

Supplementary Information

Experimental and Theoretical Studies of the ancillary ligand (*E*)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-diterbutylphenol in Rhenium(I) core

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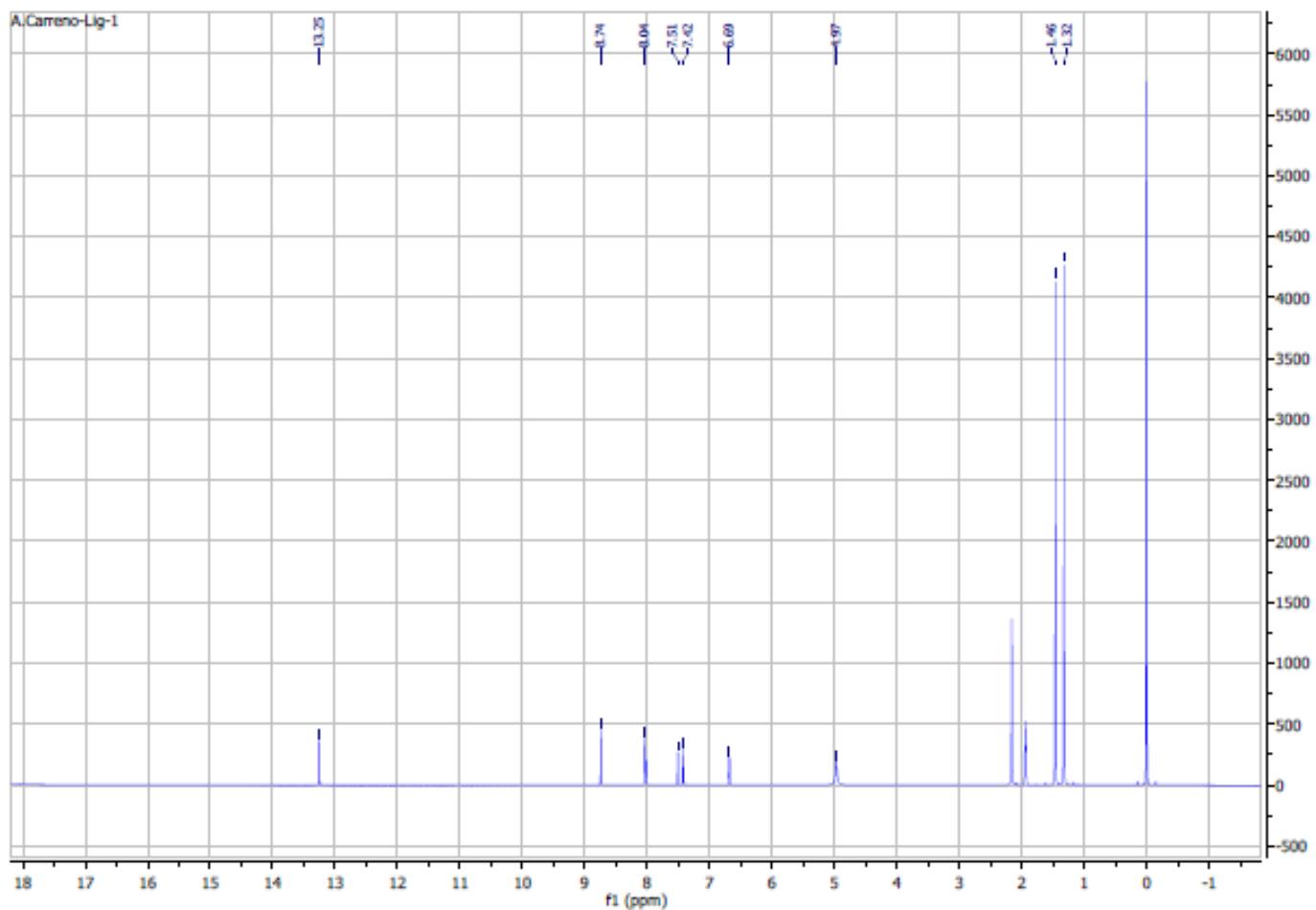


Figure S1. ^1H NMR spectra of **L** in acetonitrile deuterated.

