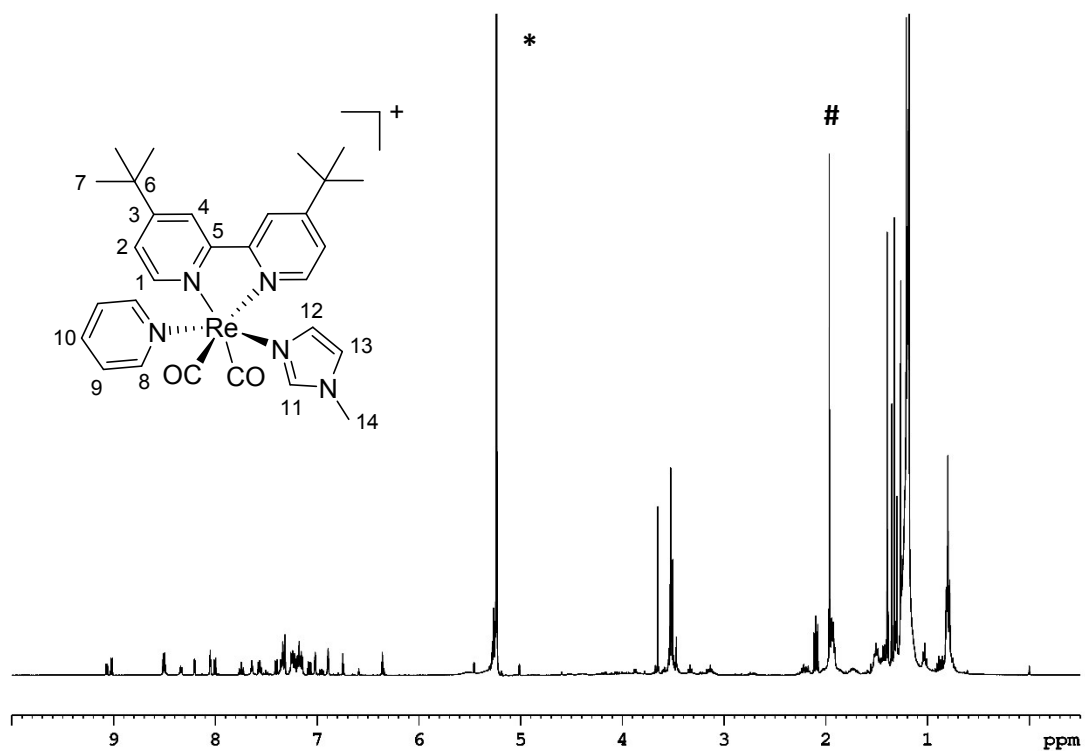


Figure S5. 400 MHz $^1\text{H-NMR}$ of **7** (in CD_2Cl_2 , * = solvent residual peak of DCM, # = solvent residual peak of ethyl acetate). Numbers correspond to the main text.

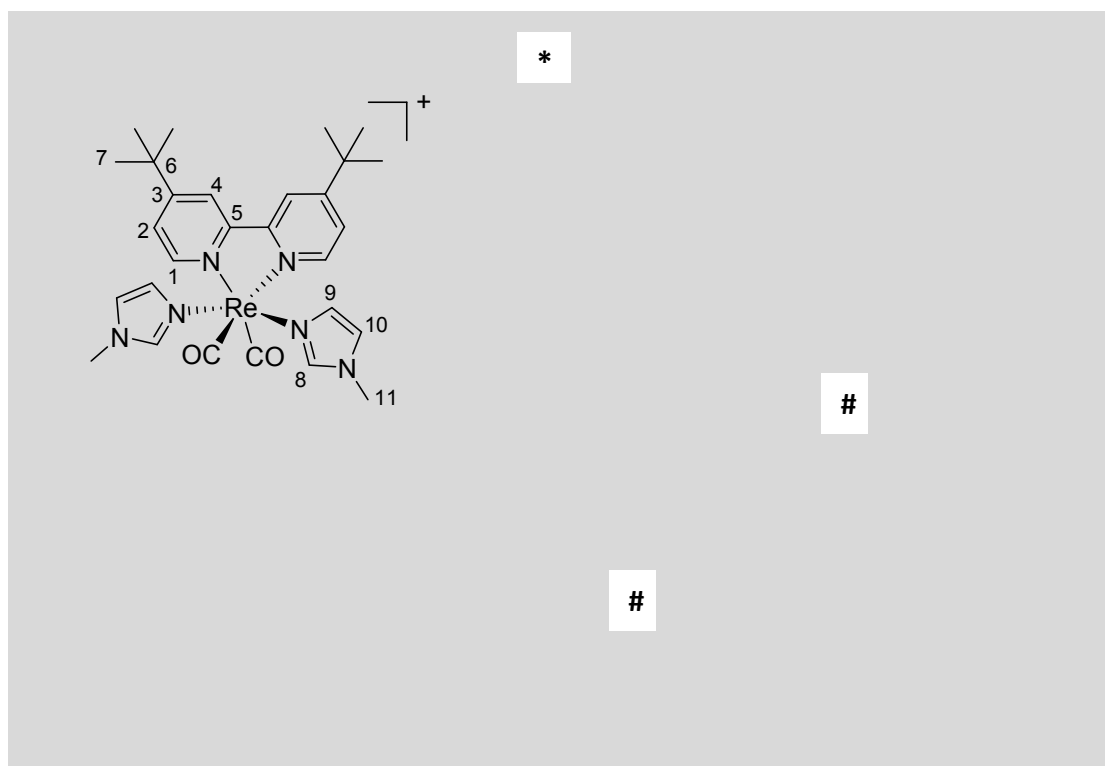


Figure S6. 400 MHz ^1H -NMR of **8** (in CD_2Cl_2 , * = solvent residual peak of DCM, # = solvent residual peaks of ethyl acetate). Numbers correspond to the main text.

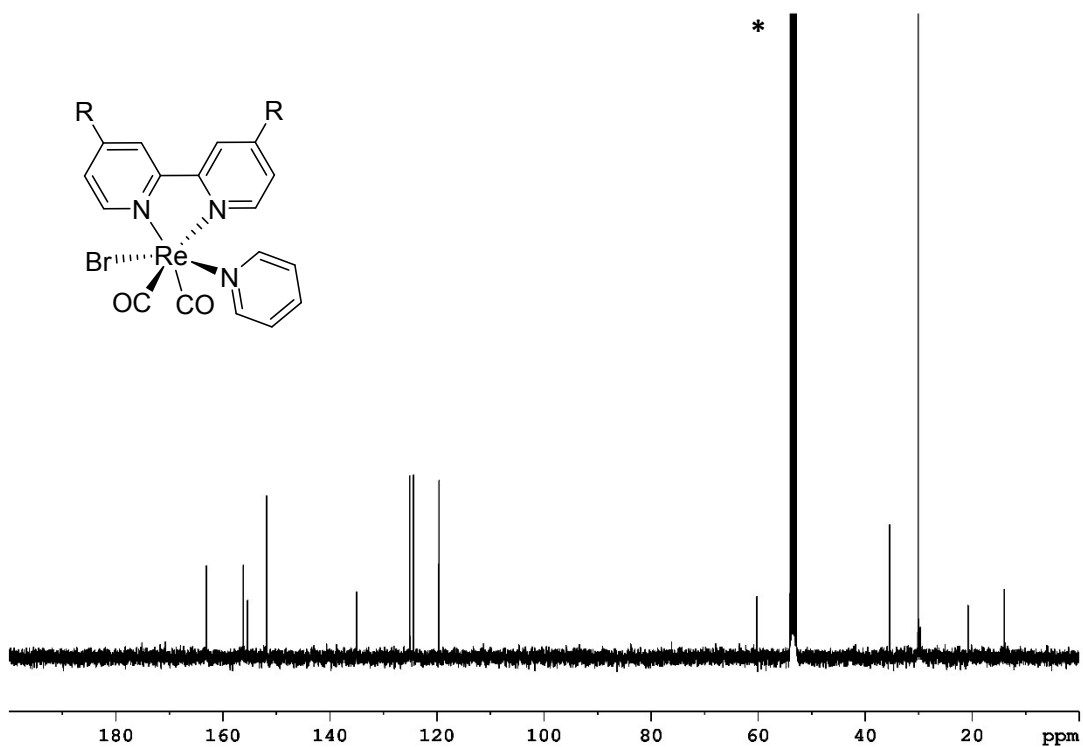


Figure S7. 101 MHz ^{13}C -NMR of **3** (in CD_2Cl_2 , * = solvent residual peak of DCM).

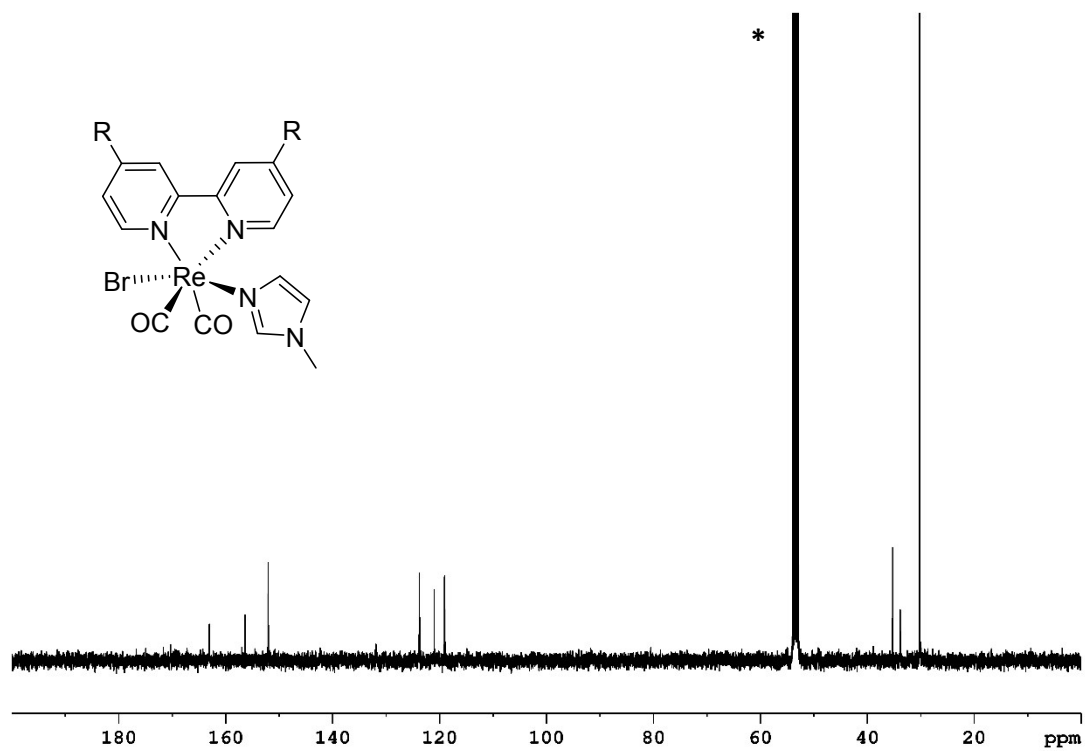


Figure S8. 101 MHz ¹³C-NMR of **t-4** (in CD₂Cl₂, * = solvent residual peak of DCM).

