Electrocatalytic reduction of CO_2 to CO by a Series of organometallic Re(I)-tpy complexes

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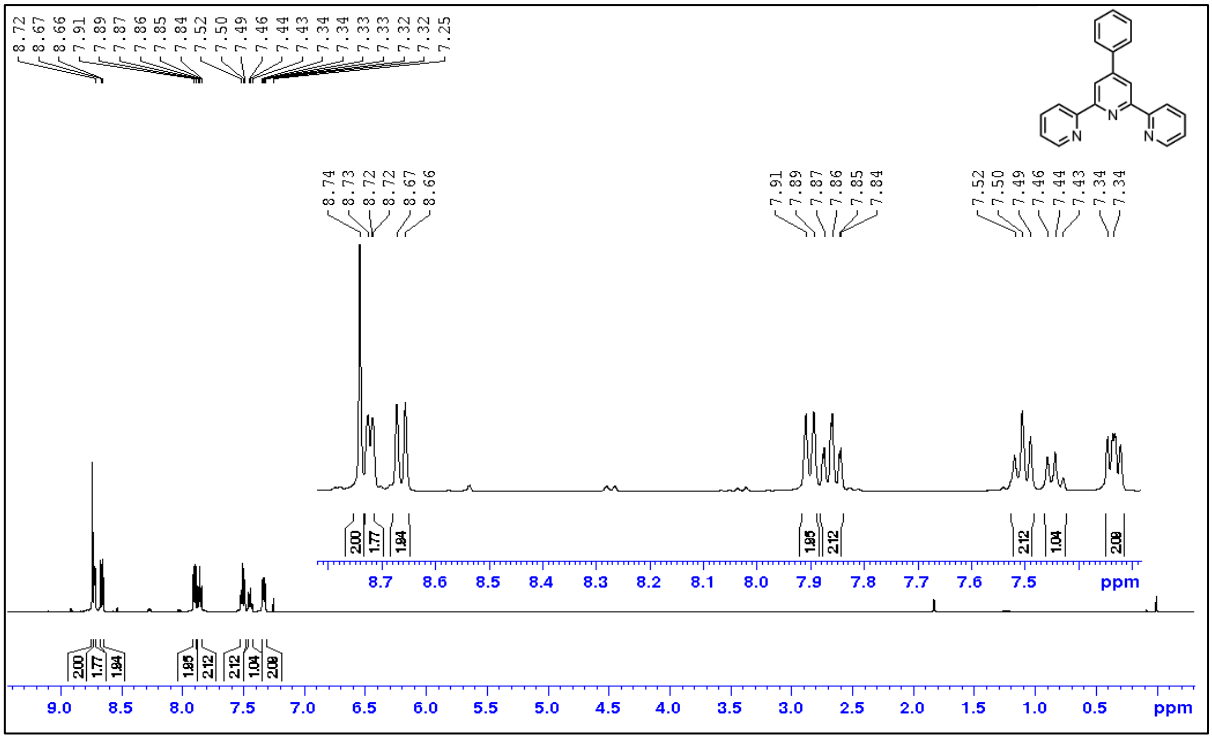