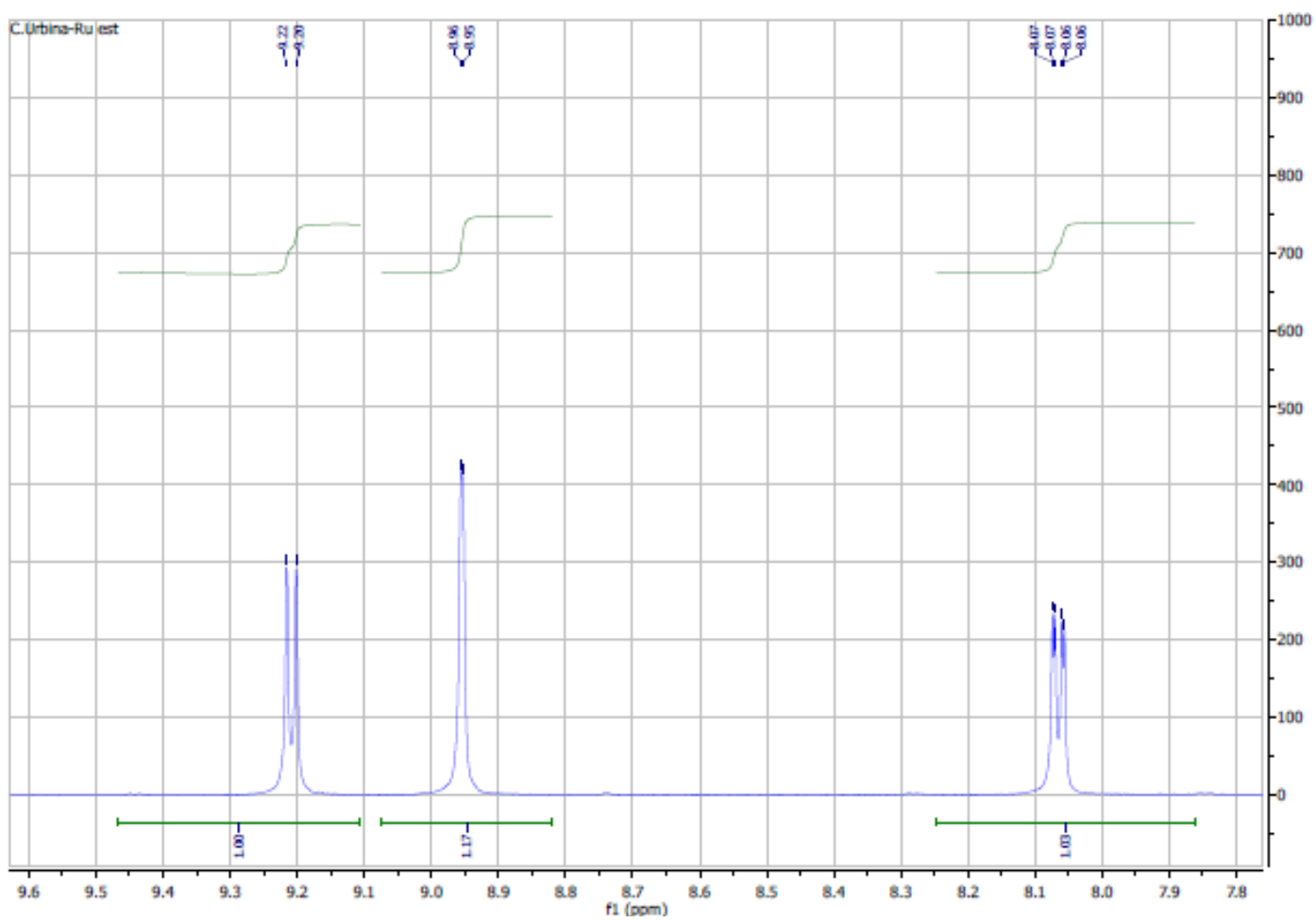


Figure S2. ^1H NMR of C1 in acetonitrile deuterated.

