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Supporting information

Understanding the photophysical properties of rhenium(I) compounds coordinated to 4,7-diamine-1,10-phenanthroline: synthetic, luminescence and biological studies

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Figure S1: ^{1}H NMR spectrum of 4,7-diamine-1,10-phenanthroline in DMSO-d6 at room temperature (400 MHz).

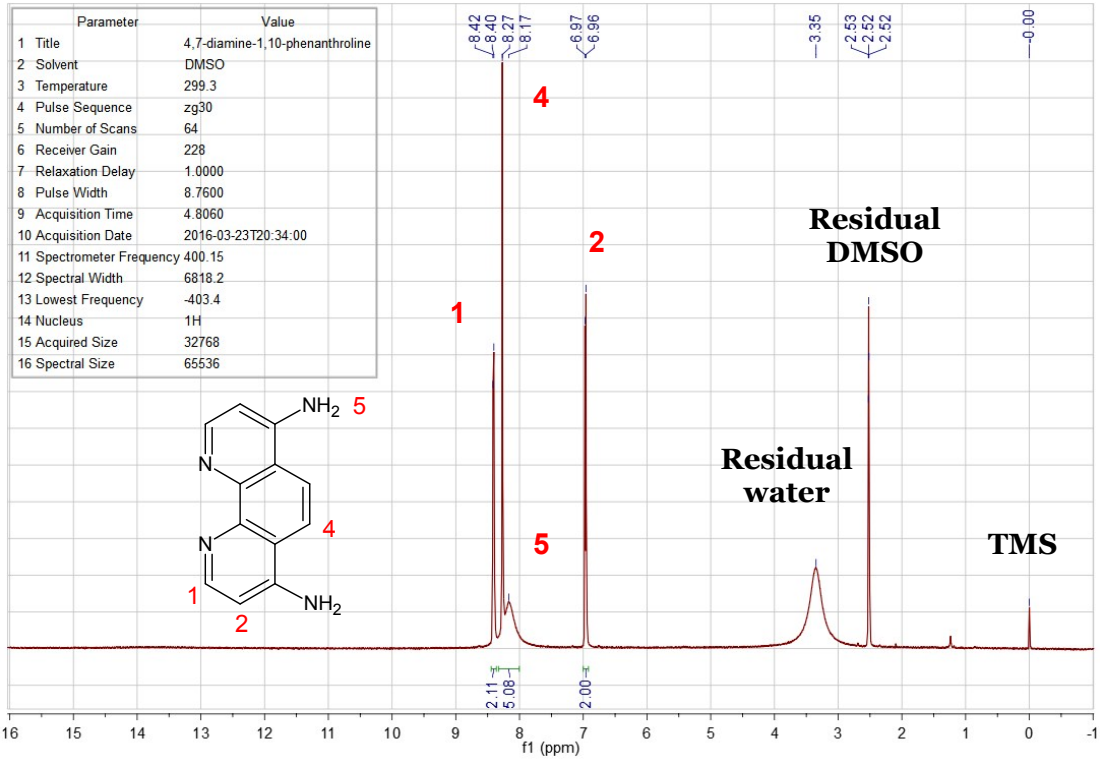
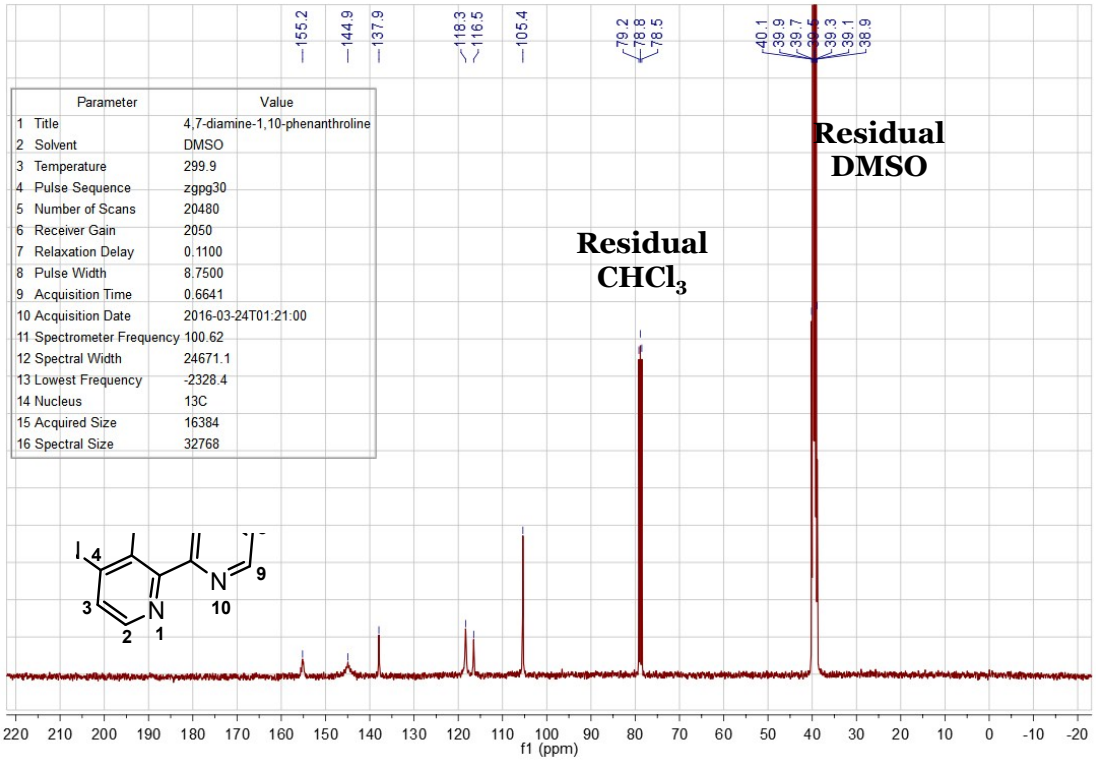


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of 4,7-diamine-1,10-phenanthroline in DMSO-d6: $CDCl_3$ at room temperature (400 MHz).



	Parameter	Value
1	Title	4,7-diamine-1,10-phenanthroline
2	Solvent	DMSO
3	Temperature	299.9
4	Pulse Sequence	zgpg30
5	Number of Scans	20480
6	Receiver Gain	2050
7	Relaxation Delay	0.1100
8	Pulse Width	8.7500
9	Acquisition Time	0.6641
10	Acquisition Date	2016-03-24T01:21:00
11	Spectrometer Frequency	100.62
12	Spectral Width	24671.1
13	Lowest Frequency	-2328.4
14	Nucleus	13C
15	Acquired Size	16384
16	Spectral Size	32768

Figure S3: IR spectrum of 4,7-diamine-1,10-phenanthroline in KBr.