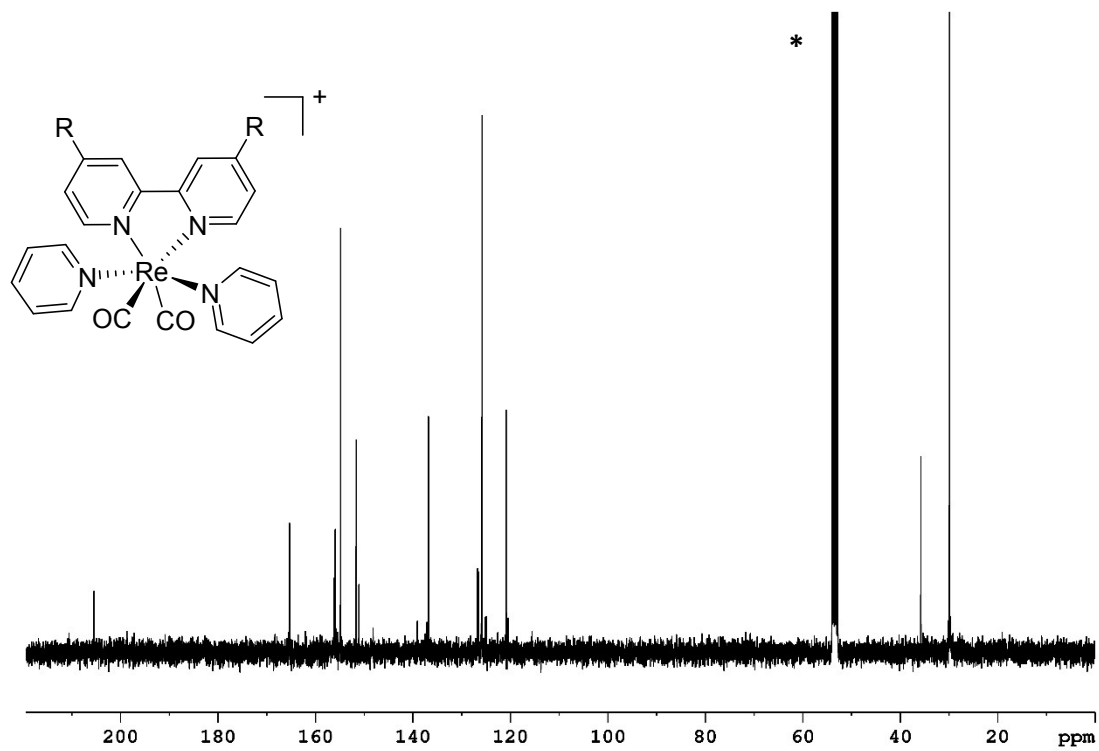


Figure S9. 101 MHz ¹³C-NMR of **6** (in CD₂Cl₂, * = solvent residual peak of DCM).

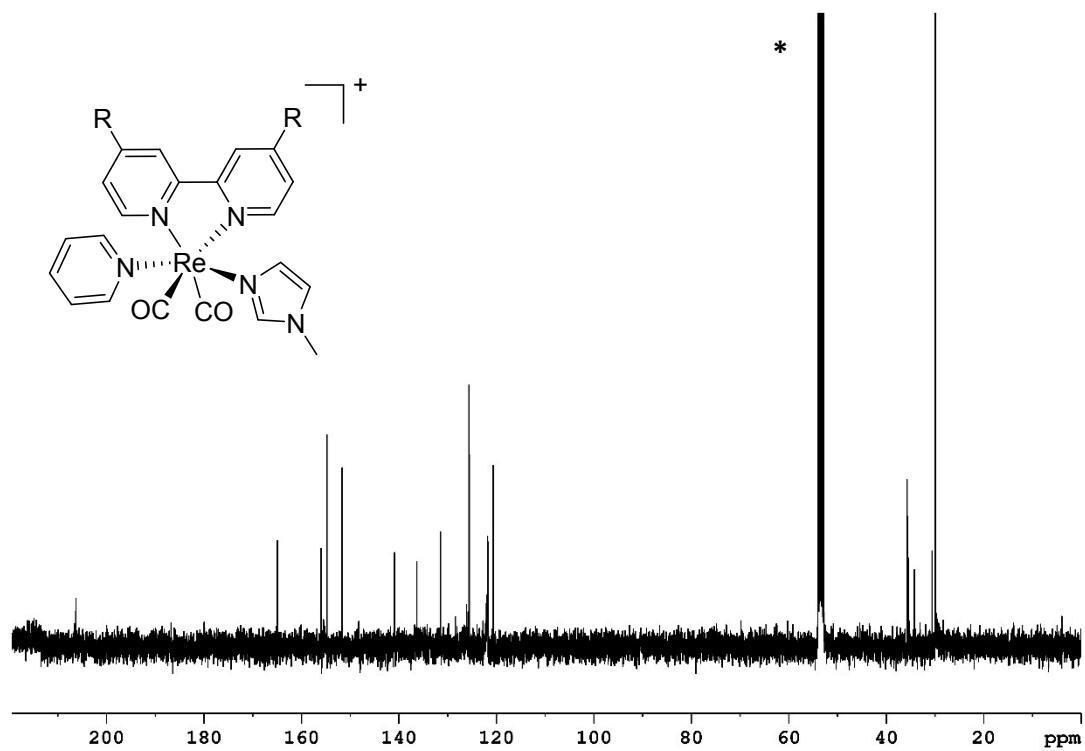


Figure S10. 101 MHz ^{13}C -NMR of **7** (in CD_2Cl_2 , * = solvent residual peak of DCM).

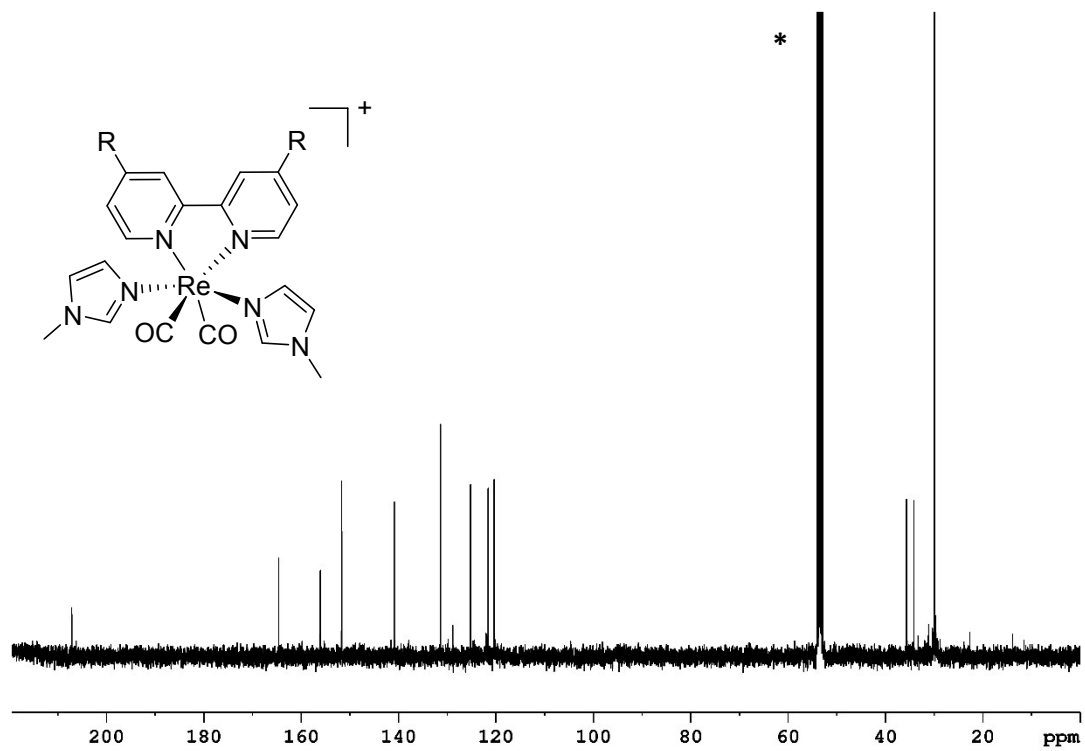


Figure S11. 101 MHz ^{13}C -NMR of **8** (in CD_2Cl_2 , * = solvent residual peak of DCM).

IR spectra

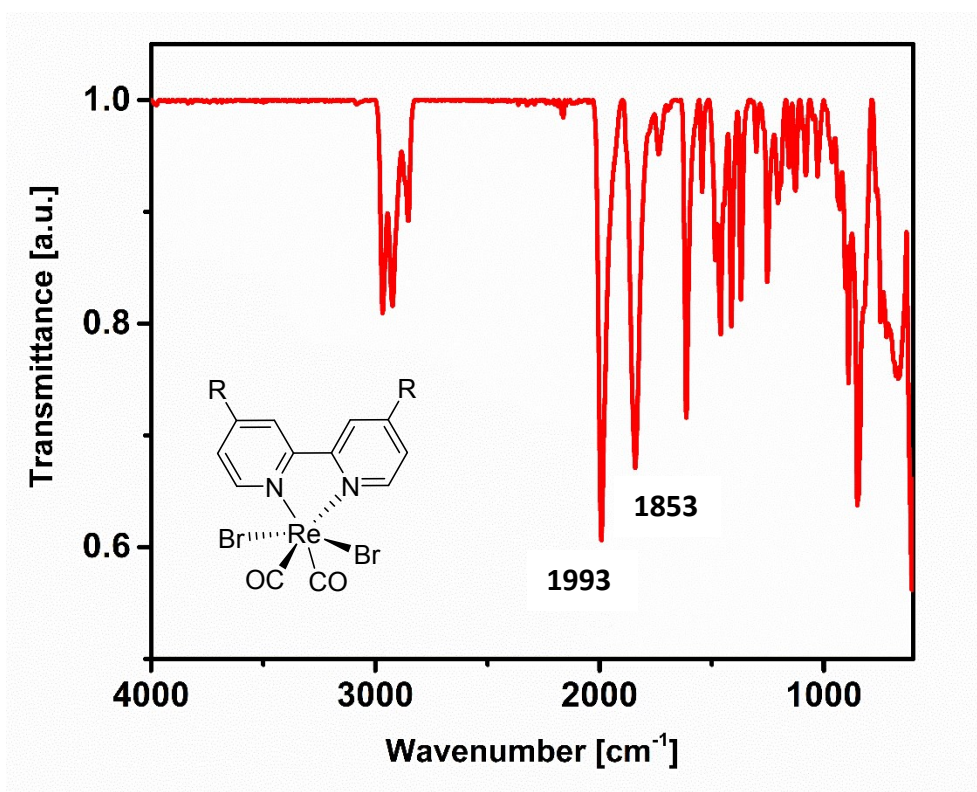


Figure S12. IR spectrum (solid state) of 1.

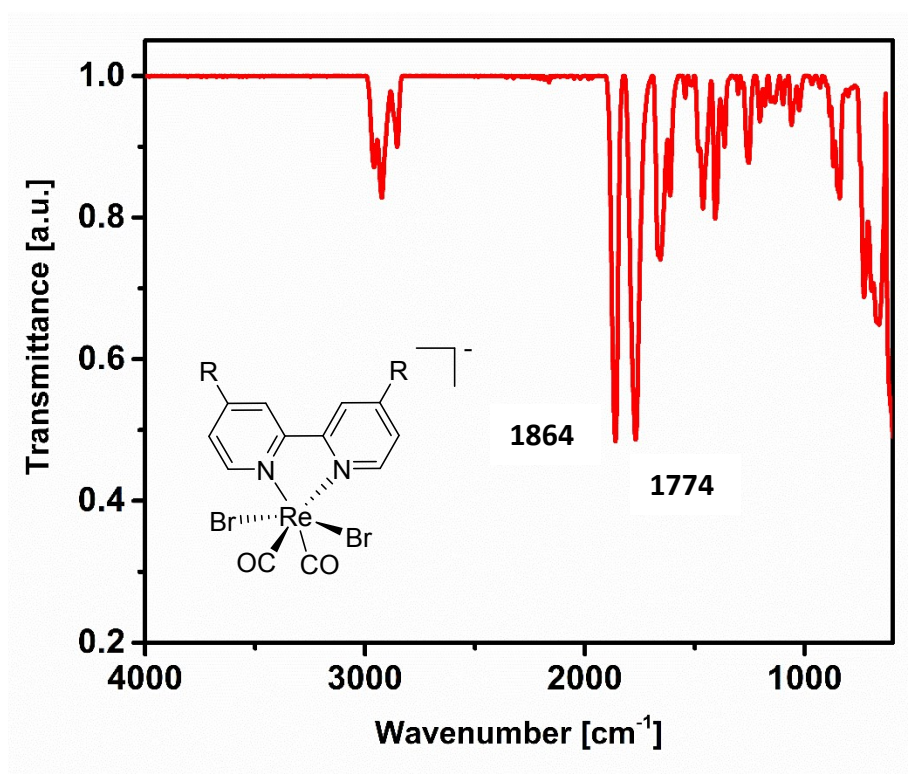


Figure S13. IR spectrum (solid state) of 2.