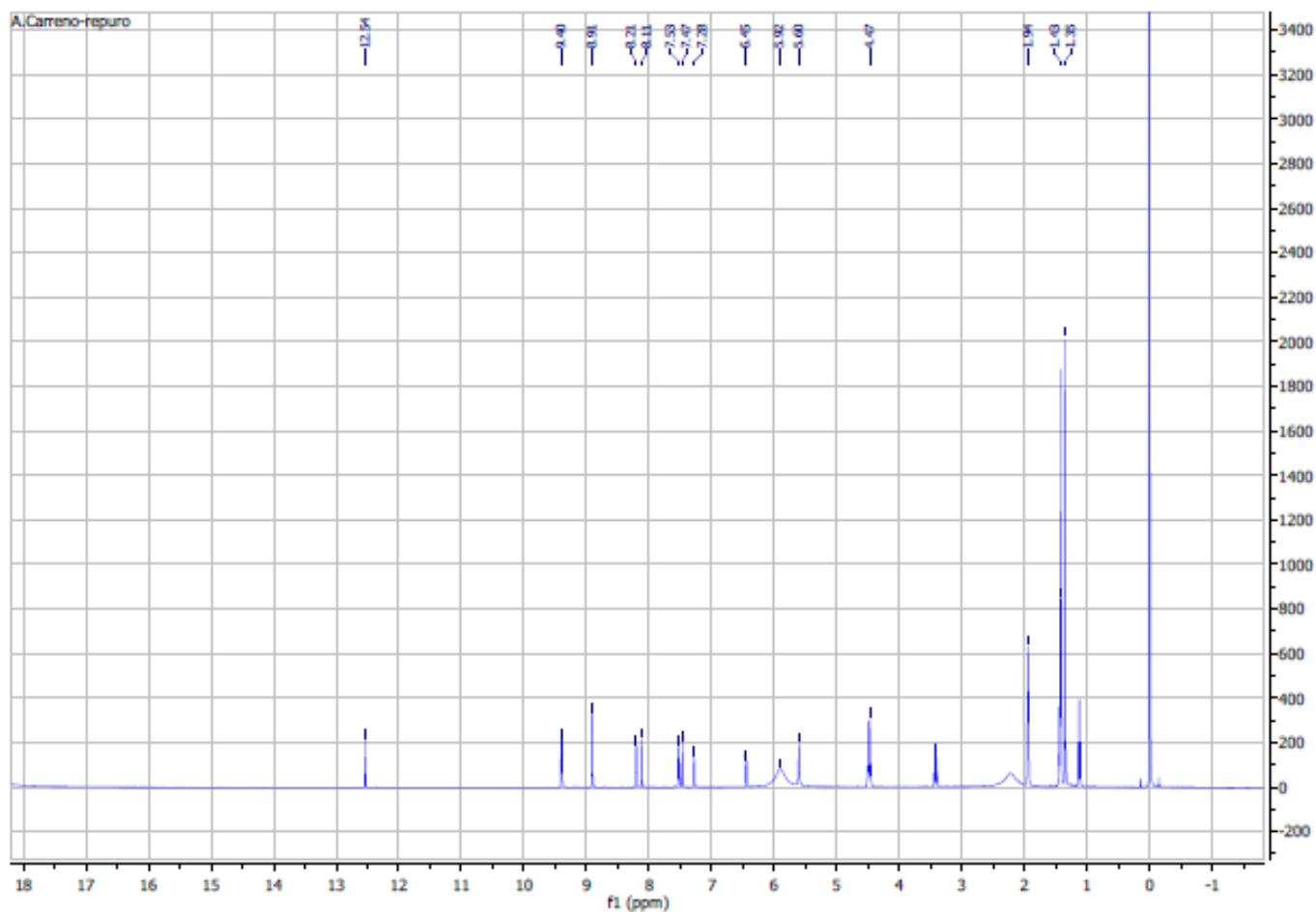


Figure S3. ^1H NMR of C2 in acetonitrile deuterated.