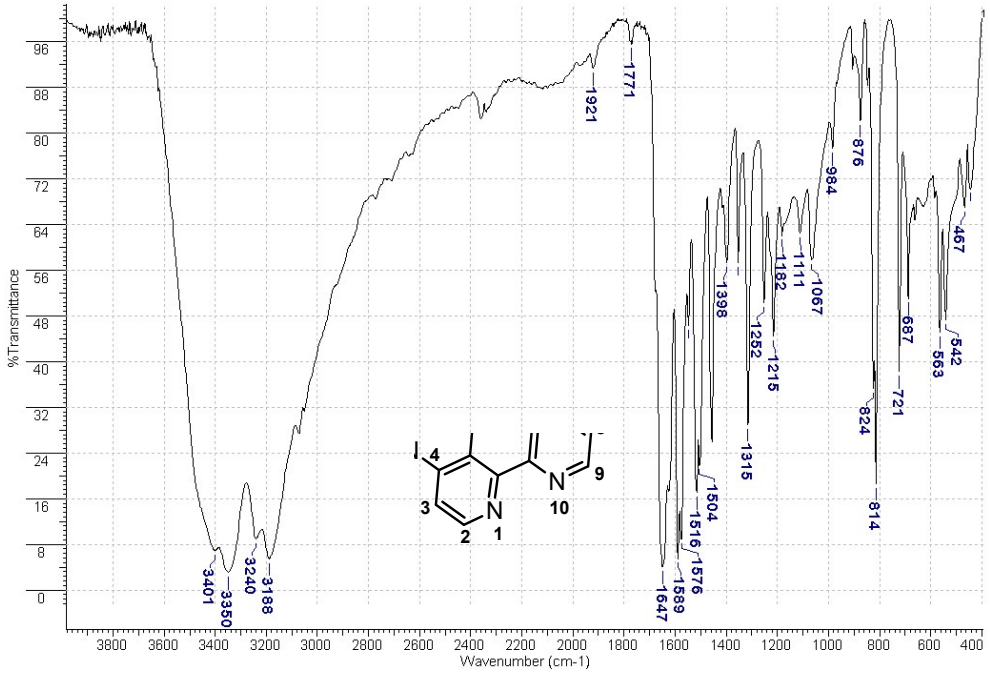


Figure S4: HRMS (ESI) of 4,7-diamine-1,10-phenanthroline. Calc. $[M+H]^+$ 211.0978; Found: 211.0975. (Error 1,7 ppm).

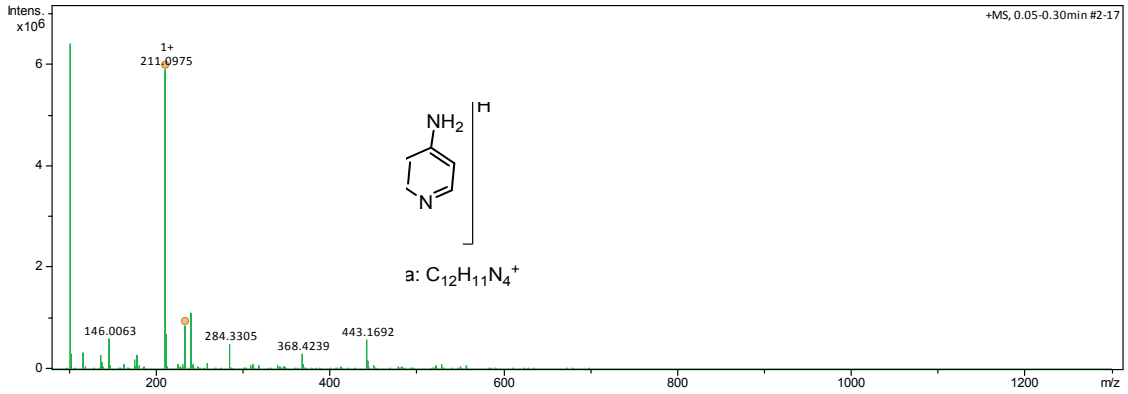


Figure S5: ^1H NMR spectrum of *fac*-[ReCl(Am$_2$phen)(CO)$_3$] in CD_3CN at room temperature (500MHz).

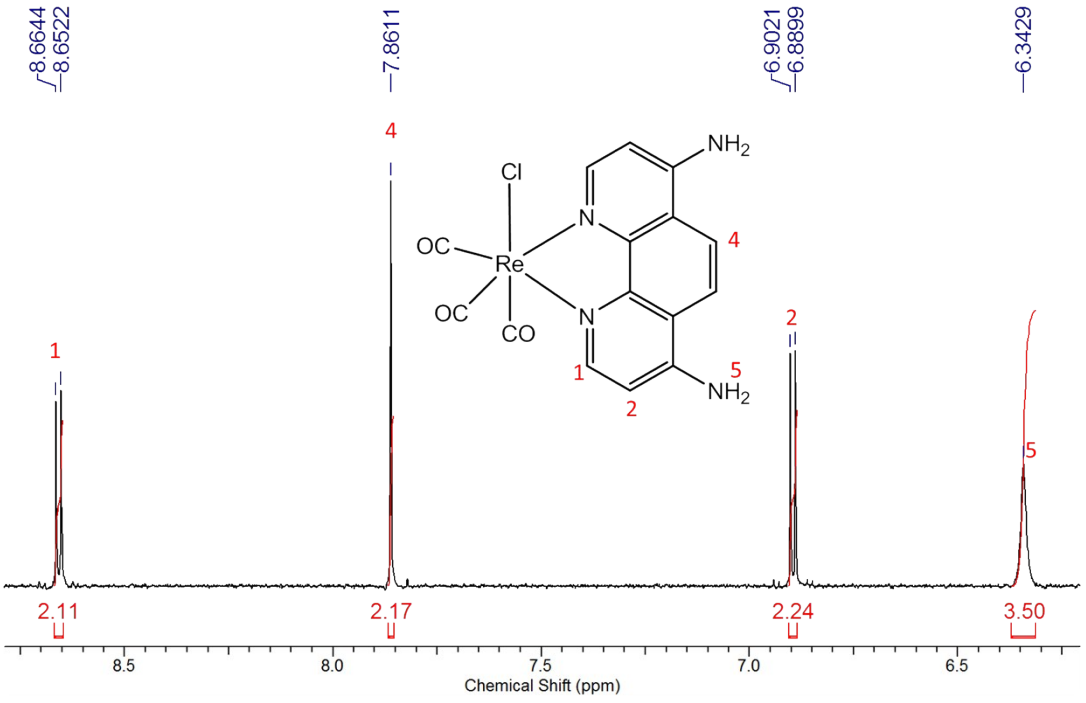


Figure S6: FTIR spectrum of *fac*-[ReCl(Am_2phen)($CO)_3$].