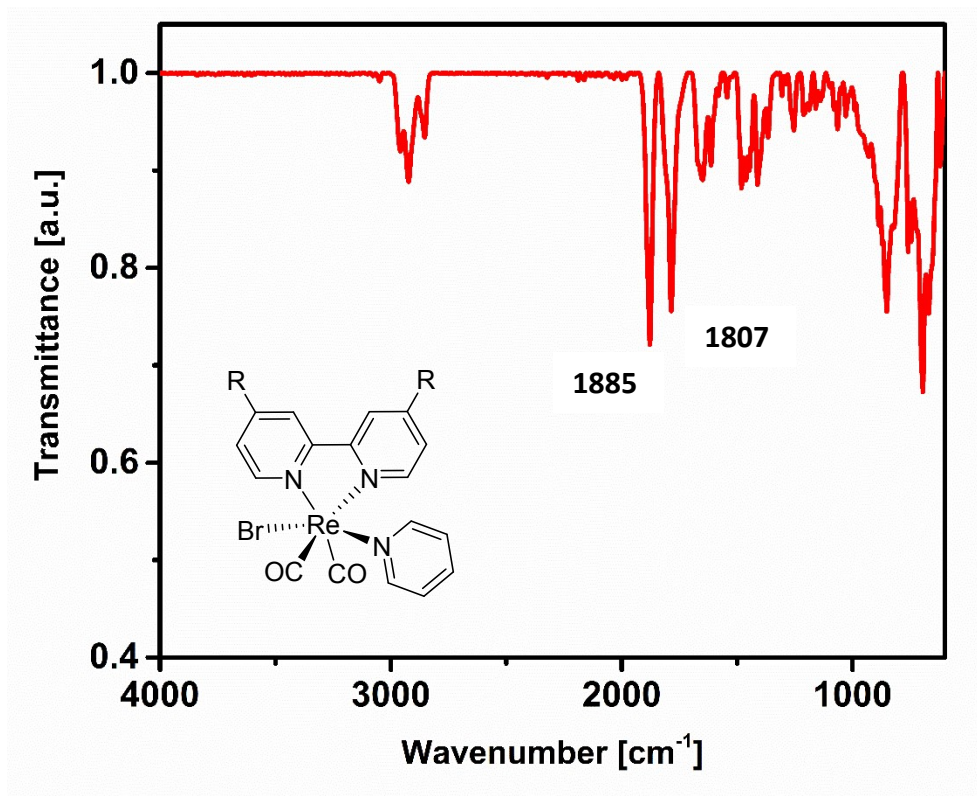


Figure S14. IR spectrum (solid state) of **3**.

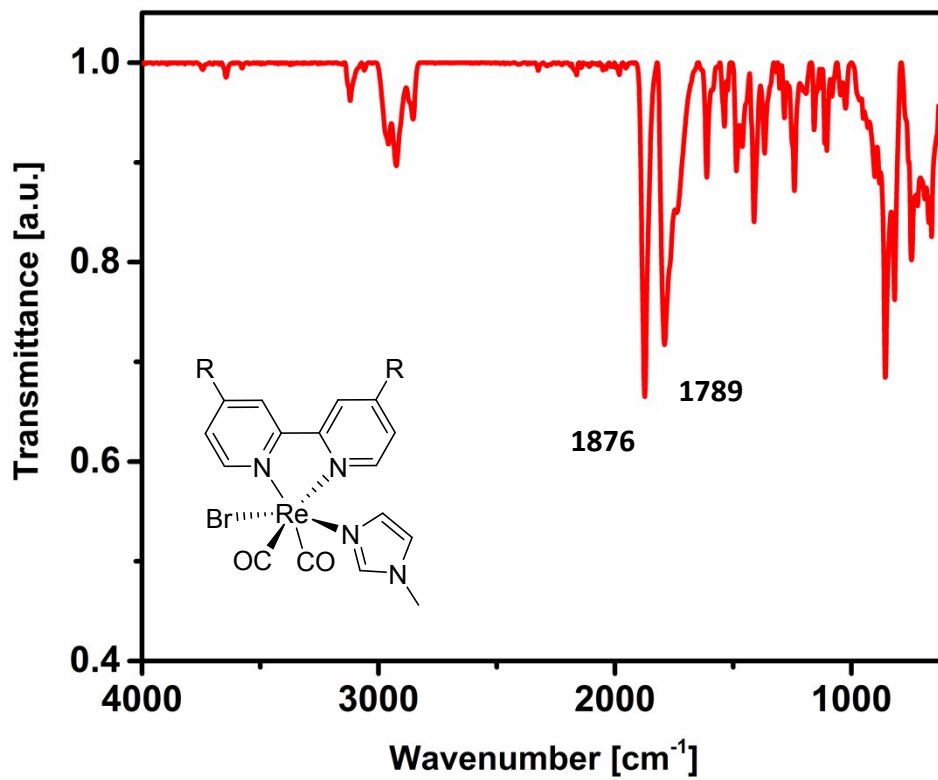


Figure S15. IR spectrum (solid state) of **t-4**.

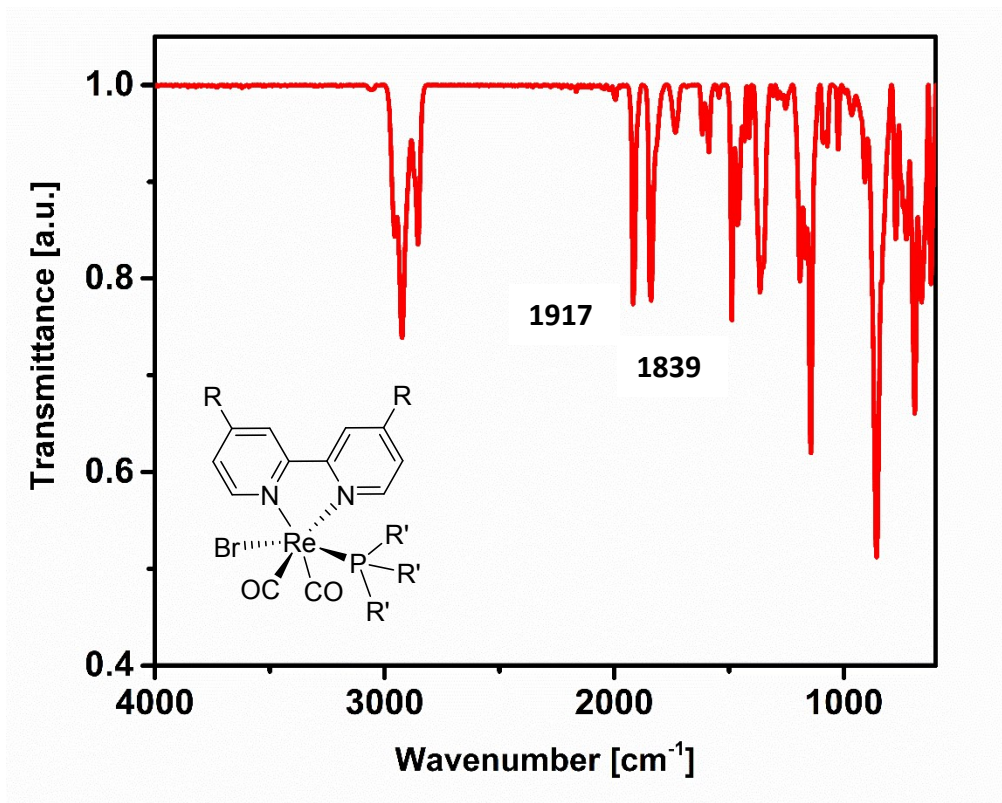


Figure S16. IR spectrum (solid state) of 5.

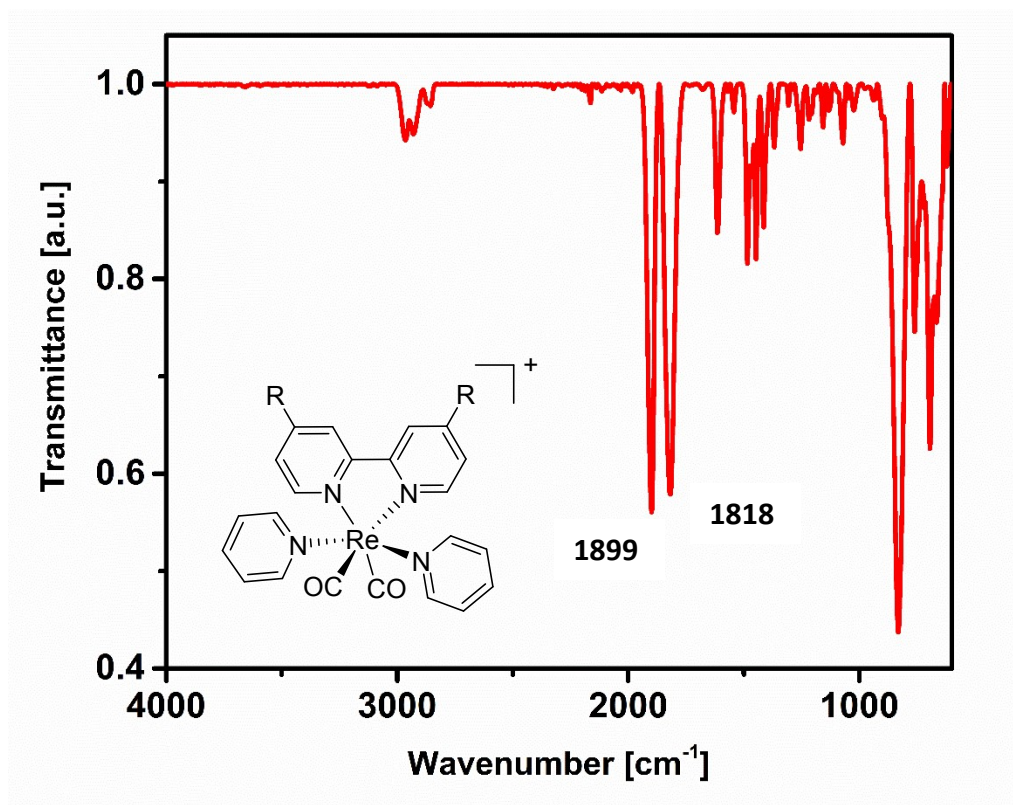


Figure S17. IR spectrum (solid state) of 6.

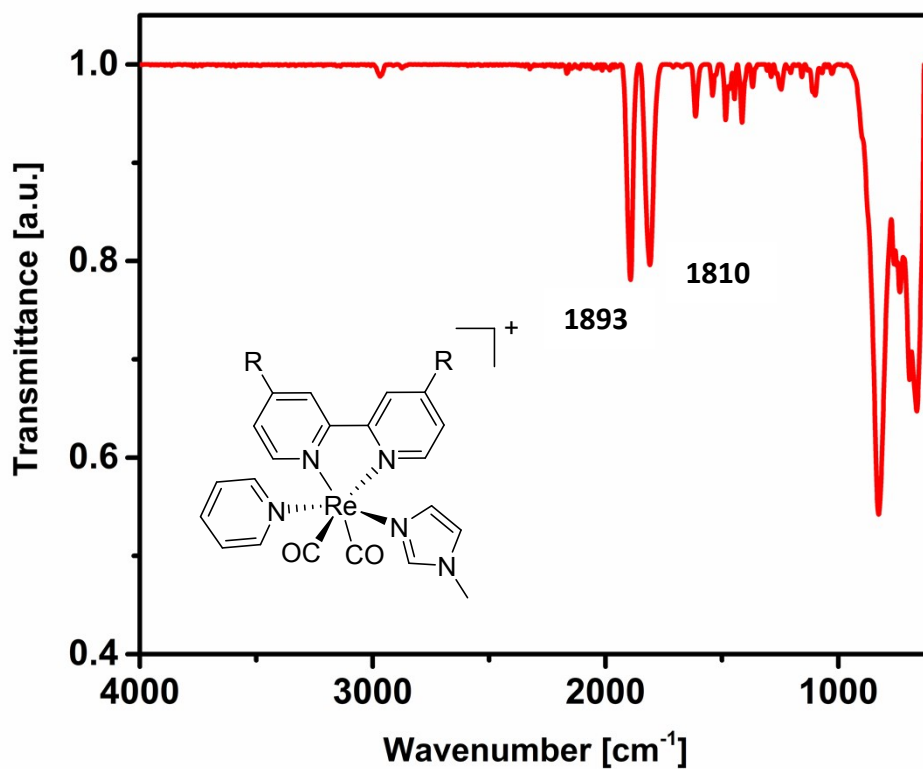


Figure S18. IR spectrum (solid state) of 7.