Figure S1a: *^{1}H NMR spectrum of **L2** (500 MHz, $CDCl_3$).*

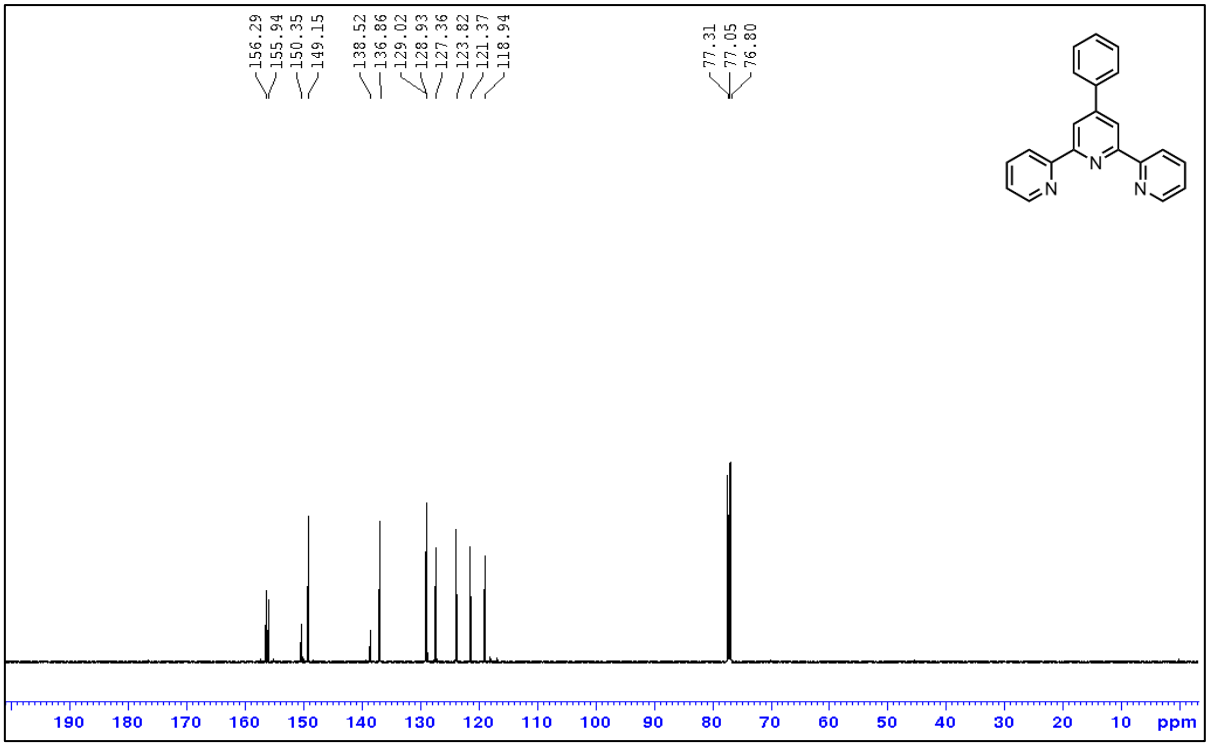

Figure S1b: *$^{13}C\{^{1}H\}$ NMR spectrum of **L2** (125 MHz, $CDCl_3$).*