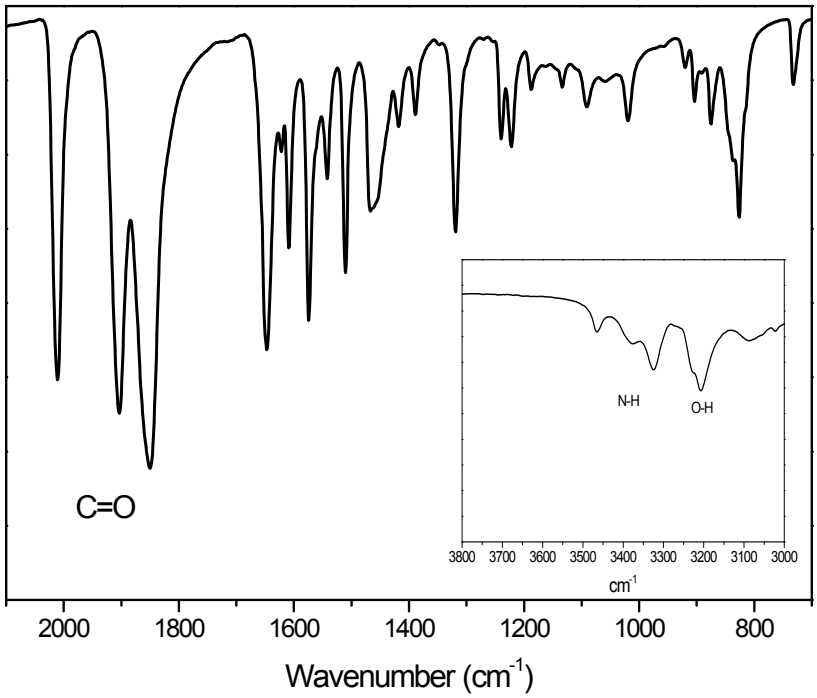


Figure S7: ^{1}H NMR spectrum of *fac*-[Re(et-isonic)(Am_2phen)($CO)_3$]$^+$ in CD_3CN at room temperature (500 MHz).

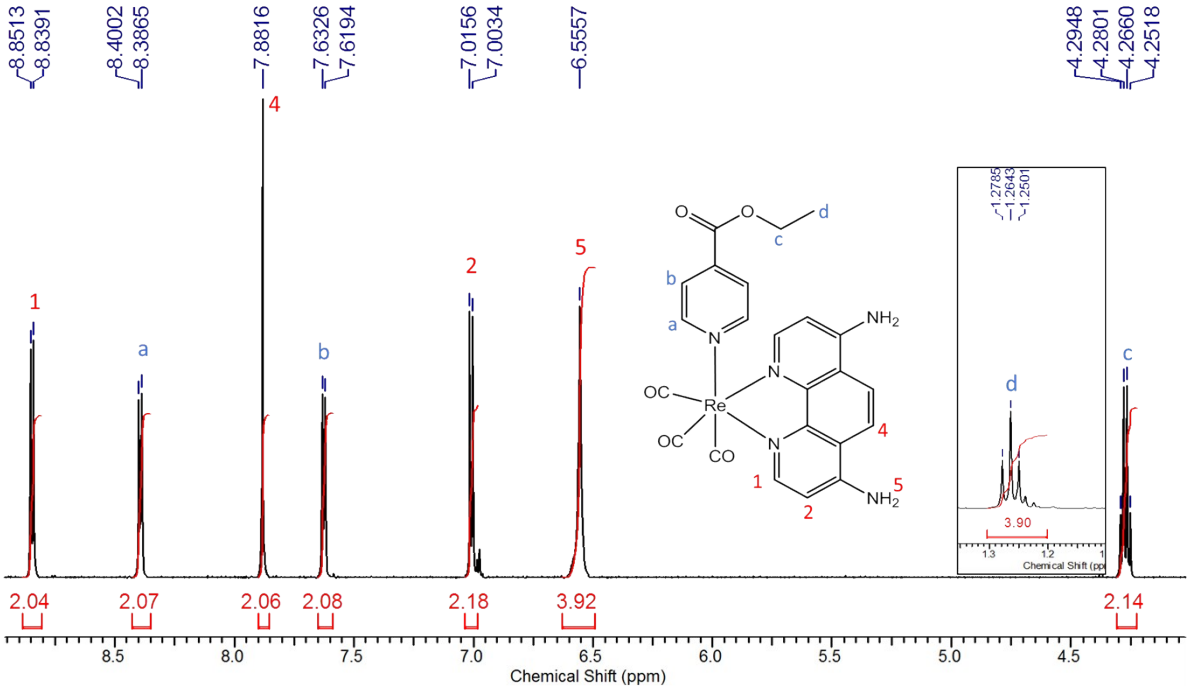


Figure S8: FTIR spectrum of *fac*-[Re(et-isonic)(Am_2phen)($CO)_3$]PF_6

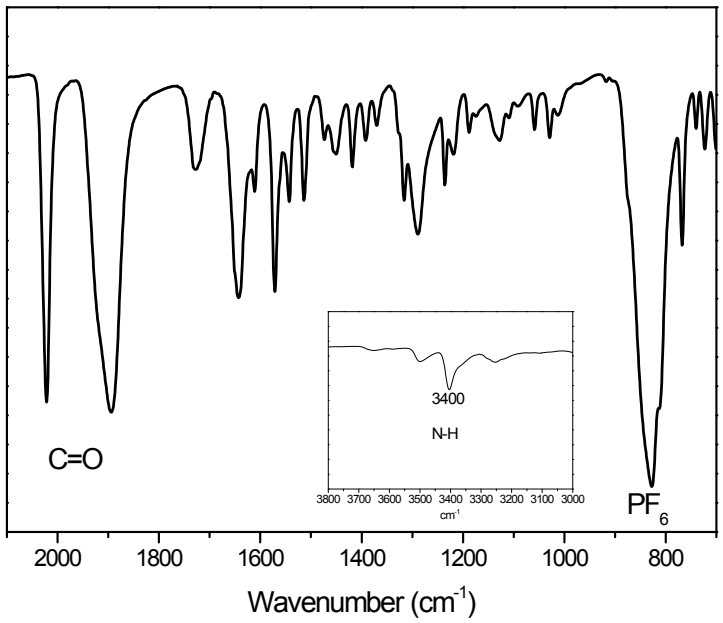


Figure S9: ^{1}H NMR spectrum of *fac*-[ReCl(et-isonic)$_2$($CO)_3$] in CD_3CN at room temperature (300 MHz).