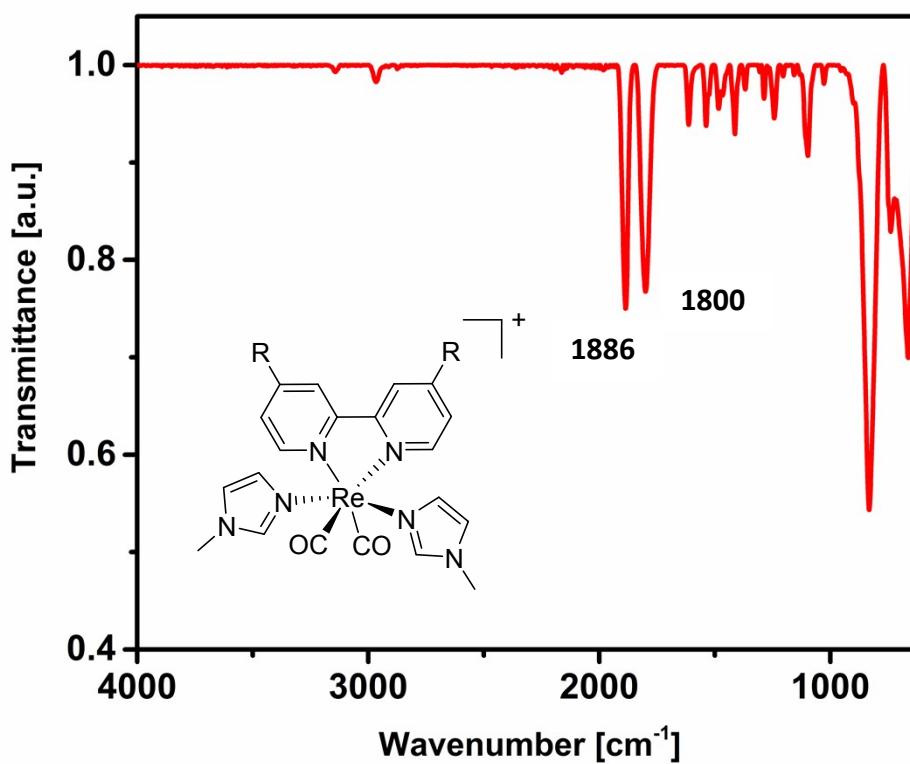


Figure S19. IR spectrum (solid state) of 8.

UV-Vis spectra

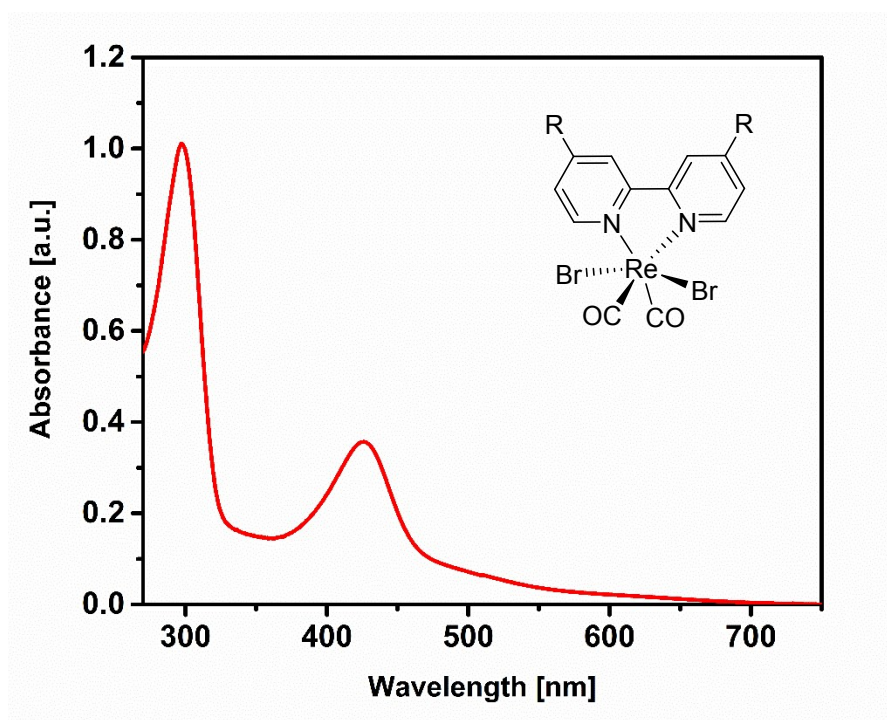


Figure S20. UV-Vis spectrum (in DMF) of 1.

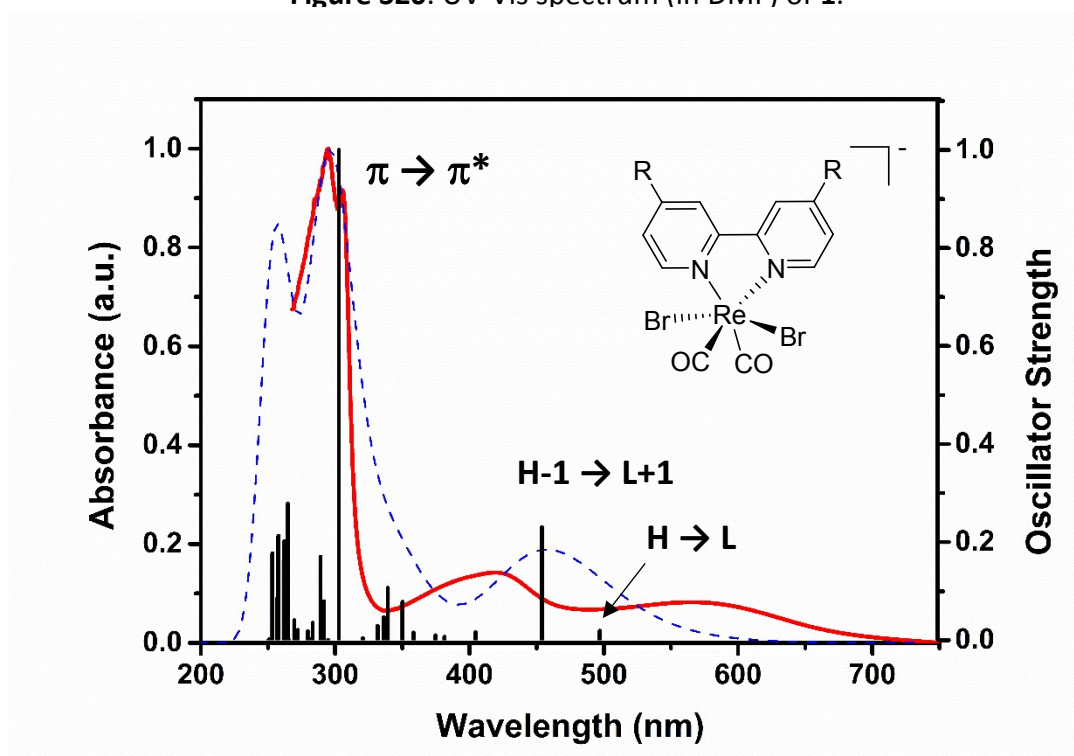


Figure S21. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of 2.

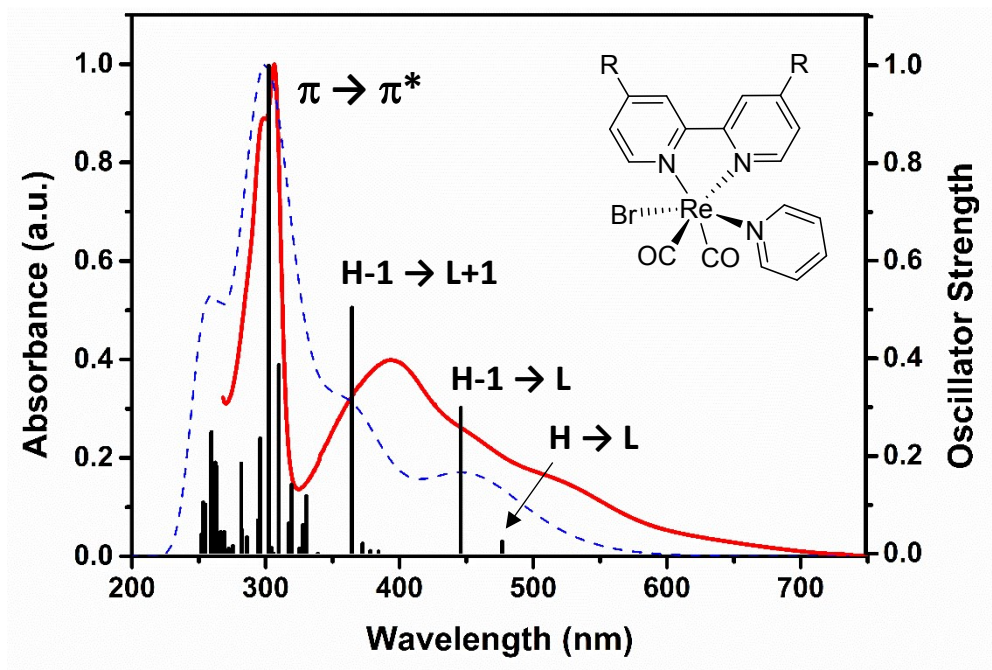


Figure S22. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of **3**.

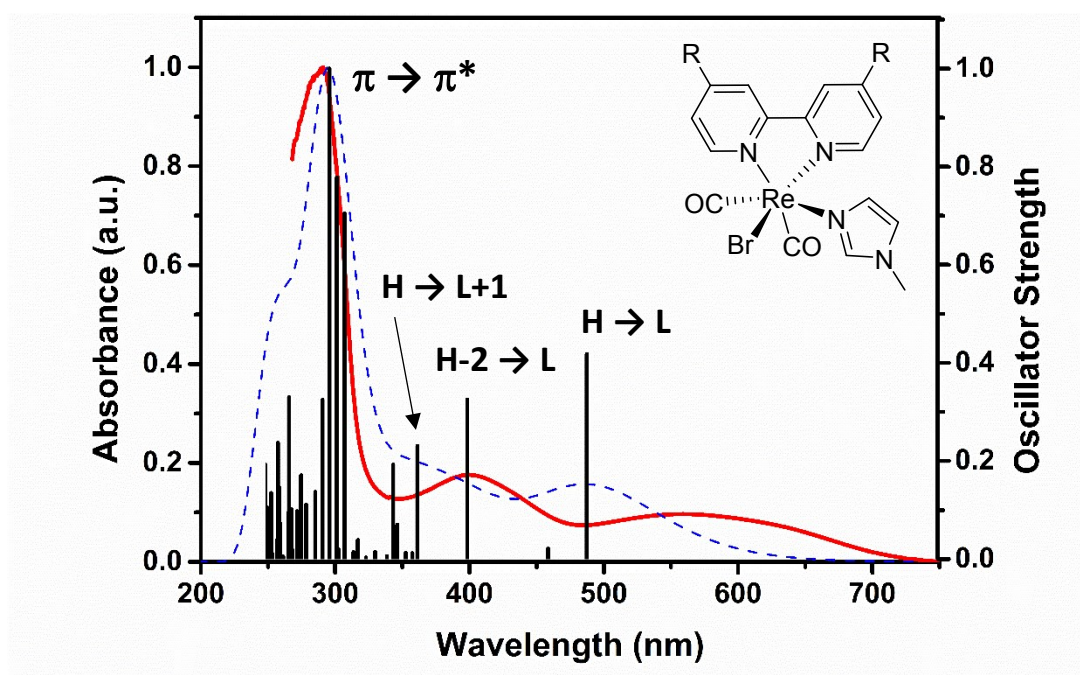


Figure S23. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of **c-4**.