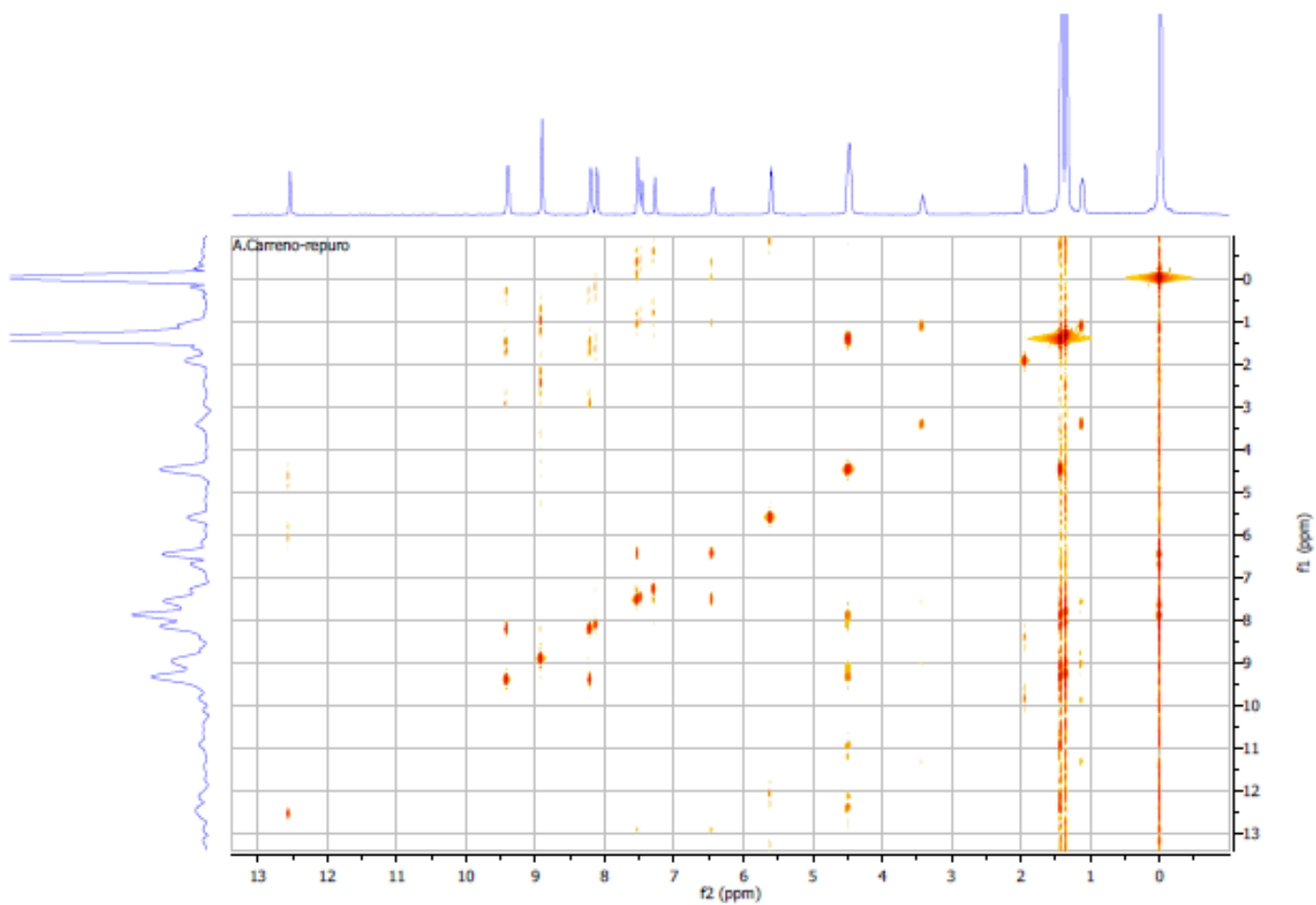


Figure S4. HHCOSY of C2 in acetonitrile deuterated.

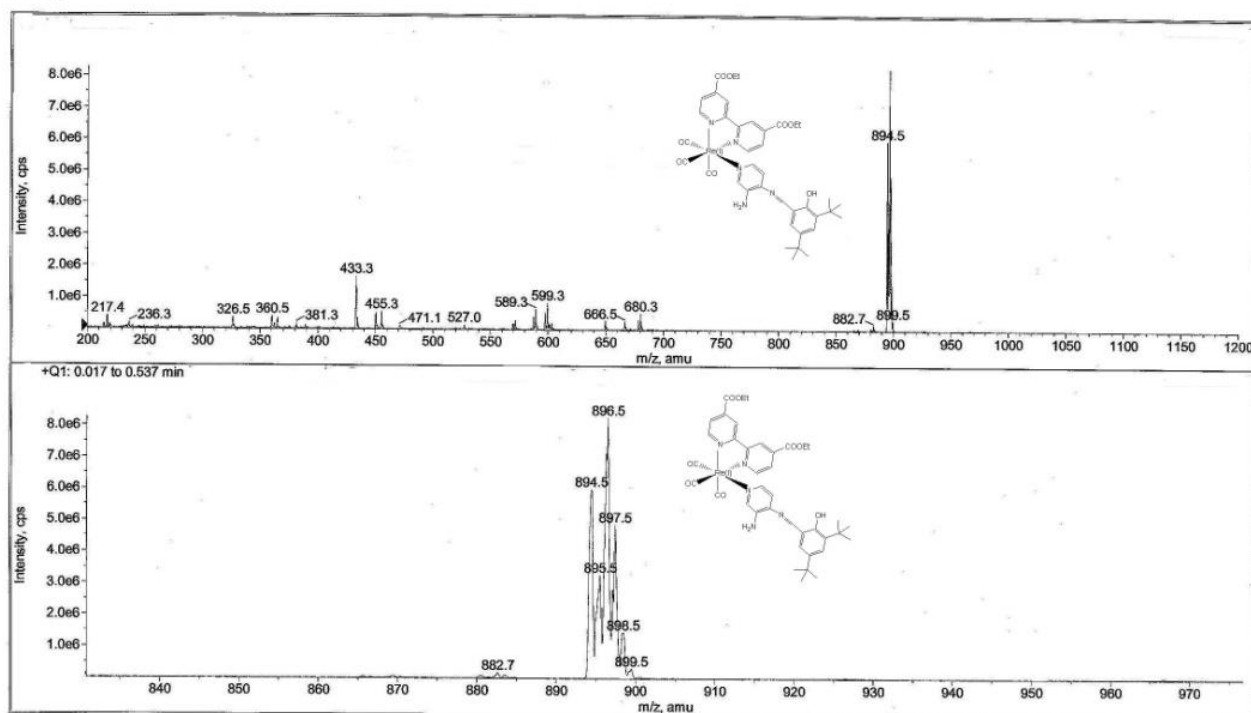


Figure S5. Mass spectra of C2.