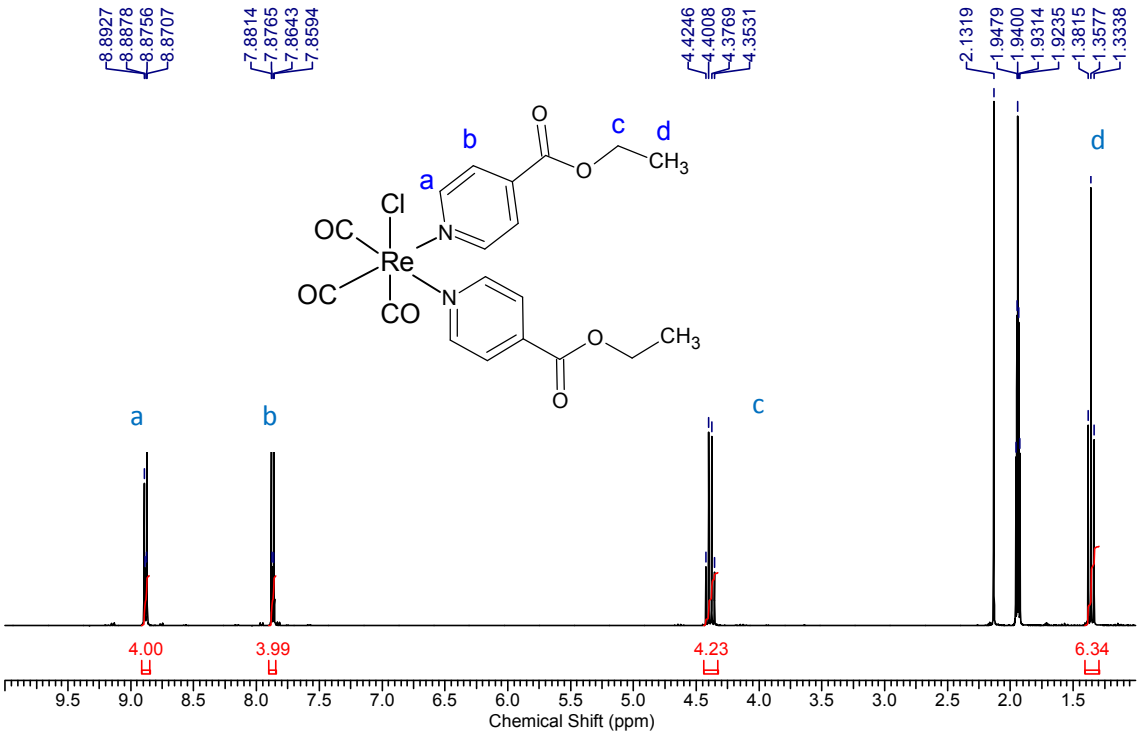


Figure S10: IR spectrum of *fac*-[ReCl(et-isonic)$_2$(CO)$_3$] in KBr

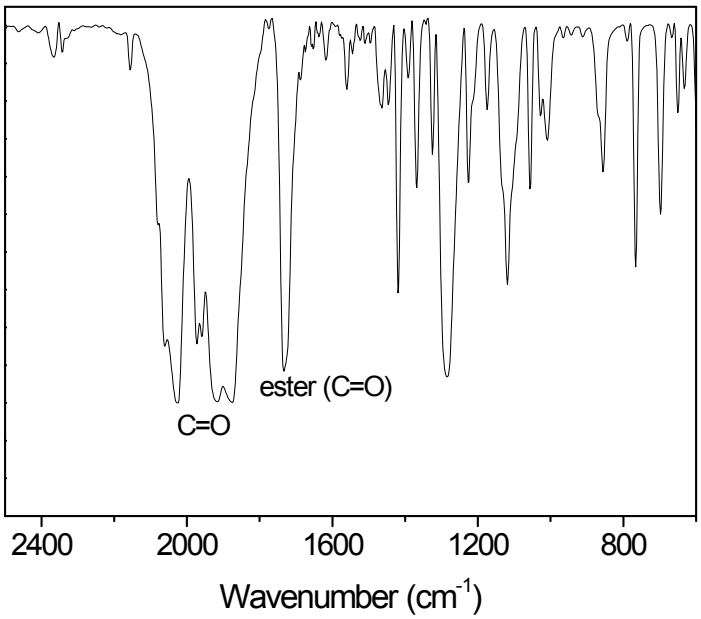


Table S1. ^{1}H NMR data for Am_2phen ligand in DMSO-d6 and for *fac*-$[Re(L)(Am_2phen)(CO)_3]^{0/+}$ compounds in CD_3CN at room temperature.

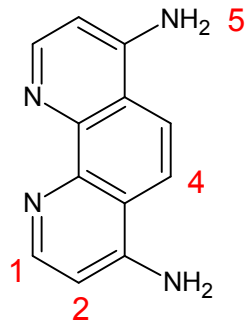
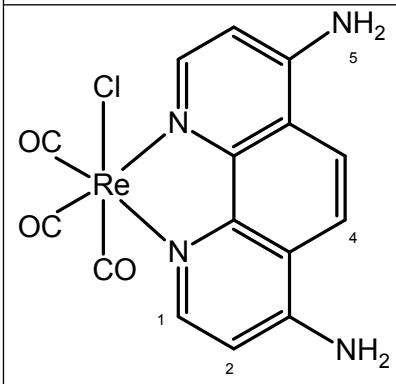
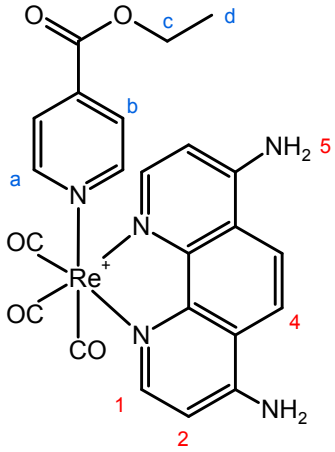
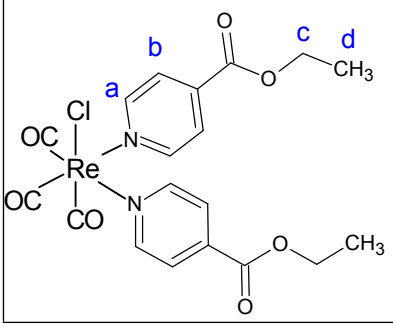
Compound	Proton	δ (ppm)	J (Hz)
	H1 (d) H4 (s) H2 (d) H5 (br)	8.41 8.27 8.17	6.1
	H1 (d) H4 (s) H2 (d) H5 (br)	8.69 7.93 6.94 6.39	6.1 6.1
	H1 (d) Ha (dd) H4 (s) Hb (dd) H2 (d) H5 (br) Hc (q) Hd (t)	8.84 8.39 7.88 7.62 7.00 6.55 4.27 1.26	6.1 5.4; 1.5 5.2; 1.5 6.1 7.1 7.1
	Ha (dd) Hb (dd) Hc (q) Hd (t)	8.88 7.87 4.39 1.36	6.6; 5.1 6.6; 5.1 7.1 7.1