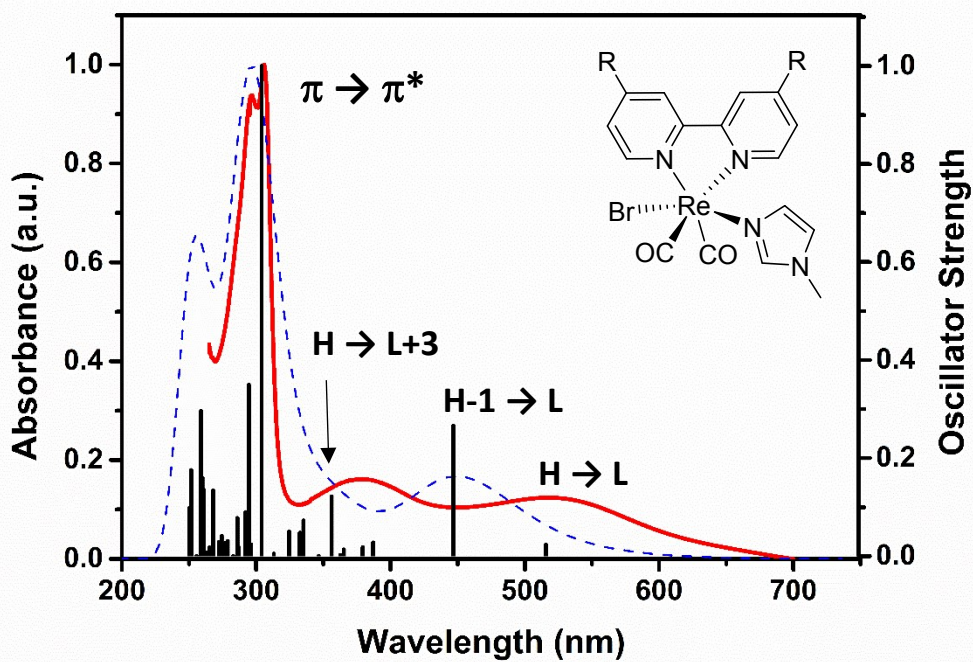


Figure S24. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of **t-4**.

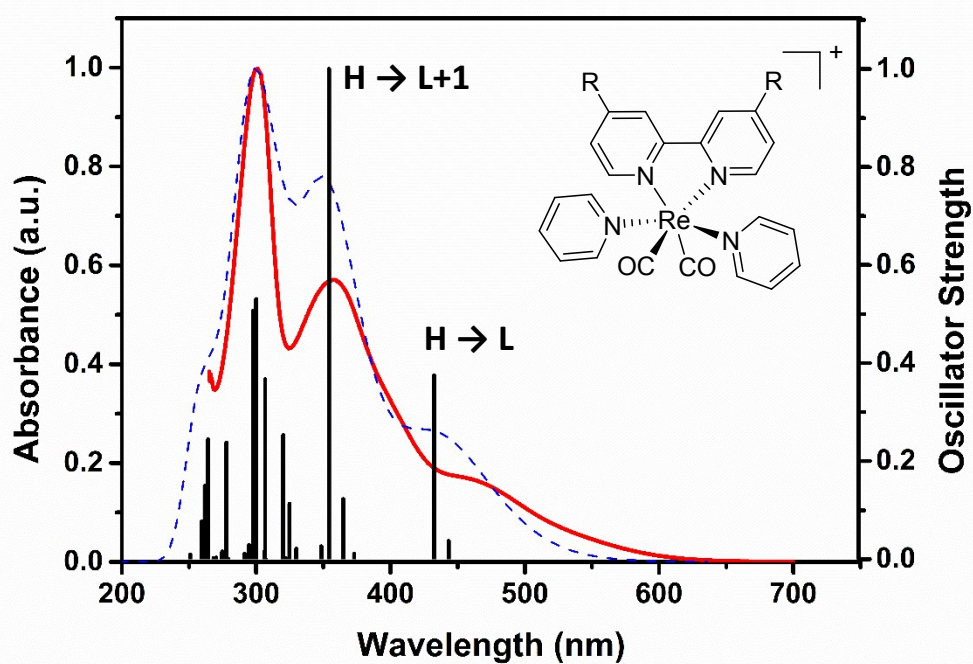


Figure S25. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of **6**.

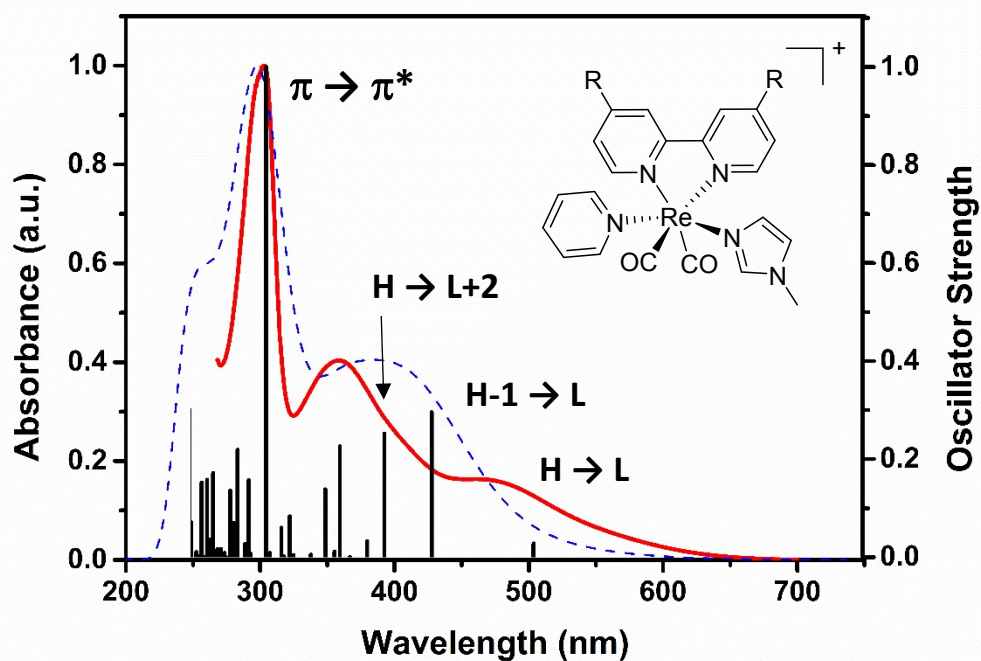


Figure S26. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of **7**.

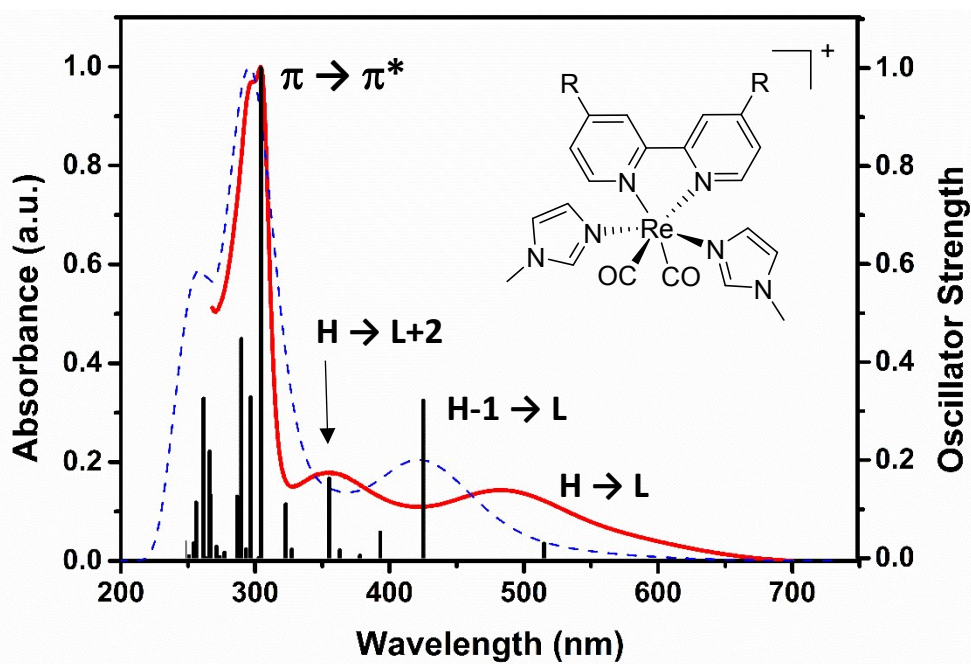


Figure S27. UV-Vis measured spectrum (red), calculated spectrum (blue) and oscillator strength (black) (all in DMF) of **8**.

Crystallography

Table S1. Crystallographic details of **1**, **Cl-1**, **3**, **t-4** and **c-4**.

Compound	1	Cl-1	3	t-4	c-4
formula	C ₄₁ H ₅₀ Br ₄ Cl ₂ N ₄ O ₄ Re ₂	C ₂₁ H ₂₅ BrCl ₄ N ₂ O ₂ Re	C ₂₅ H ₂₉ BrN ₃ O ₂ Re	C ₂₄ H ₃₀ BrN ₄ O ₂ Re	C ₂₉ H ₄₂ BrN ₄ O ₂ Re
fw	1425.79	745.34	669.62	672.63	744.77
T, K	250(2)	250(2)	200(2)	293(2)	200(2)
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	P2 ₁ /c	Pnma	Cmce	Pnma	Pnma
a, Å	12.9090(4)	12.4068(8)	13.5302(2)	14.2929(3)	15.1687(3)
b, Å	31.7496(12)	13.9121(6)	34.6388(7)	17.3769(3)	17.1375(3)
c, Å	12.5191(4)	16.1781(7)	15.2486(2)	10.1717(2)	12.0964(2)
α, deg	90	90	90	90	90
β, deg	103.998(2)	90	90	90	90
γ, deg	90	90	90	90	90
V, Å ³	4978.7(3)	2792.4(2)	7146.6(2)	2526.31(8)	3144.50(10)
Z	4	4	8	4	4
ρ _{calc} , g/cm ³	1.902	1.773	1.245	1.768	1.573
R1 ^a , (wR2) ^a	0.0509, 0.0992	0.0778, 0.2133	0.0439, 0.1308	0.0227, 0.0566	0.0234, 0.0614
Largest diff. peak/hole (e Å ⁻³)	0.90/-1.17	1.19/-2.21	0.80/-1.60	0.85/-0.78	0.75/-1.01

Table S2. Crystallographic details of **5**, **6**, **7** and **8**.

Compound	5	6	7	8
formula	C ₃₈ H ₃₉ BrN ₂ O ₂ PRE	C ₃₀ H ₃₄ F ₆ N ₄ O ₂ PRE	C ₂₉ H ₃₅ F ₆ N ₅ O ₂ PRE	C ₂₈ H ₃₆ F ₆ N ₆ O ₂ PRE
fw	852.79	813.78	816.79	819.80
T, K	200(2)	200(2)	250(2)	250(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pbca	I2/a	C2/c	P2 ₁ /c
a, Å	18.8689(3)	32.6007(5)	32.1948(10)	12.3996(3)
b, Å	13.4662(2)	12.21990(10)	12.3447(3)	13.8863(3)
c, Å	28.4268(5)	18.8003(3)	28.1669(9)	19.1424(5)
α, deg	90	90	90	90
β, deg	90	101.7040(10)	144.0940(10)	100.747(2)
γ, deg	90	90	90	90
V, Å ³	7223.0(2)	7333.89(17)	6565.1(3)	3238.21(14)
Z	8	8	8	4
ρ _{calc} , g/cm ³	1.568	1.474	1.653	1.682
R1 ^a , (wR2) ^a	0.0204, 0.0516	0.0422, 0.1171	0.0438, 0.1009	0.0288, 0.0659
Largest diff. peak/hole (e Å ⁻³)	0.79/-0.61	1.60/-1.51	0.77/-0.78	0.49/-0.60

Table S3. Bond lengths and angles of **1**, **Cl-1**, **3**, **t-4** and **c-4**.