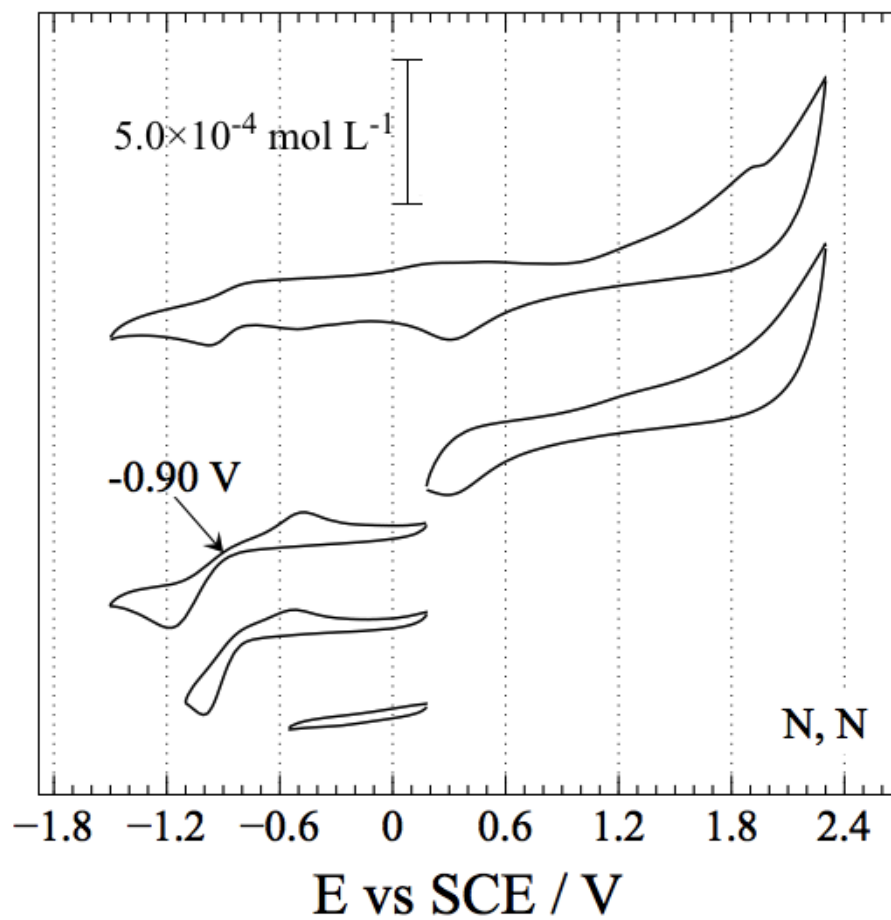


Figure S6. CV working-window study of **deeb**. Interface: Interface: Pt | 1.0×10^{-5} M of analyte + 1.0×10^{-4} M TBAPF₆ in anhydrous CH₃CN under an argon atmosphere.