Table S2. Calculated bond lengths and angle of *fac*-[Re(L)(Am_2phen)$(CO)_3]^{0/+1}$, *fac*-[Re(L)(phen)$(CO)_3]^{0/+1}$ and *fac*-[ReCl(et-isonic)$_2(CO)_3$] compounds.

Bond Lenght	***fac*-[Re(L)(Am_2phen)$(CO)_3]^{0/+1}$**	
	Cl	**et-isonic**
Re-C (equatorial) (Å)	1.92	1.93
Re-C (ancillary) (Å)	1.90	1.93
Re-$N_{(NN)}$ (Å)	2.18	2.18
Re-L (Å)	2.56	2.23
$N_{(NN)}$-Re-$N_{(NN)}$ (°)	75.55	75.42
Bond Lenght	***fac*-[Re(L)(phen)$(CO)_3]^{0/+1}$**	
	Cl	**et-isonic**
Re-C (equatorial) (Å)	1.92	1.93
Re-C (ancillary) (Å)	1.91	1.93
Re-$N_{(NN)}$ (Å)	2.18	2.19
Re-L (Å)	2.55	2.24
$N_{(NN)}$-Re-$N_{(NN)}$ (°)	76.33	76.20

Bond Lenght	***fac*-[ReCl(et-isonic)$_2(CO)_3$]**
Re-C (equatorial) (Å)	1.93
Re-C (ancillary) (Å)	1.90
Re-N (Å)	2.22
Re-Cl (Å)	2.55
N-Re-N (°)	85.94

Table S3. Vibrational data (ν_{CO}) of *fac*-[ReCl(NN)$(CO)_3$], *fac*-[Re(et-isonic)(NN)$(CO)_3]PF_6$ and *fac*-[ReCl(et-isonic)$_2(CO)_3$] compounds.

Compound	**Experimental (cm^{-1})**	**Calculated (cm^{-1})**
fac-[ReCl(Am_2phen)$(CO)_3$]	2010; 1903; 1850	1976.70; 1891.57; 1868.60
fac-[Re(et-isonic)(Am_2phen)$(CO)_3]PF_6$	2021; 1894	1996.23; 1913.43; 1902.32
fac-[ReCl(phen)$(CO)_3$]	2014; 1925; 1887	1982.76; 1902.41; 1879.08
fac-[Re(et-isonic)(phen)$(CO)_3]PF_6$	2030; 1930; 1910	2002.86; 1924.31; 1913.34
fac-[ReCl(et-isonic)$_2(CO)_3$]	2027; 1917; 1873	1990.95; 1914.75; 1867.16

Figure S11. Isosurface plots of frontier orbitals of *fac*-[ReCl(Am$_2$phen)(CO)$_3$].

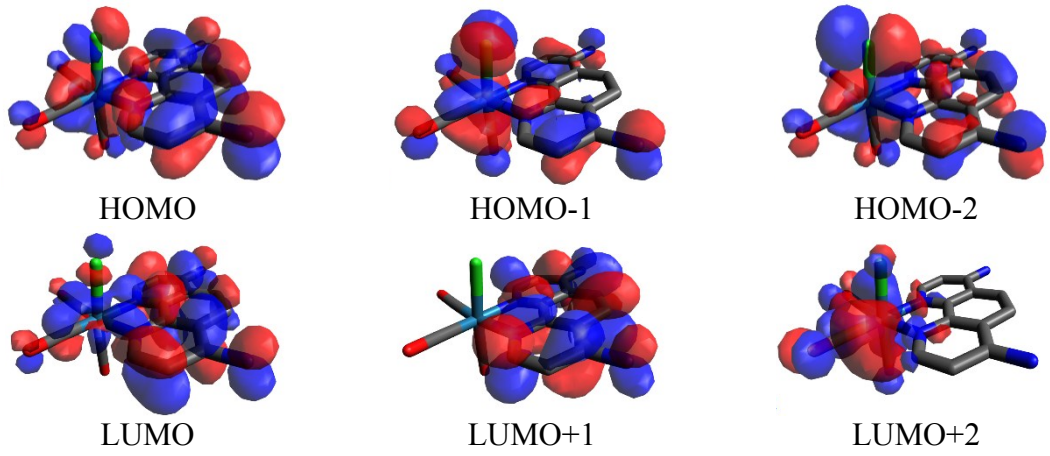


Table S4. Calculated spectral parameters of *fac*-[ReCl(et-isonic)$_2$(CO)$_3$] complex in CH_3CN.

Transition (contribution)	**λ (nm)**	**Oscillator strength**	**Main Character**
H → L (84%)	393	0.0261	$MLCT_{Re\rightarrow \text{ et-isonic}}$
H-1 →L+1 (82%)	388	0.0123	$MLCT_{Re\rightarrow \text{et-isonic}}$
H-1→ L (30%)	387	0.0370	$MLCT_{Re\rightarrow \text{et-isonic}}$
H → L+1 (38%)			$MLCT_{Re\rightarrow \text{et-isonic}}$
H-2 → L (86%)	363	0.1287	$MLCT_{Re\rightarrow \text{et-isonic}}$
H-2 → L+1 (71%)	353	0.1664	$MLCT_{Re\rightarrow \text{et-isonic}}$
H-5 → L+1 (13%)	263	0.0500	LLCT
H-2 → L+3 (14%)			$MLCT_{Re\rightarrow \text{et-isonic}}$
H-1 → L+5 (15%)			$MLCT_{Re\rightarrow \text{et-isonic}}$
H → L+5 (15%)			$MLCT_{Re\rightarrow \text{et-isonic}}$
H-11 → L (45%)	232	0.1021	$ILCT_{\text{ethyl ester}\rightarrow py}$
H-11 → L+1 (22%)			$ILCT_{\text{ethyl ester}\rightarrow py}$
H-10 → L+1 (23%)			$ILCT_{\text{ethyl ester}\rightarrow py}$

Figure S12. Isosurface plots of frontier orbitals of *fac*-[ReCl(et-isonic)$_2$(CO)$_3$] that are not presented at the text.