Compound	1	Cl-1^a	3^b	t-4^c	c-4^d
Re(1)-C(1)	1.971(14)	2.01(2)	1.889(6)	1.892(4)	1.883(5)
Re(1)-C(2)	1.958(12)	2.01(2)	1.889(6)	1.892(4)	1.874(11)
Re(1)-Br(1)	2.4940(14)	2.491(4)	2.5944(9)	2.5963(6)	2.5782(14)
Re(1)-Br(2)	2.5234(12)	2.403(5)			
C(1)-O(1)	1.047(13)	1.02(2)	1.154(7)	1.143(5)	1.148(6)
C(2)-O(2)	1.114(12)	1.02(2)	1.154(7)	1.143(5)	1.214(11)
Re(1)-N(1)	2.166(7)	2.184(10)	2.178(4)	2.177(2)	2.136(2)
Re(1)-N(2)	2.161(7)	2.184(10)	2.178(4)	2.177(2)	2.136(2)
Re(1)-N(3)			2.140(7)	2.147(4)	2.222(3)
Re(1)-N(4)					
angles	1	Cl-1^a	3	t-4	c-4
C(1)-Re(1)-C(2)	85.2(5)	85.7(10)	88.2(3)	87.8(2)	87.1(3)
C(1)-Re(1)-Br(1)	91.3(4)	88.5(3)	93.68(16)	95.69(10)	93.72(10)
C(1)-Re(1)-Br(2)	91.0(4)	86.4(3)			
Br(1)-Re(1)-Br(2)	171.87(4)	173.63(15)			
Br(1)-Re(1)-N(3)			172.38(18)	169.38(10)	179.65(16) ^e
C(1)-Re(1)-N(1)	101.3(4)	100.0(6)	98.96(19)	99.02(12)	94.19(13)
C(1)-Re(1)-N(2)	176.2(4)	173.6(5)	172.77(19)	173.13(12)	179.65(16)
N(1)-Re(1)-N(2)	75.0(3)	74.1(5)	73.8(2)	74.15(13)	74.97(12)
Br(1)-Re(1)-N(1)	86.5(2)	88.5(3)	85.39(11)	84.44(7)	94.85(6)
Br(1)-Re(1)-N(2)	87.7(2)	88.5(3)	85.39(11)	84.45(7)	86.04(6)

^aBr(2) refers to Cl(1), N(2) to N(1)#1, C(2) to C(1)#1

^bN(2) refers to N(1)#1, N(3) to N(2), C(2) to C(1)#1

^cN(2) refers to N(1)#1, N(3) to N(2), C(2) to C(1)#1

^dN(2) refers to N(1)#1, N(3) to N(2)

^eBr(1) refers to C(1)

Table S4. Bond lengths and angles of **5**, **6**, **7** and **8**.

Compound	5^f	6	7^g	8^g
Re(1)-C(1)	1.899(3)	1.878(6)	1.879(8)	1.881(5)
Re(1)-C(2)	1.890(3)	1.883(5)	1.863(9)	1.877(5)
Re(1)-Br(1)	2.6204(3)			
C(1)-O(1)	1.157(3)	1.175(7)	1.167(9)	1.164(6)
C(2)-O(2)	1.160(3)	1.168(6)	1.194(9)	1.156(5)
Re(1)-N(1)	2.177(2)	2.182(4)	2.194(5)	2.184(3)
Re(1)-N(2)	2.1731(19)	2.177(4)	2.180(5)	2.184(3)
Re(1)-N(3)	2.3367(6)	2.145(4)	2.160(5)	2.154(3)
Re(1)-N(4)		2.150(4)	2.163(6)	2.156(3)
angles	5	6	7	8
C(1)-Re(1)-C(2)	89.29(11)	88.8(2)	88.1(3)	87.5(2)
C(1)-Re(1)-Br(1)	96.45(8)			
C(1)-Re(1)-N(1)	170.34(9)	98.07(19)	98.3(3)	97.66(16)
C(1)-Re(1)-N(2)	95.99(9)	171.35(19)	172.9(3)	171.87(16)
N(1)-Re(1)-N(2)	74.41(7)	73.99(14)	73.9(2)	74.24(12)
Br(1)-Re(1)-P(1)	173.845(16)			
N(3)-Re(1)-N(4)		173.15(16)	171.8(2)	171.98(13)
Br(1)-Re(1)-N(1)	81.57(5)			
Br(1)-Re(1)-N(2)	82.67(5)			

^fN(3) refers to P(1)^gN(4) refers to N(5)

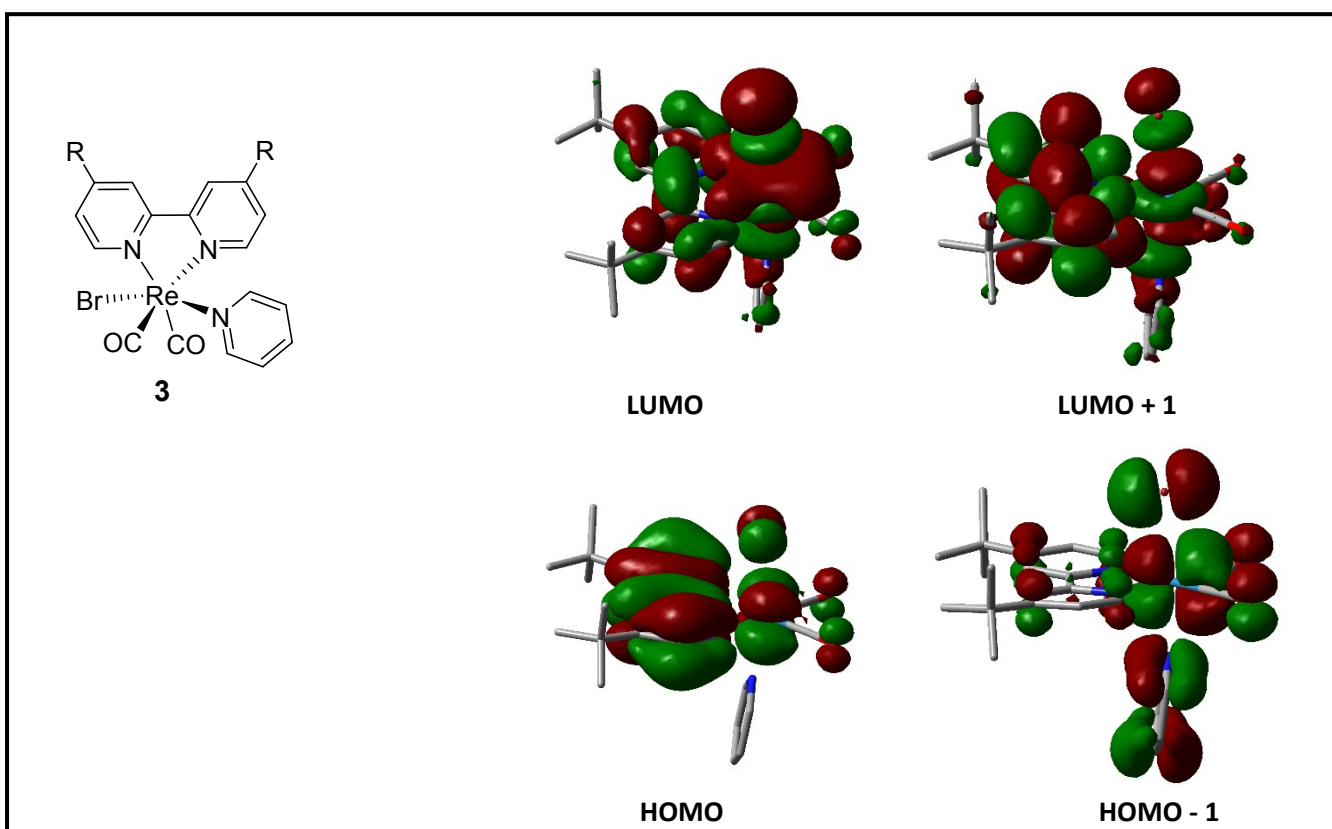
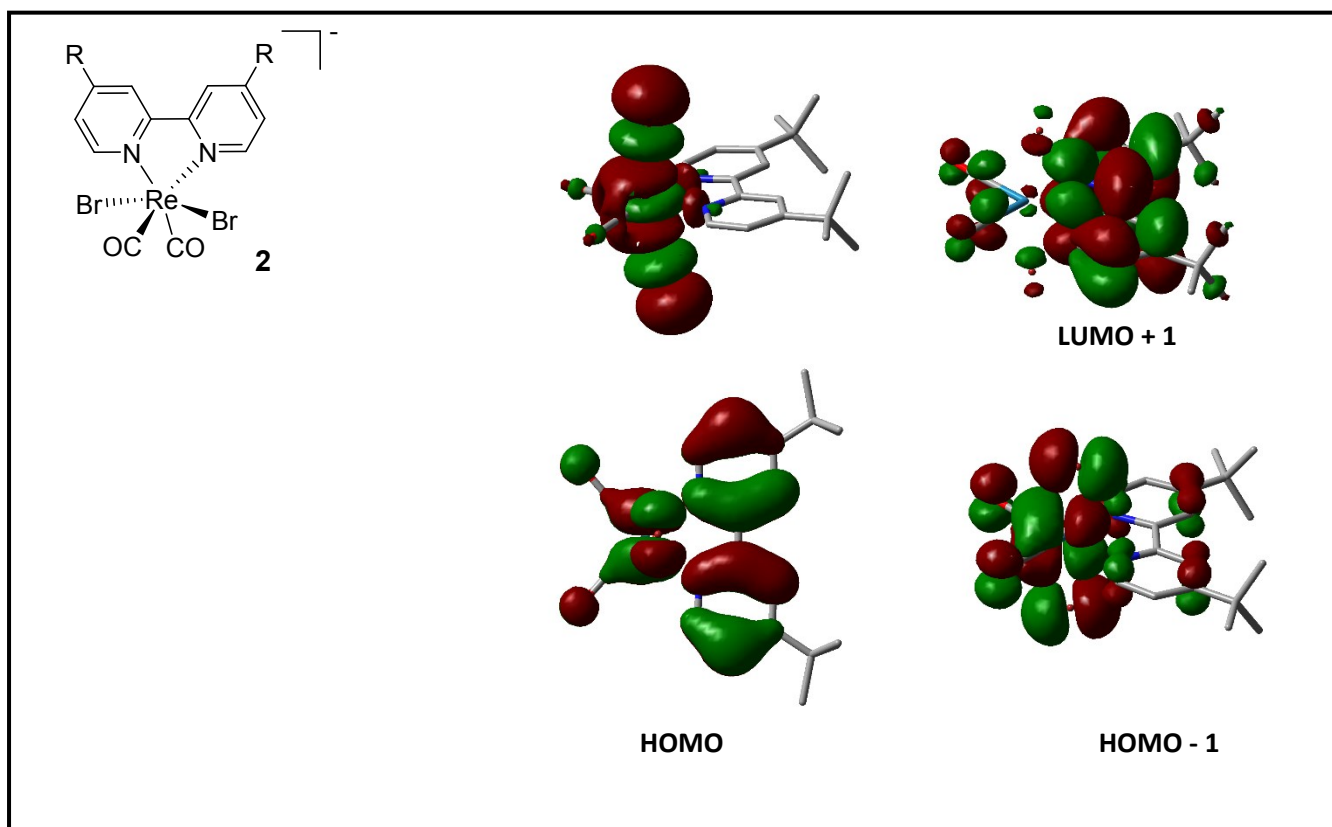


Figure S28. Calculated molecular orbitals of complexes **2** and **3**.