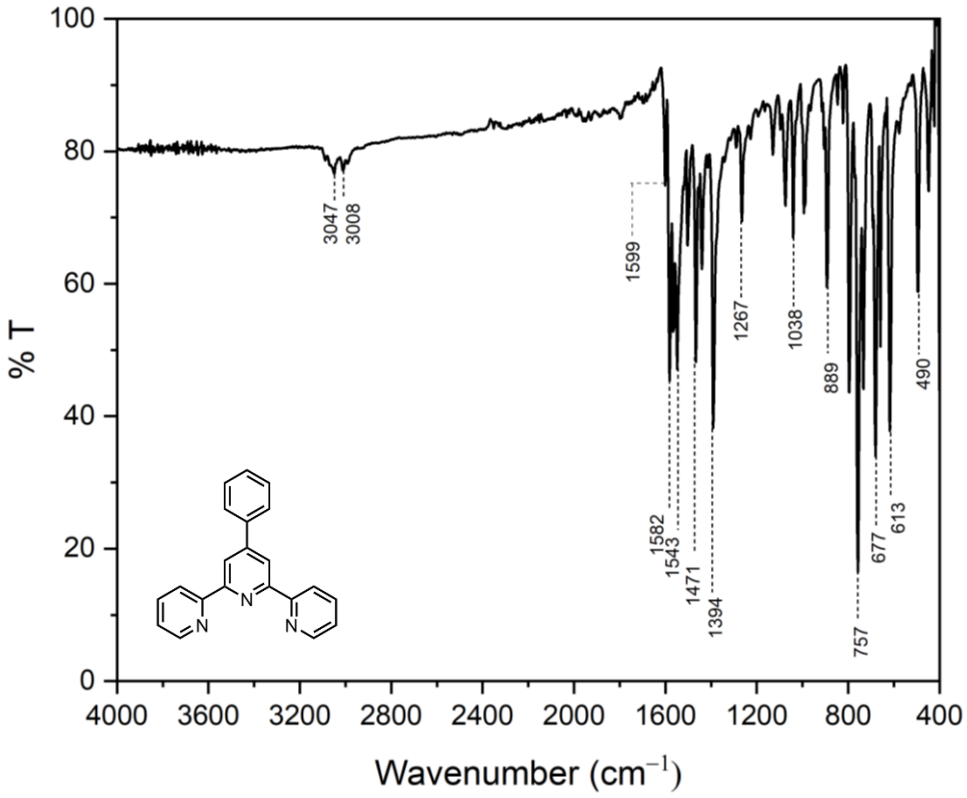

Figure S1c: *ATR–IR spectrum of* ***L2****.*

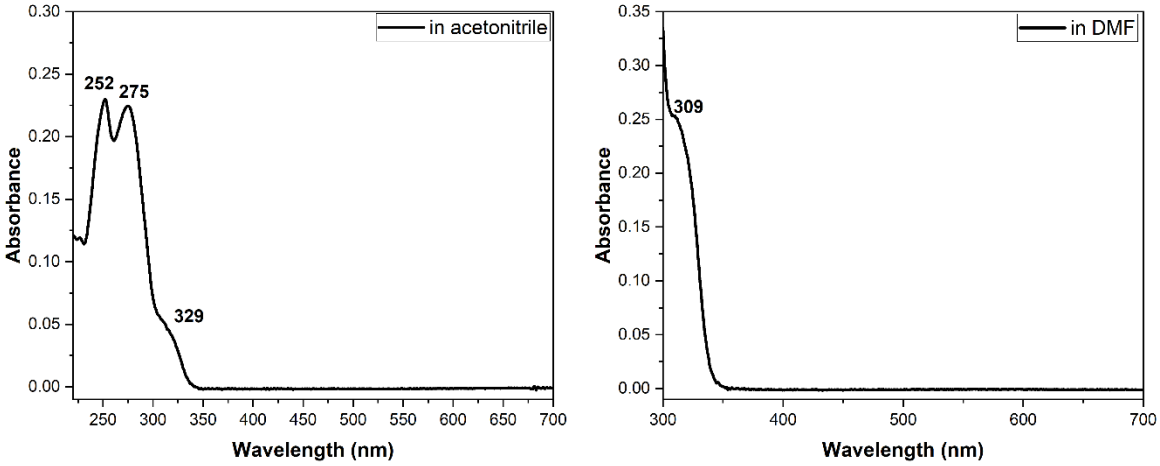

Figure S1d: *Absorbance spectra of* ***L2*** *(0.01 mM) in acetonitrile and DMF.*