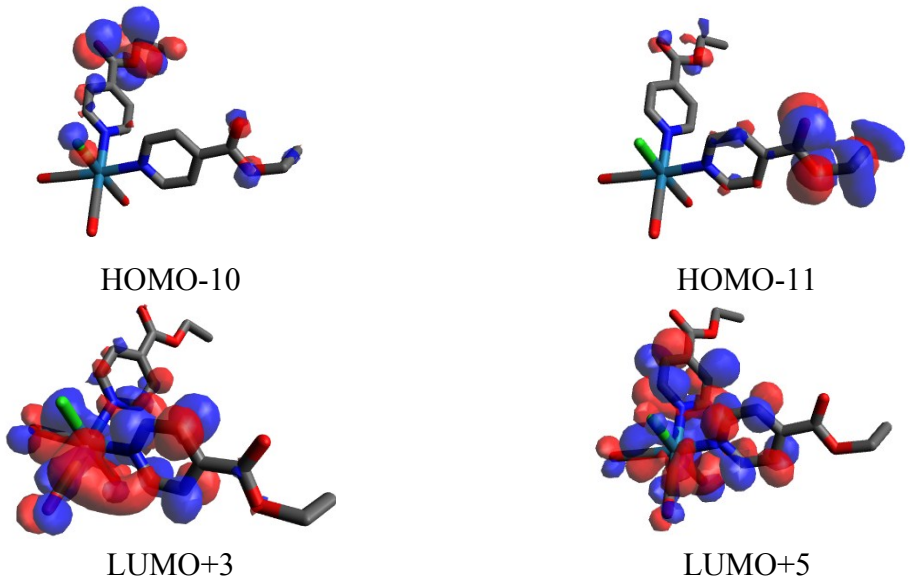


Figure S13: Experimental (line) and theoretical (bars) UV-Vis spectra of *fac*-[ReCl(et-isonic)$_2$(CO)$_3$] in CH_3CN at room temperature.

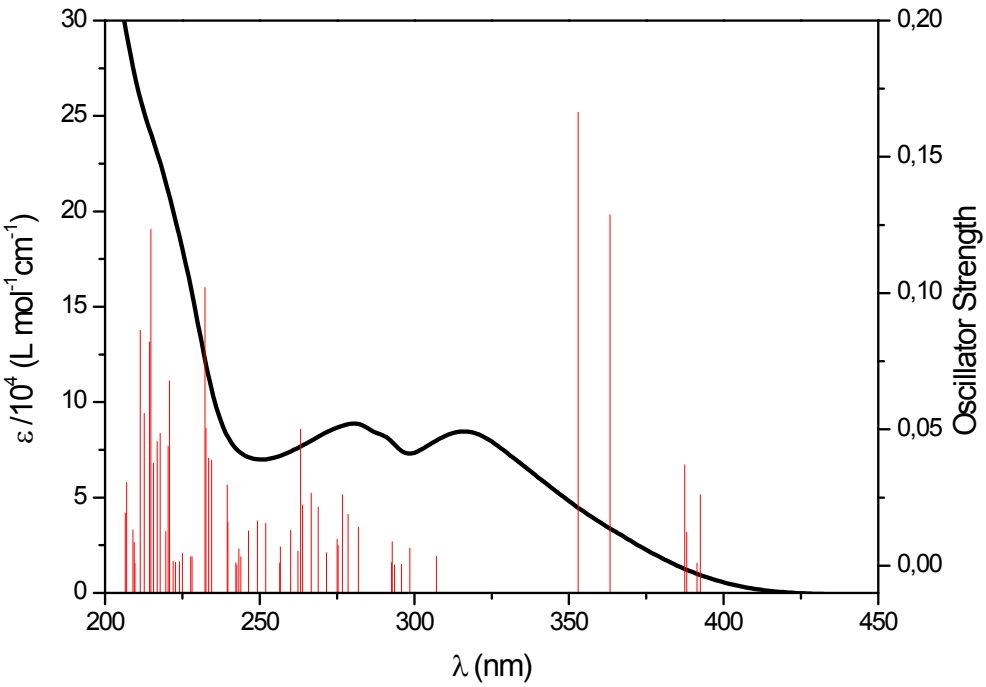
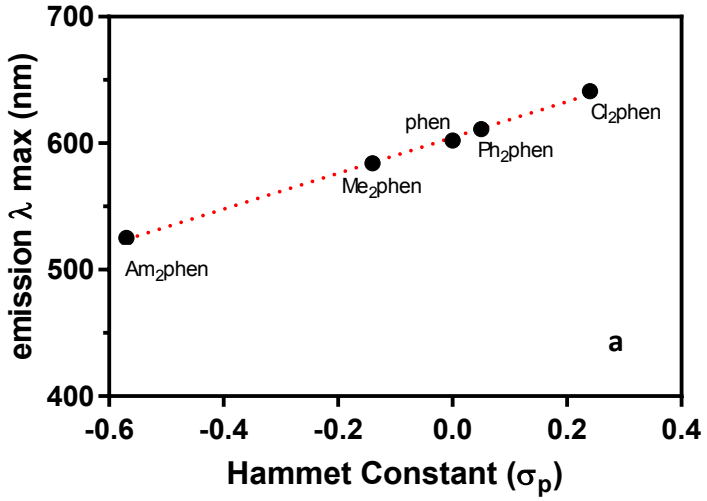


Figure S14. Plot of emission maxima versus Hammet Constant for a) *fac*-[ReCl(NN)(CO)$_3$] and b) *fac*-[Re(et-isonic)(NN)(CO)$_3$]$^+$ compounds.



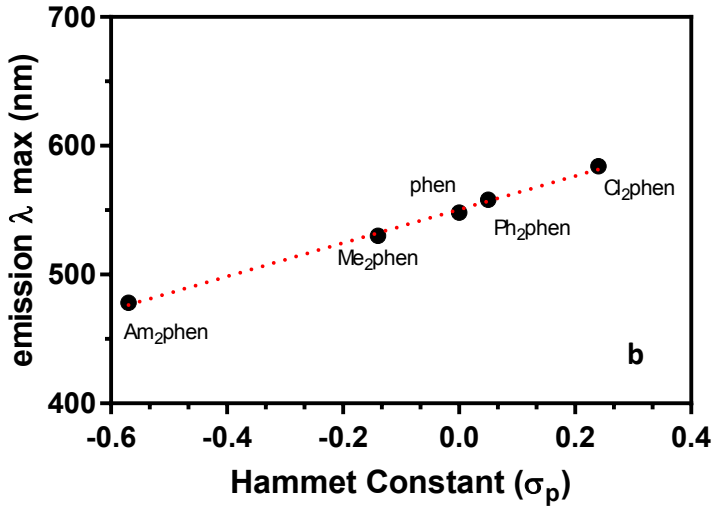


Figure S15: Emission spectra of (a) *fac*-[ReCl(Am_2phen)($CO)_3$], (b) *fac*-[Re(et-isonic)(Am_2phen)($CO)_3]^+$ and (c) free Am_2phen in CH_3CN at room temperature (continuous line) and in ethanol: methanol (4:1) at 77 K (dashed line).