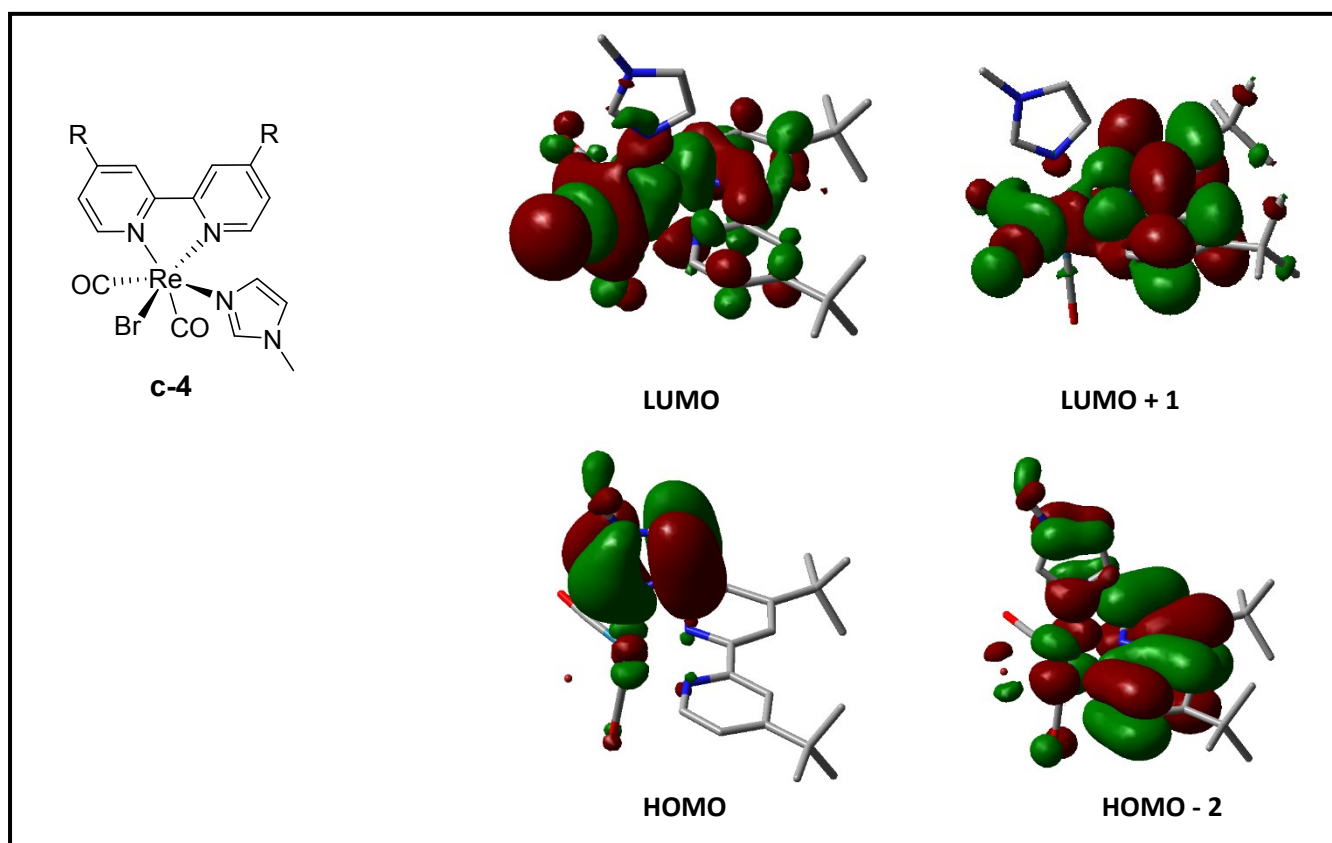
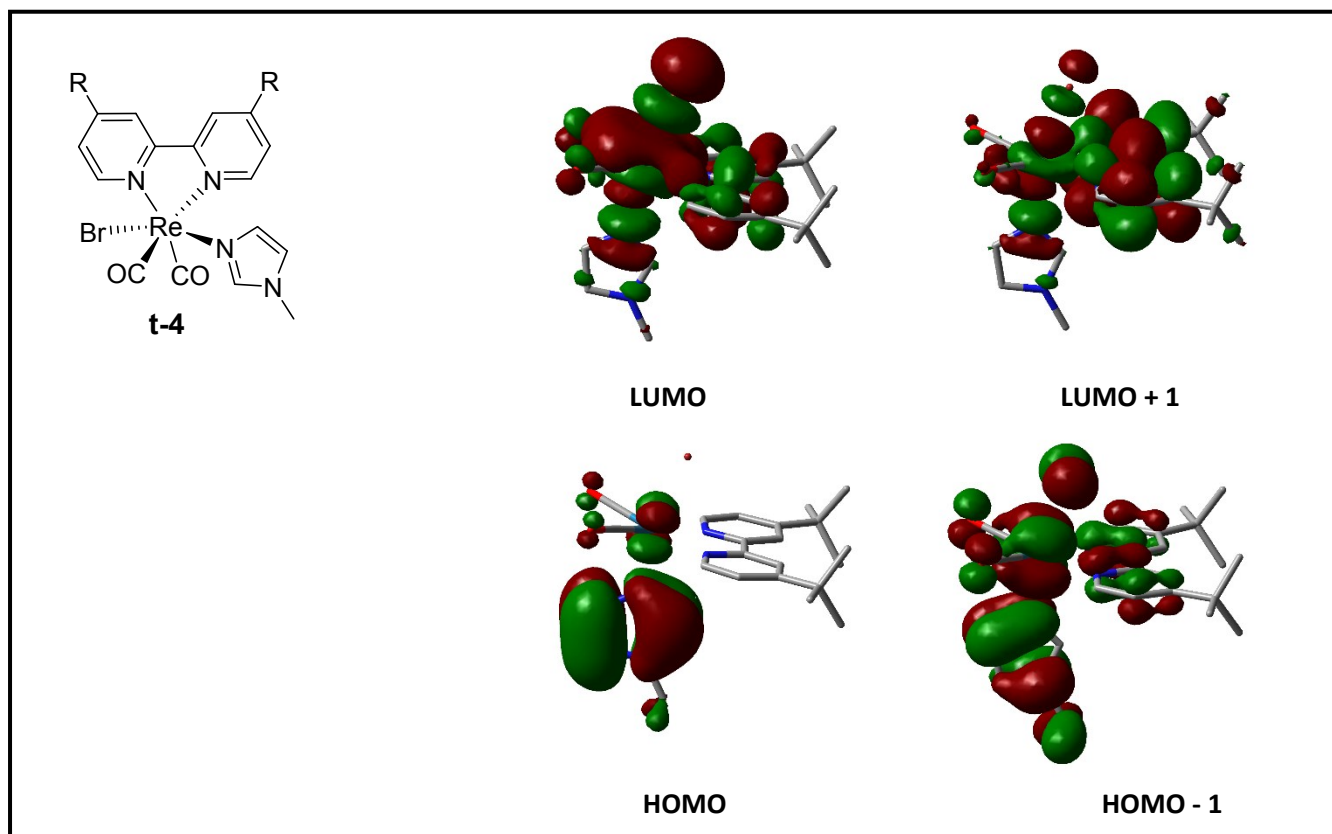


Figure S29. Calculated molecular orbitals of complexes **t-4** and **c-4**.

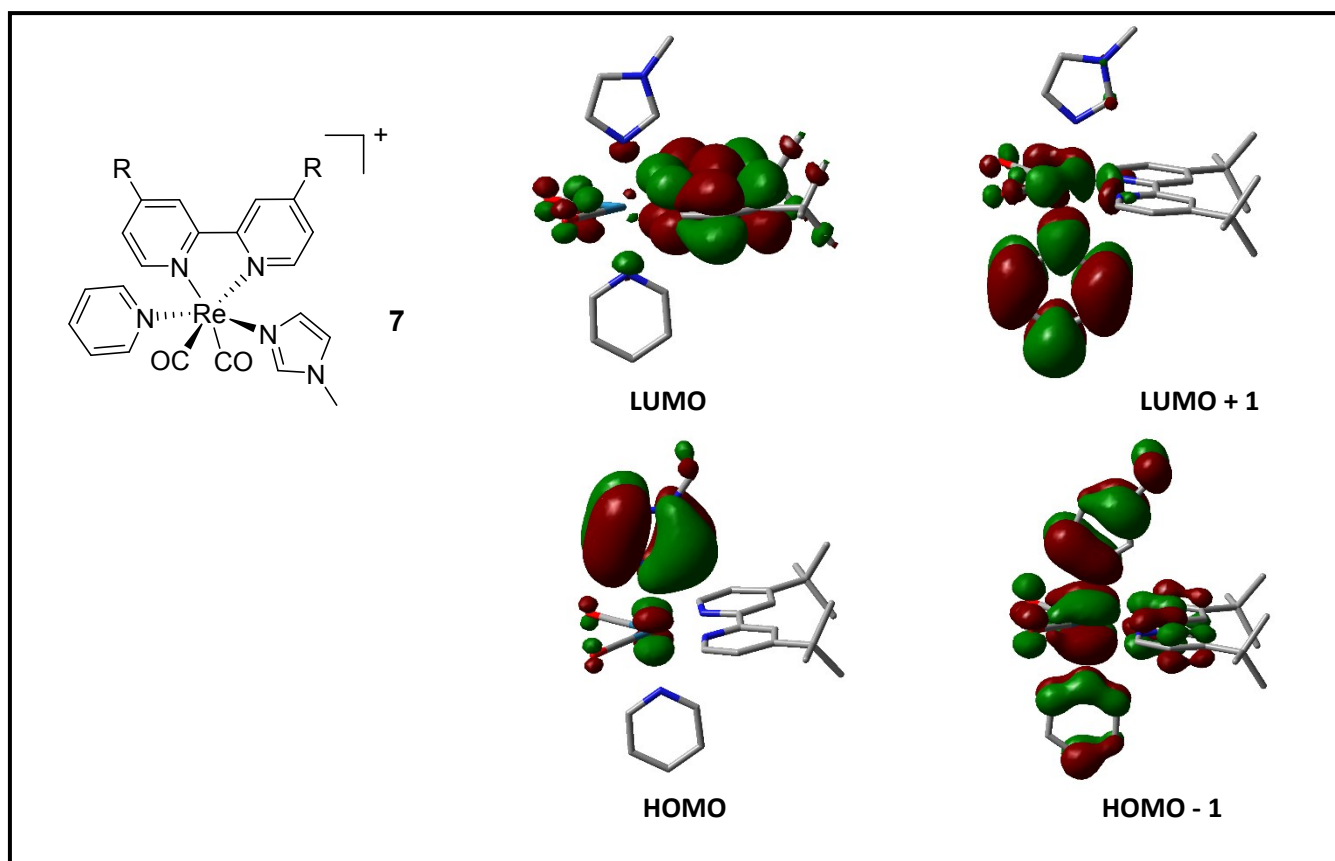
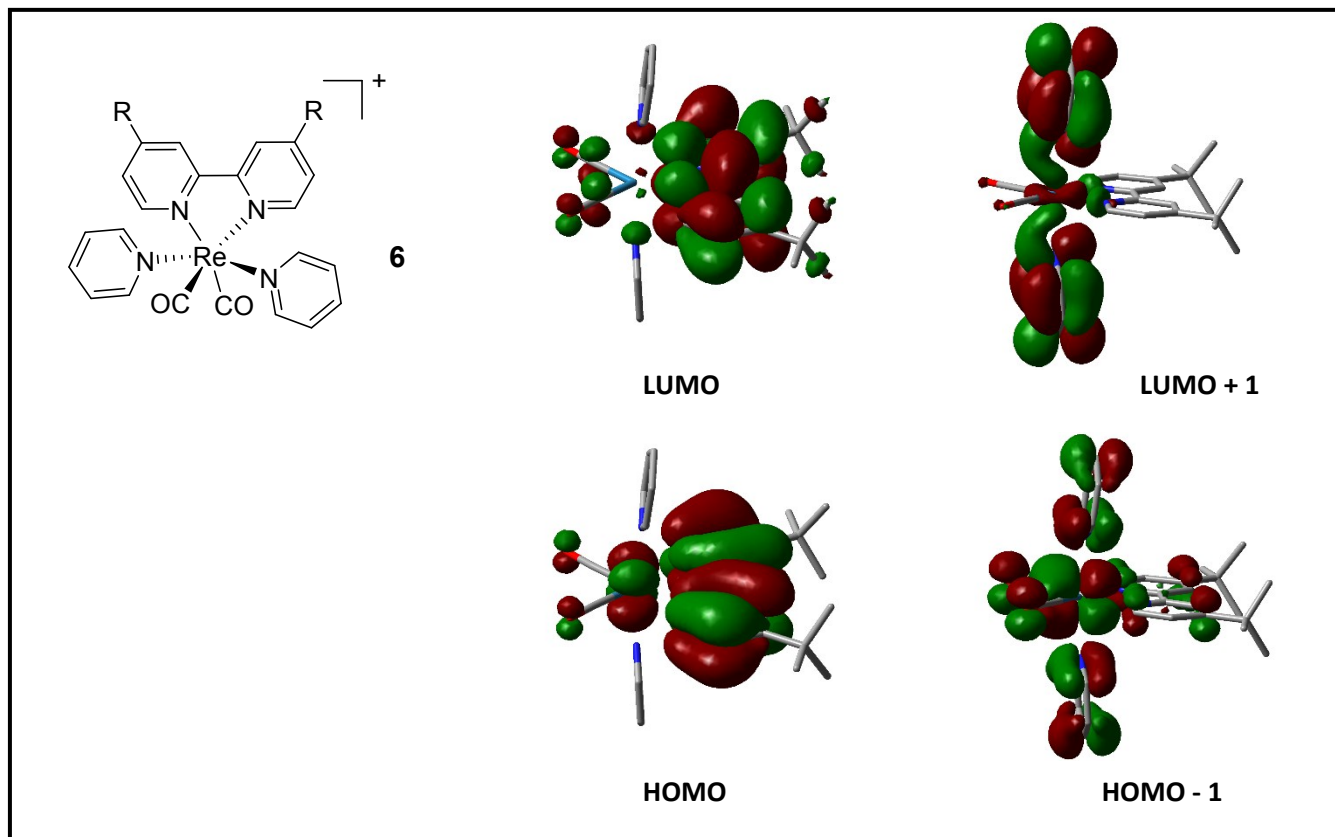