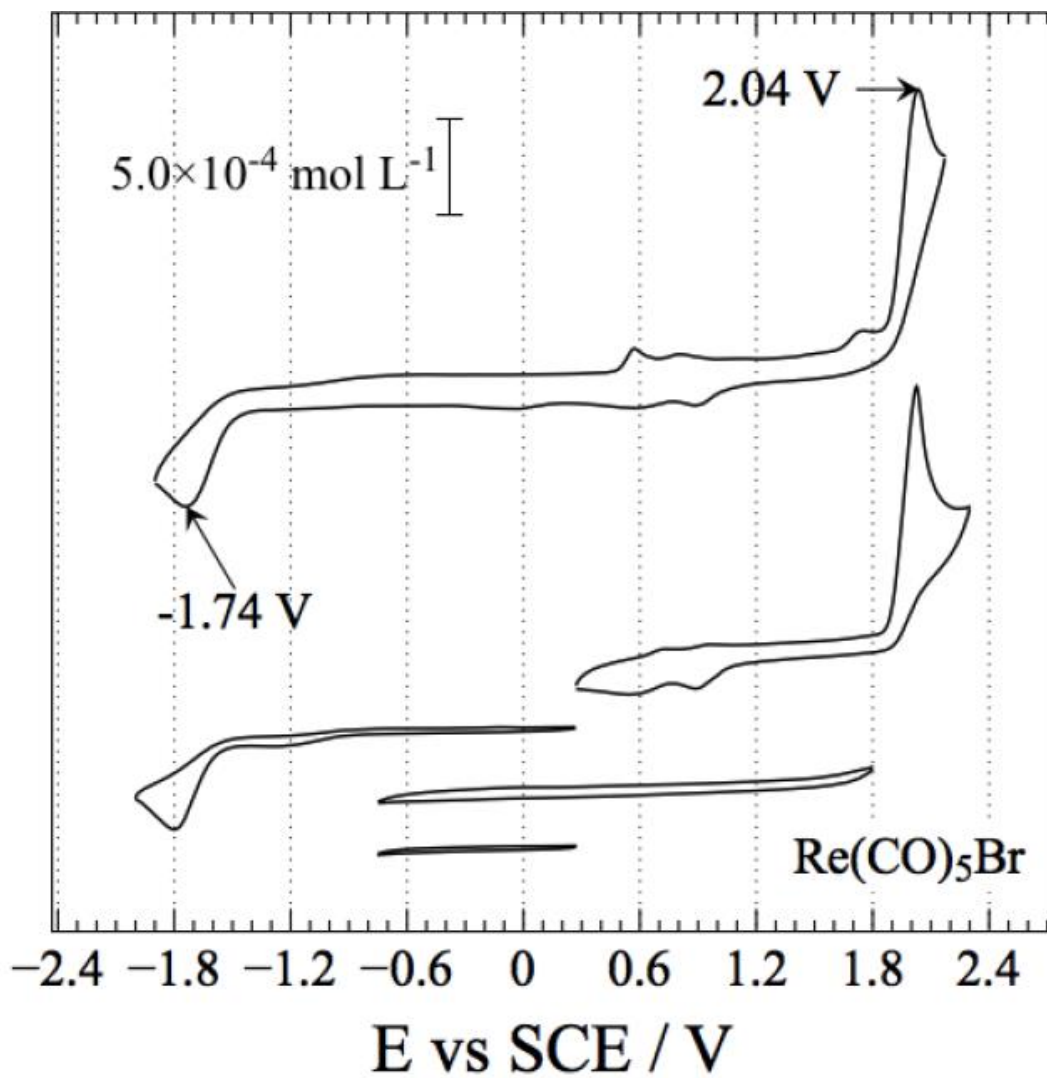


Figure S7. CV working-window study of $\text{Re}(\text{CO})_5\text{Br}$. Interface: Interface: Pt | $1.0 \times 10^{-5} \text{ M}$ of analyte + $1.0 \times 10^{-4} \text{ M}$ TBAPF₆ in anhydrous CH₃CN under an argon atmosphere.

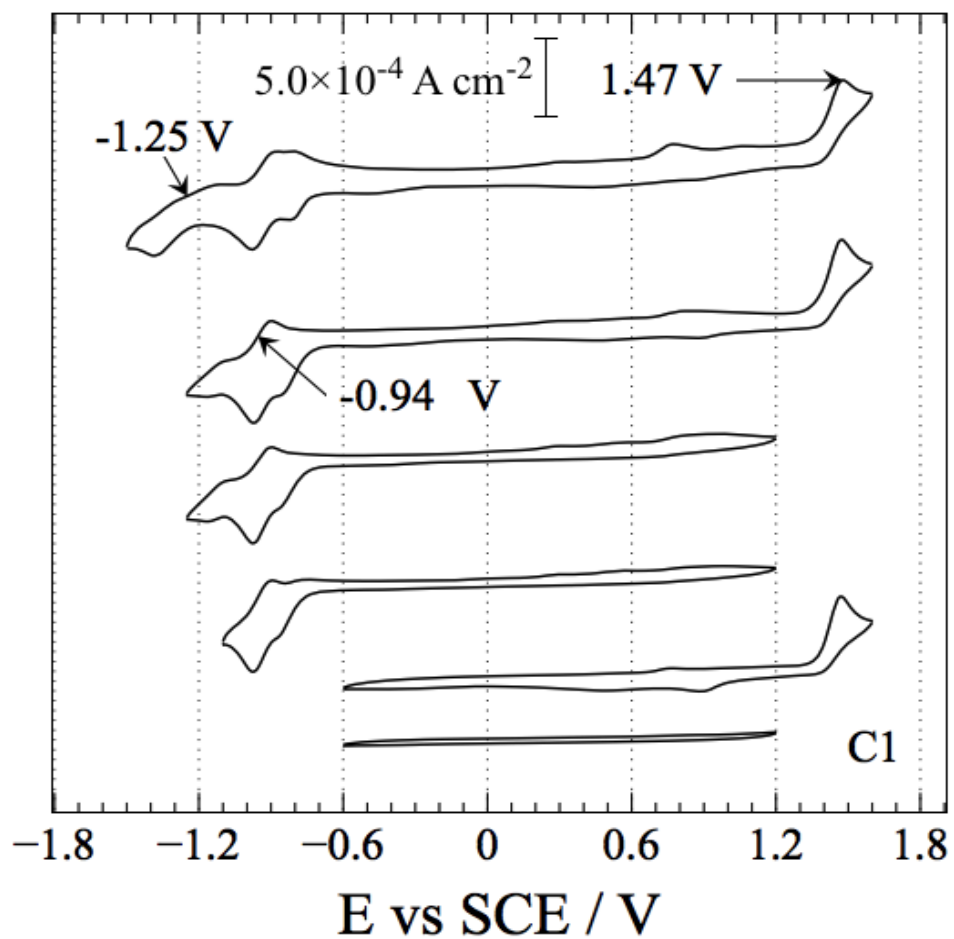


Figure S8. CV working-window study of **C1**. Interface: Interface: Pt | $1.0 \times 10^{-5} \text{ M}$ of analyte + $1.0 \times 10^{-4} \text{ M}$ TBAPF₆ in anhydrous CH₃CN under an argon atmosphere.