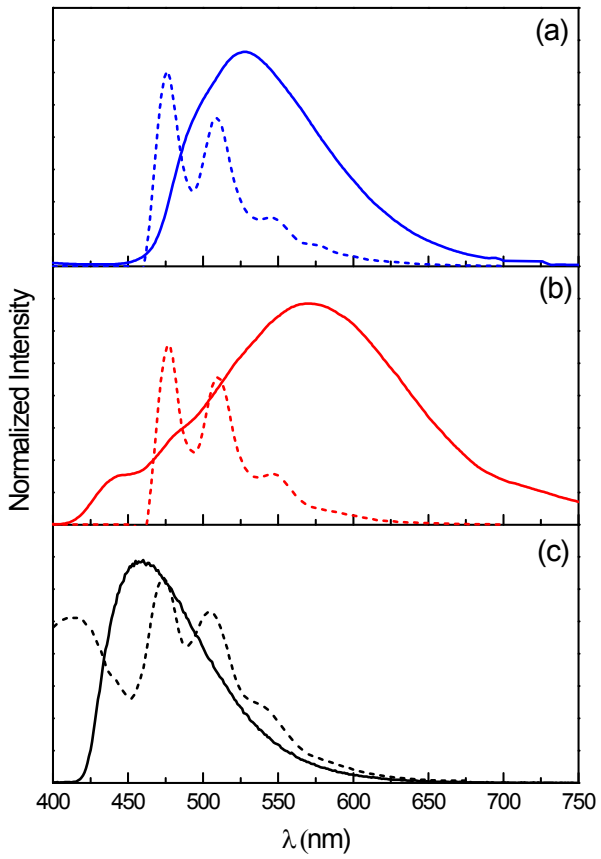


Figure S16. Microscopy fluorescence of Re(I) complexes (50 µmol.L^{-1}) for 15 min in SkMel-147 cell line. (1) *fac*- [ReCl(Am$_2$phen)(CO)$_3$]; (2) *fac*-[Re(et-isonic)(Am$_2$phen)(CO)$_3$]$^+$.

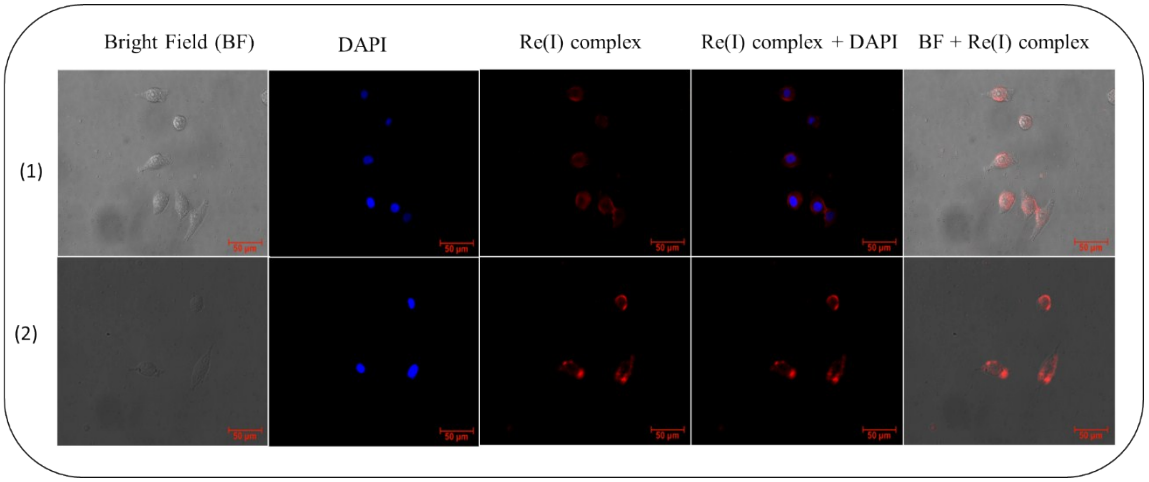


Figure S17. Microscopy fluorescence of Re(I) complexes (50 µmol.L^{-1}) for 15 min in SkMel-29 cell line.. (1) *fac*- [ReCl(Am$_2$phen)(CO)$_3$]; (2) *fac*-[Re(et-isonic)(Am$_2$phen)(CO)$_3$]$^+$.