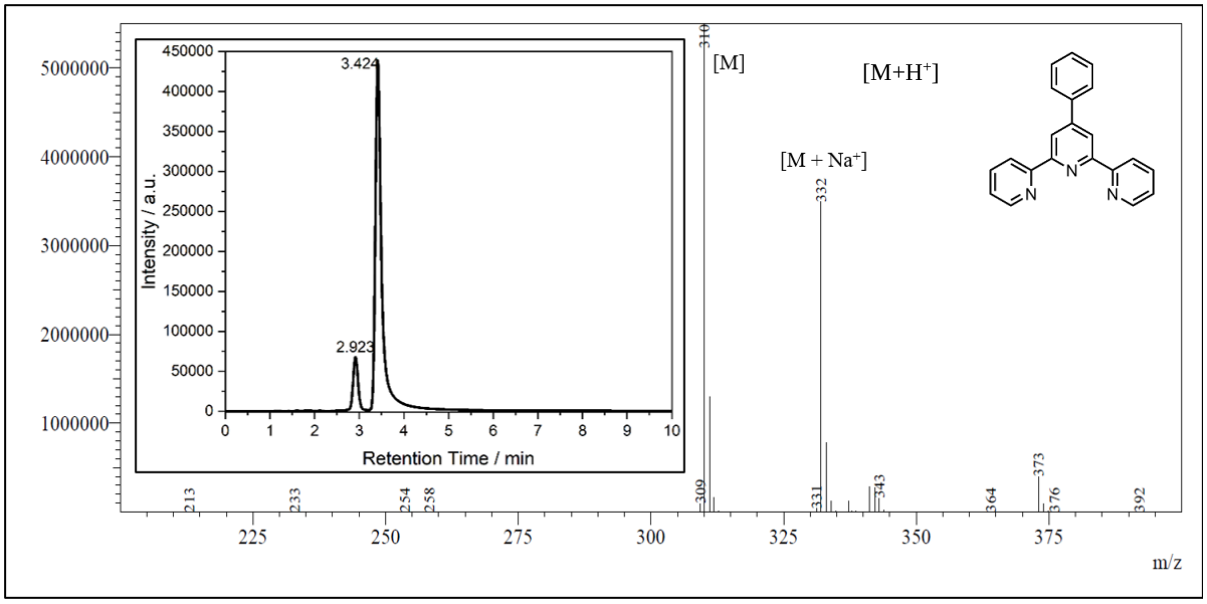

Figure S1e: *LC-MS spectrum of* ***L2****, mass values shown at 3.424 min; Mass fragmentation pattern for* ***L2*** *[$C_{21}H_{15}N_3$ = M]; m/z = 310 $[M+H]^+$ ($C_{21}H_{16}N_3$), m/z = 332 $[M+Na]^+$ ($C_{21}H_{16}N_3Na$).*