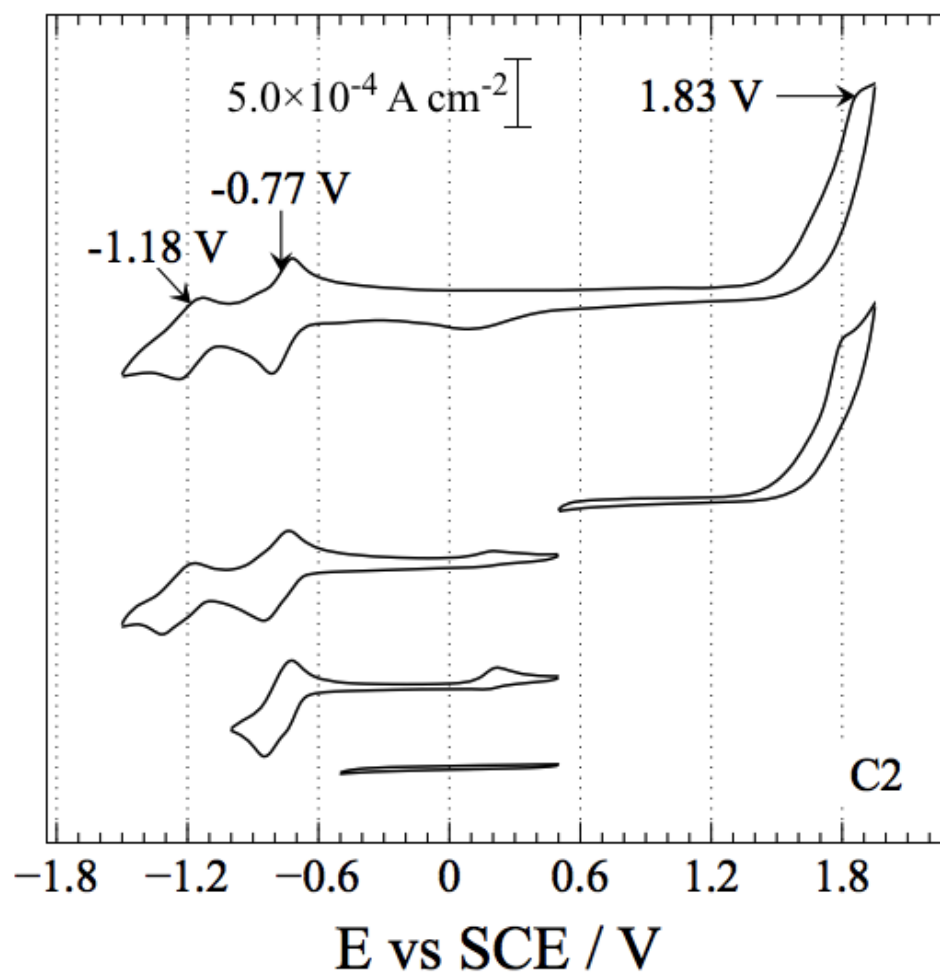


Figure S9. CV working-window study of **C2**. Interface: Interface: Pt | 1.0×10^{-5} M of analyte + 1.0×10^{-4} M TBAPF₆ in anhydrous CH₃CN under an argon atmosphere.