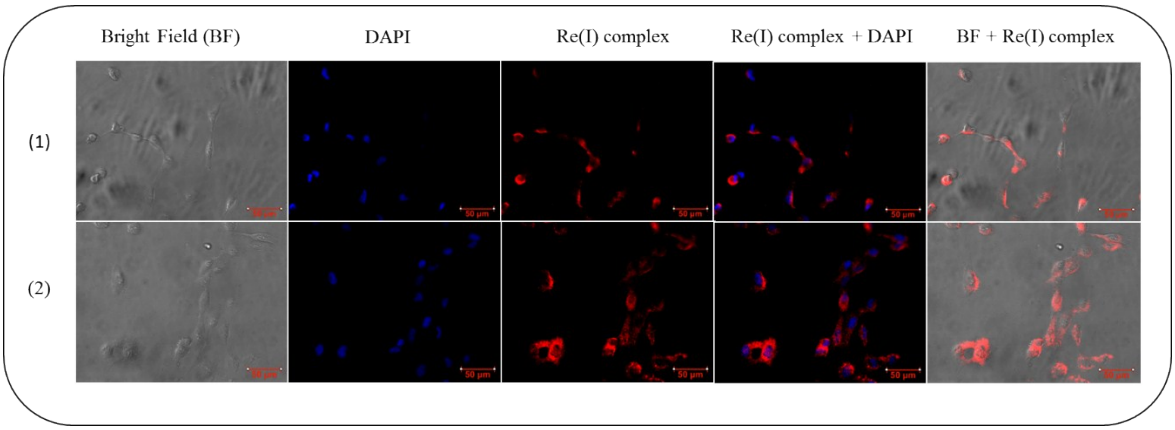
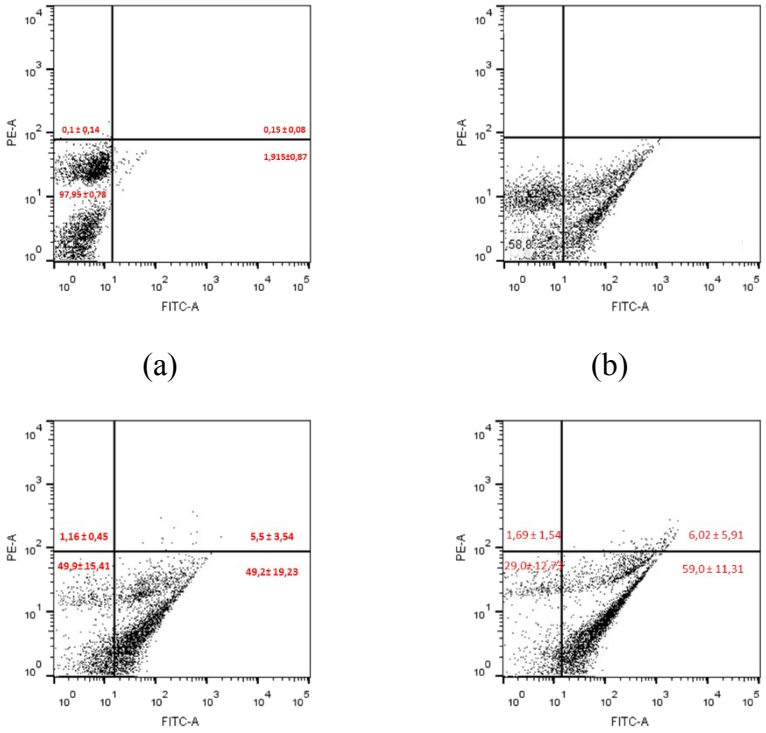


Figure S18: Dot plot of flow cytometry using Annexin V/FITC and PI in the MCF-7 cell line, treatment time of 24h at IC_{50} concentration using 1% DMSO (v/v) as vehicle, at 5% CO_2 atmosphere at 37 ° C. Negative control (a); Positive control (b), *fac*-[$ReCl(Am_2phen)(CO)_3$] (c); *fac*-[$Re(et\text{-}isonic)(Am_2phen)(CO)_3]^+$ (d).



(a) (b)

(c) (d)

Figure S19: Dot plot of flow cytometry using Annexin V/FITC and PI in the SkMel-147 cell line, treatment time of 24h at IC_{50} concentration using 1% DMSO (v/v) as vehicle, at 5% CO_2 atmosphere at 37 ° C. Negative control (a); Positive control (b), *fac*-[$ReCl(Am_2phen)(CO)_3$] (c); *fac*-[$Re(et\text{-}isonic)(Am_2phen)(CO)_3]^+$ (d).

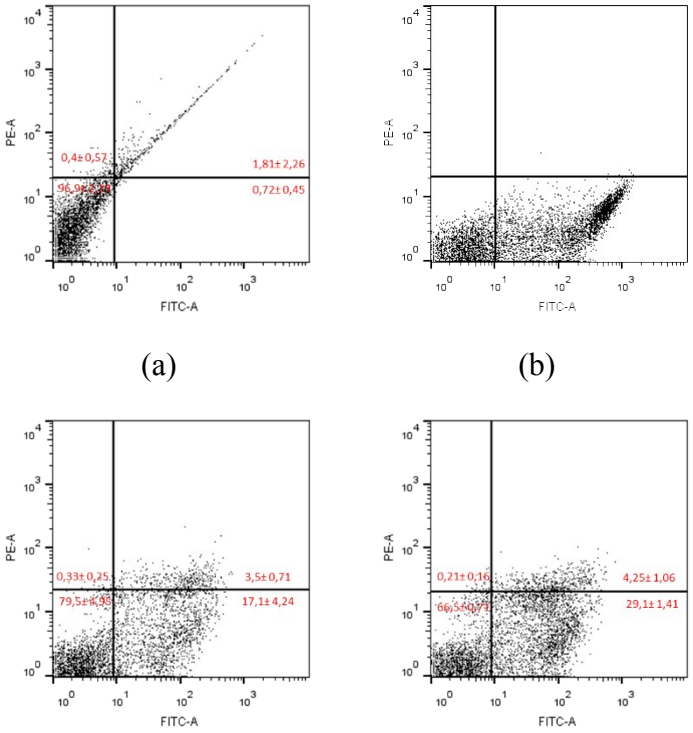
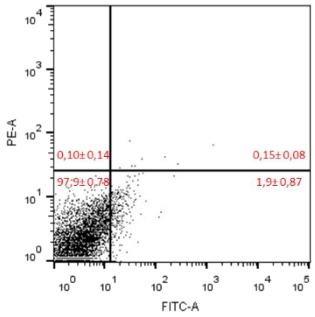
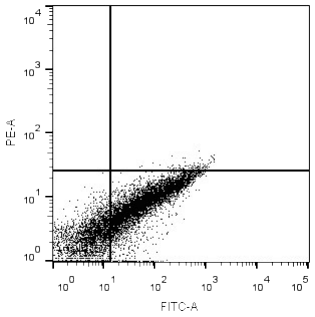


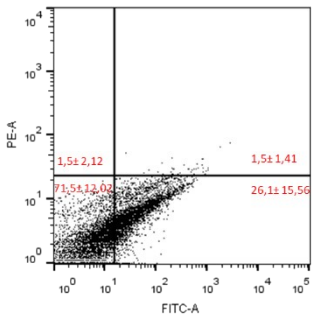
Figure S20: Dot plot of flow cytometry using Annexin V/FITC and PI in the SkMel-29 cell line, treatment time of 24h at IC_{50} concentration using 1% DMSO (v/v) as vehicle, at 5% CO_2 atmosphere at 37 ° C. Negative control (a); Positive control (b), *fac*-[$ReCl(Am_2phen)(CO)_3$] (c); *fac*-[$Re(et\text{-}isonic)(Am_2phen)(CO)_3]^+$ (d).



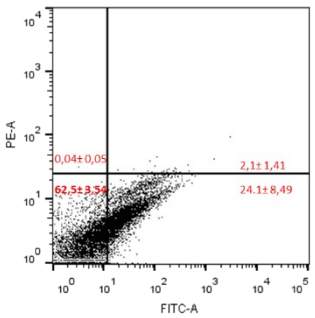
(a)



(b)



(c)



(d)