Figure S30. Calculated molecular orbitals of complexes **6** and **7**.

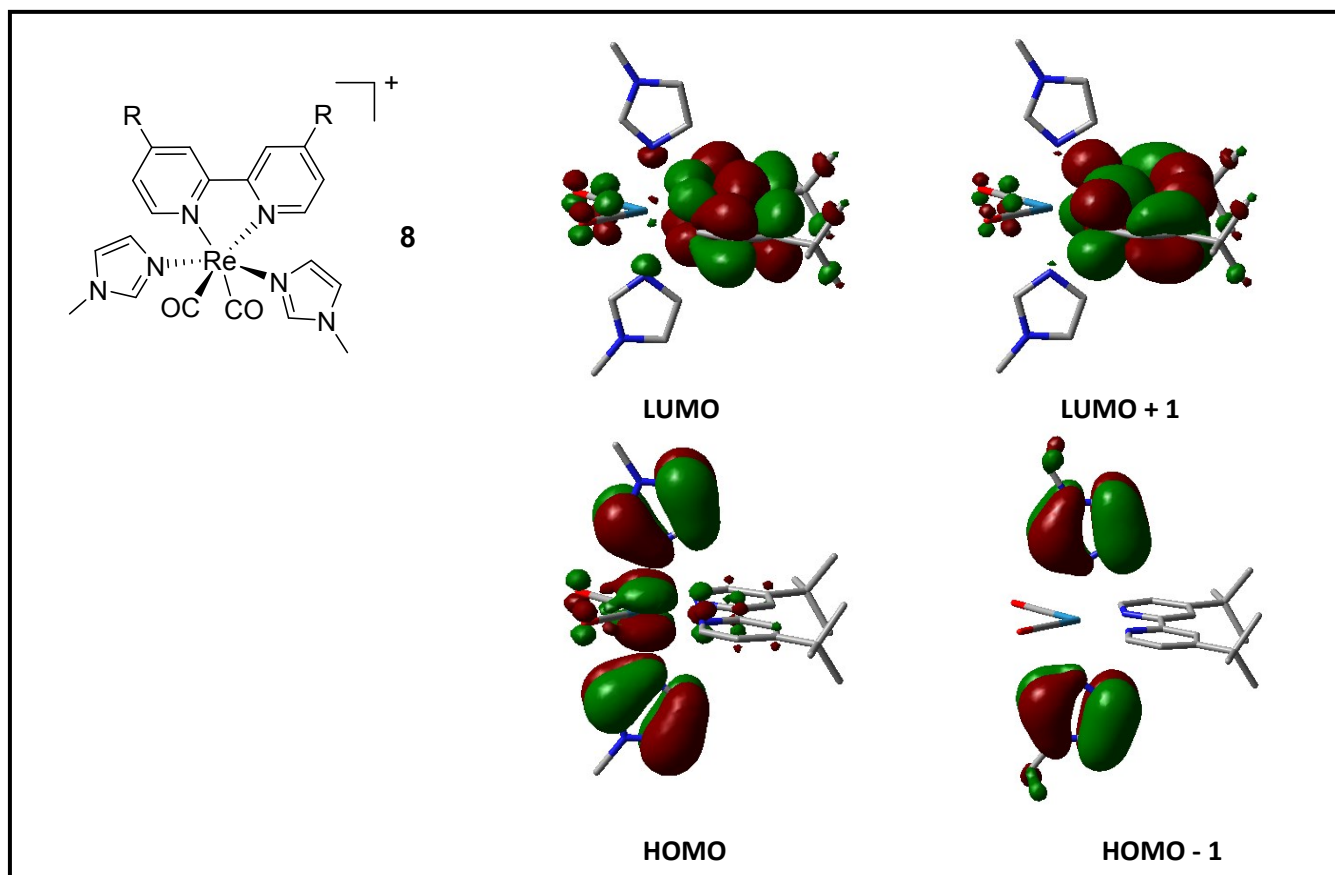


Figure S31. Calculated molecular orbitals of complex 8.

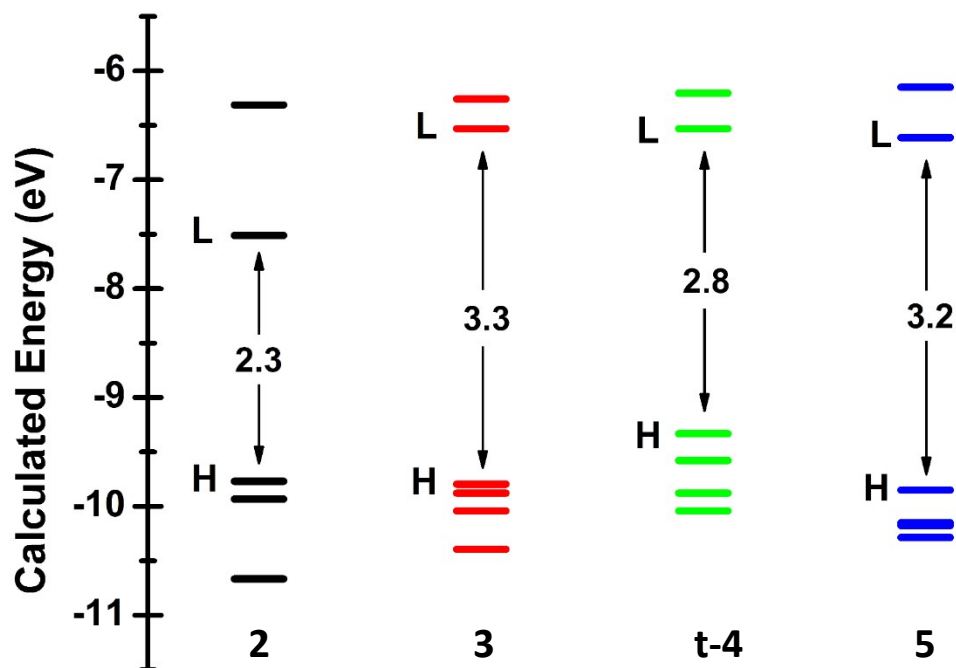


Figure S32. DFT energy diagram of $[\text{Re}(\text{CO})_2(\text{tBu}_2\text{bpy})\text{Br}(\text{L})]$ complexes, highlighting the HOMO – LUMO energy gap.

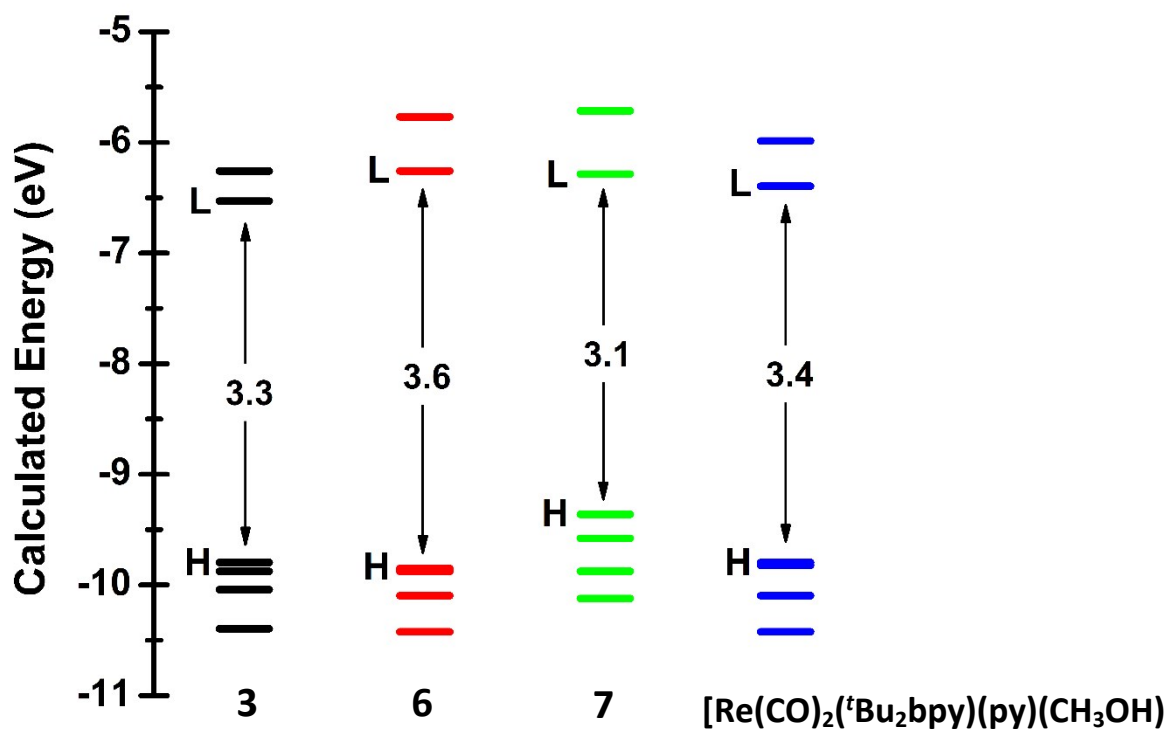


Figure S36. DFT energy diagram of $[\text{Re}(\text{CO})_2(\text{tBu}_2\text{bpy})(\text{py})(\text{L})]^n$ complexes, highlighting the HOMO – LUMO energy gap.