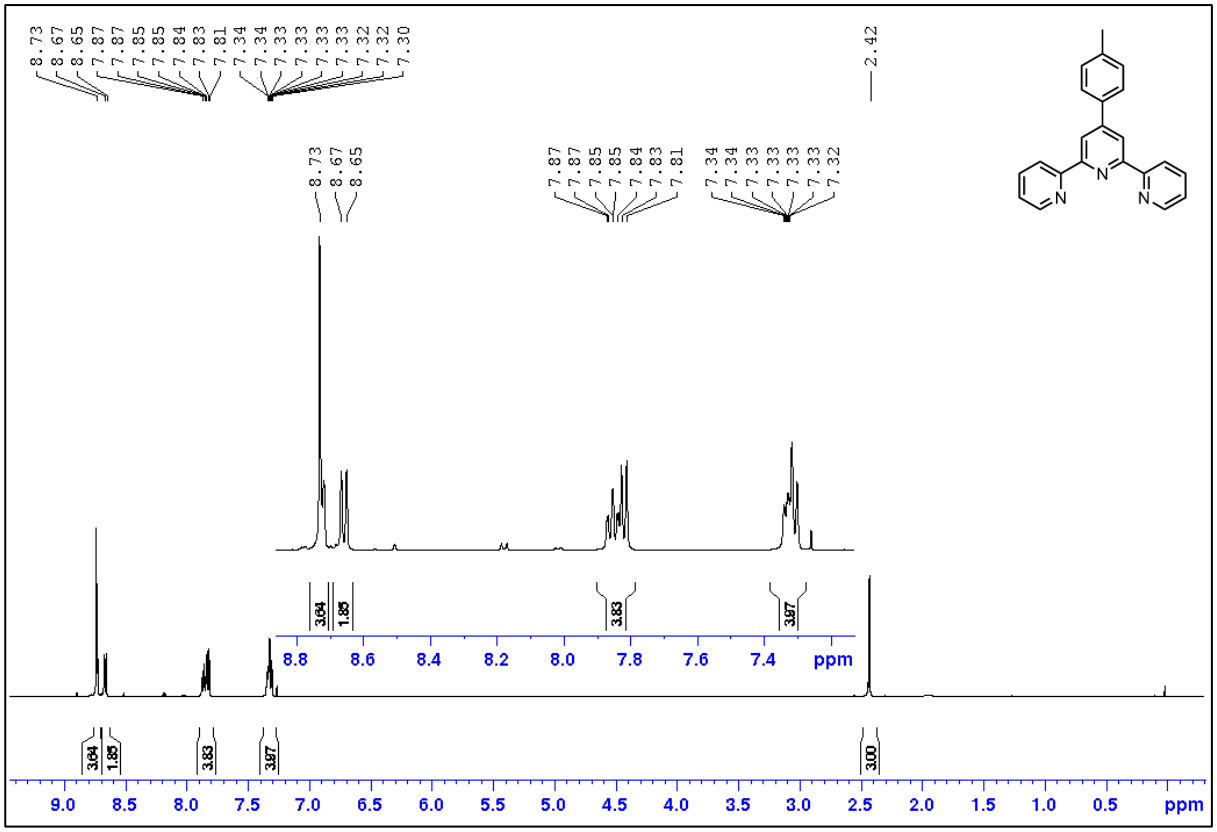

Figure S2a: *^{1}H NMR spectrum of* ***L3*** *(500 MHz, $CDCl_3$).*

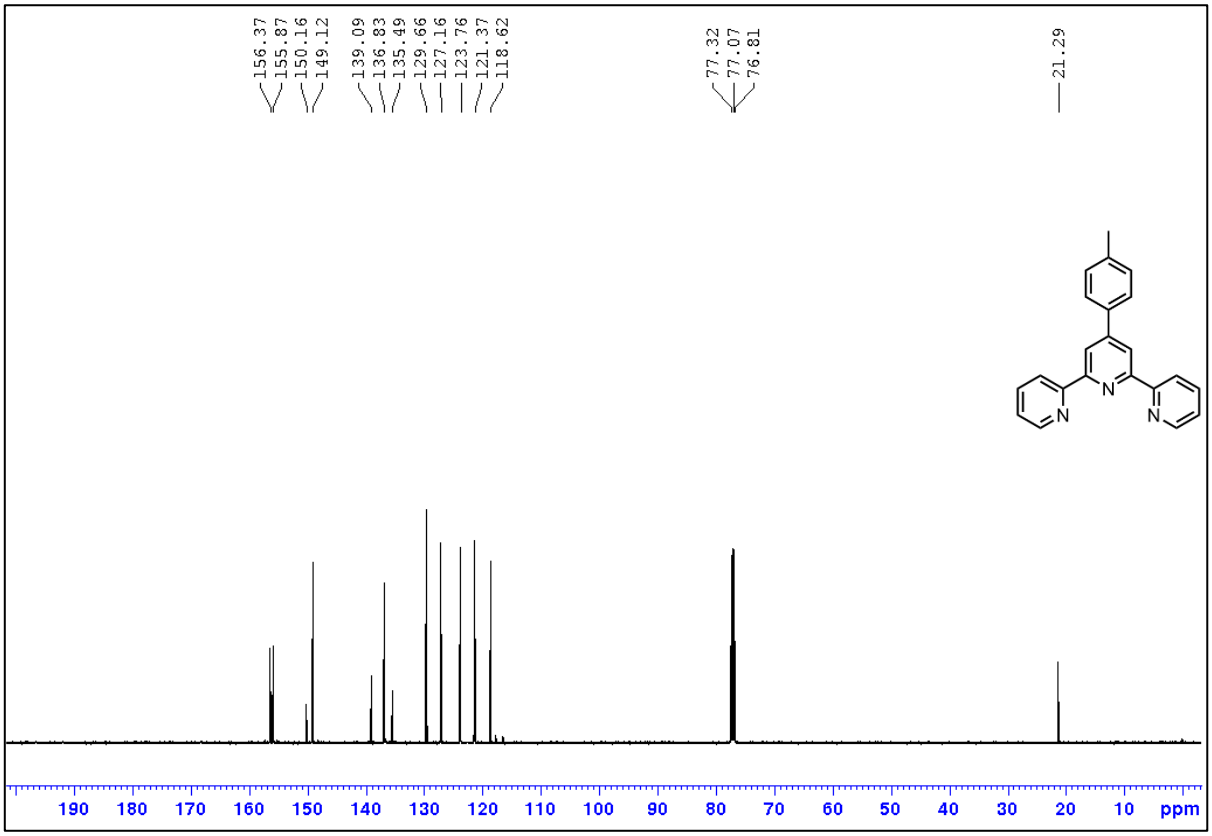

Figure S2b: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***L3*** *(125 MHz, $CDCl_3$).*