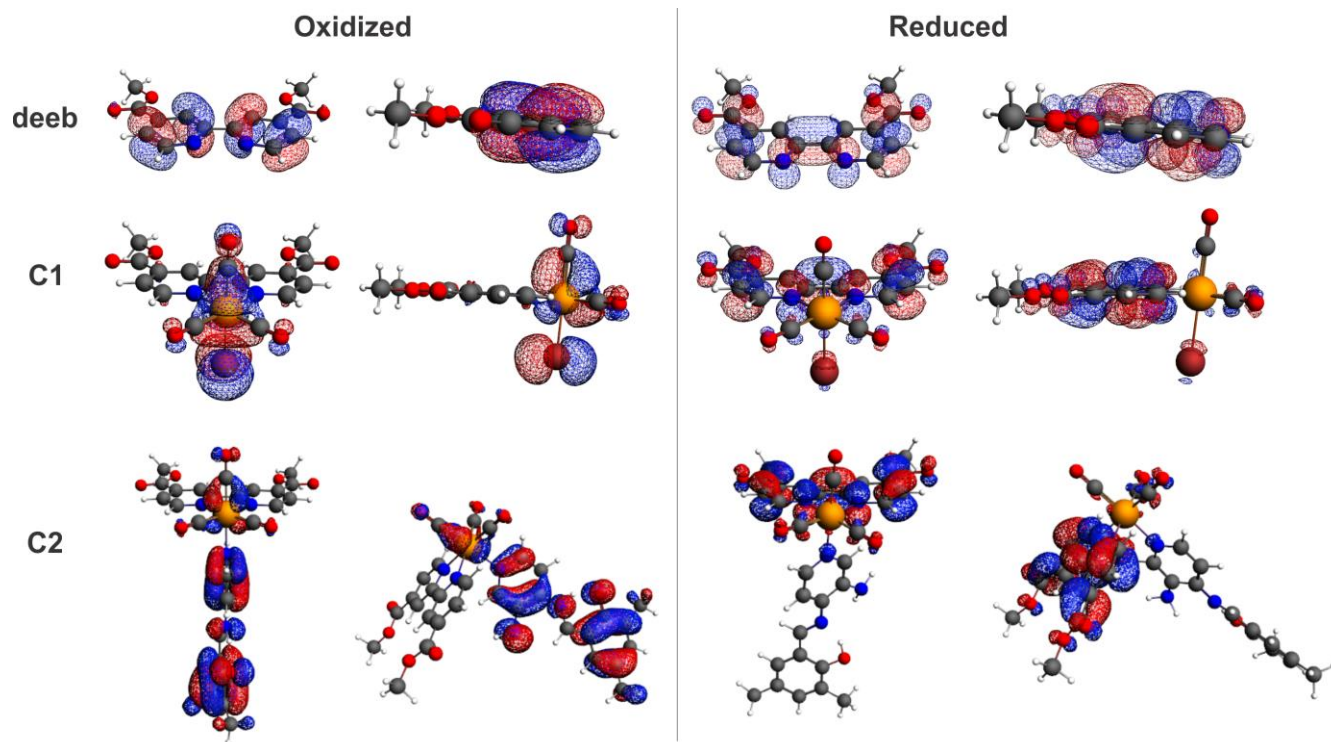


Figure S10. Two sides of view of the highest occupied orbitals of the oxidized and reduced states for deeb, C1 and C2.

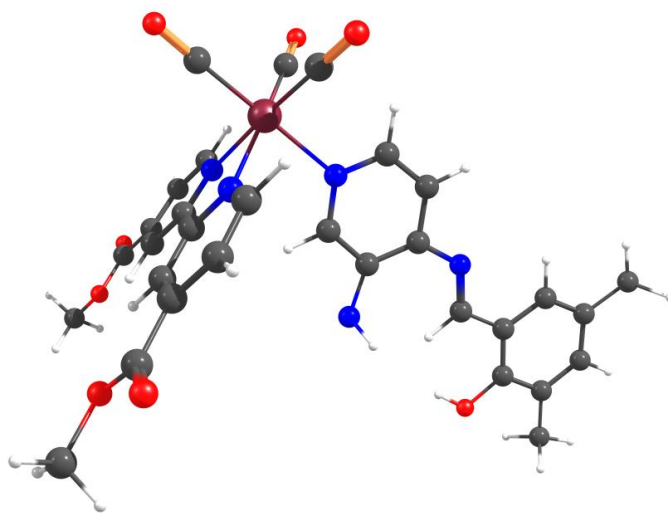


Figure S11. Optimized structure of C2 without the hydrogen bond in the L.

Table S1. Composition in percentage (%) of the frontier molecular orbitals for C1. The HOMO is indicated in bold.

Orb.	C≡O	Br	Re	deeb
80 γ 1/2	0	0	0	100
79 γ 1/2	0	0	0	100
78 γ 1/2	3	3	4	90
77γ1/2	37	48	11	0
76 γ 1/2	9	75	16	0
75 γ 1/2	29	9	60	2
64 γ 1/2	1	0	2	97

Table S2. Composition in percentage (%) of the frontier molecular orbitals for C2. The HOMO is indicated in bold.

Orb.	C≡O	L	Re	deeb
130 γ 1/2	100	0	0	0
126 γ 1/2	14	48	4	34
123 γ 1/2	1	99	0	0
121 γ 1/2	0	0	0	100
120 γ 1/2	4	0	3	94
119γ1/2	0	100	0	0
118 γ 1/2	9	88	3	0
116 γ 1/2	6	76	18	0
114 γ 1/2	30	4	65	2
111 γ 1/2	0	100	0	0