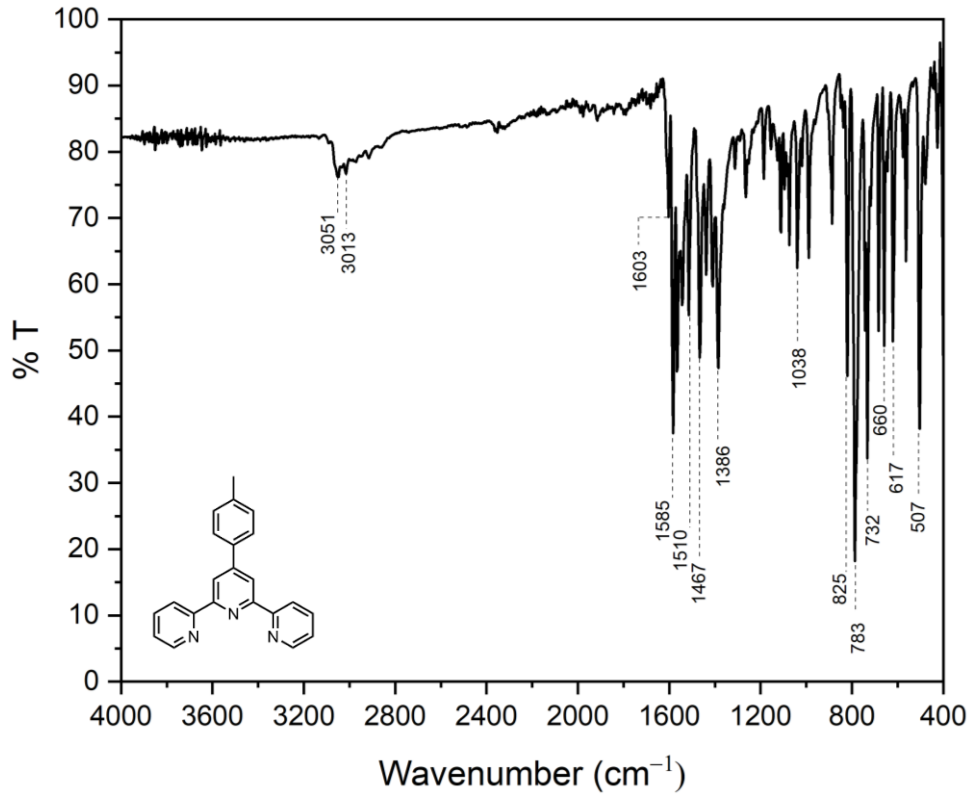

Figure S2c: *ATR–IR spectrum of* ***L3****.*

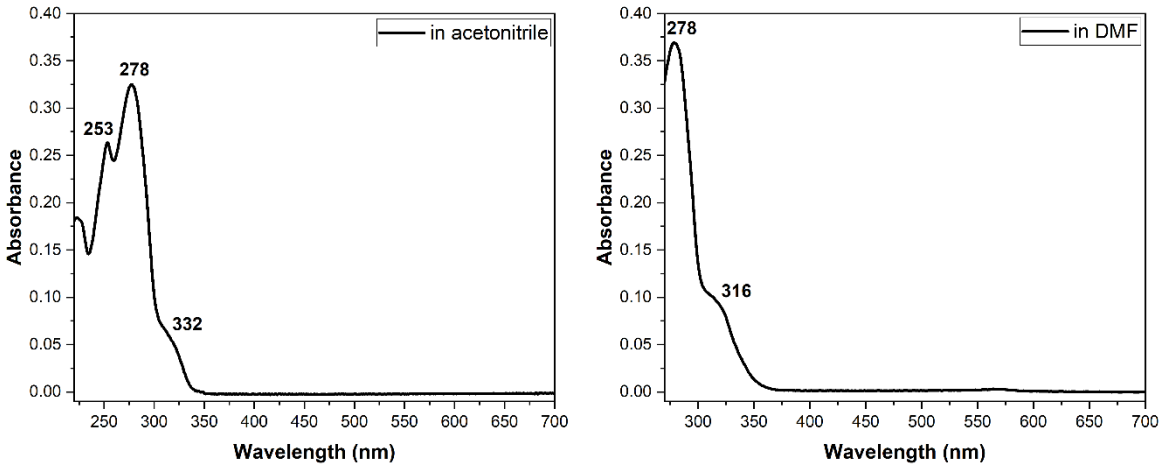

Figure S2d: *Absorbance spectra of* ***L3*** *(0.01 mM) in acetonitrile and DMF.*

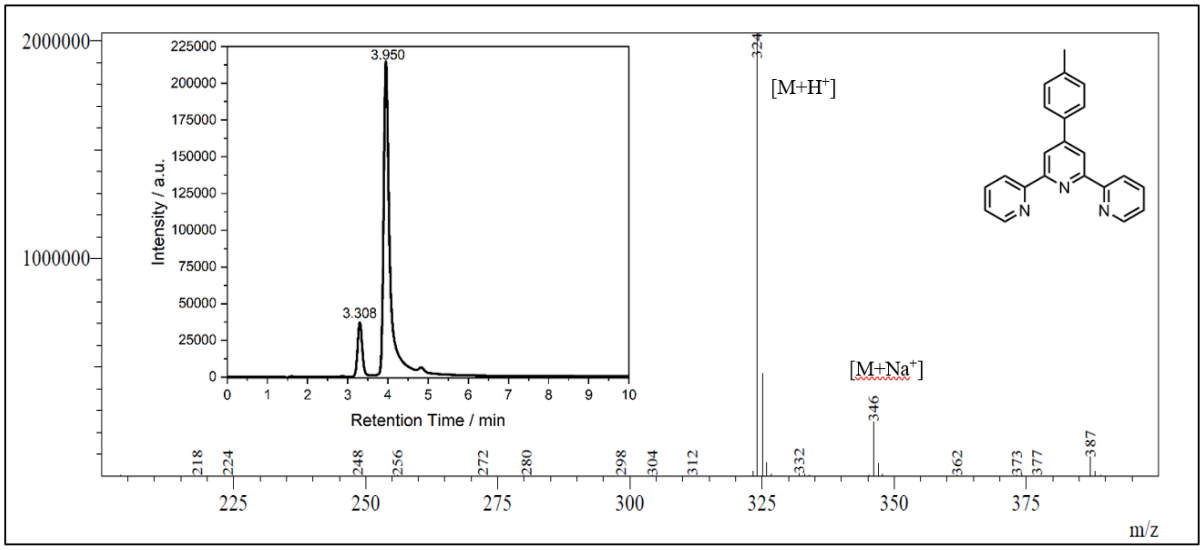

Figure S2e: *LC-MS spectrum of* ***L3****, mass values shown at 3.950 min; Mass fragmentation pattern for* ***L3*** *[$C_{22}H_{17}N_3$ = M]; m/z = 324 $[M+H]^+$ ($C_{22}H_{18}N_3$), m/z = 346 $[M+Na]^+$ ($C_{22}H_{18}N_3Na$).*

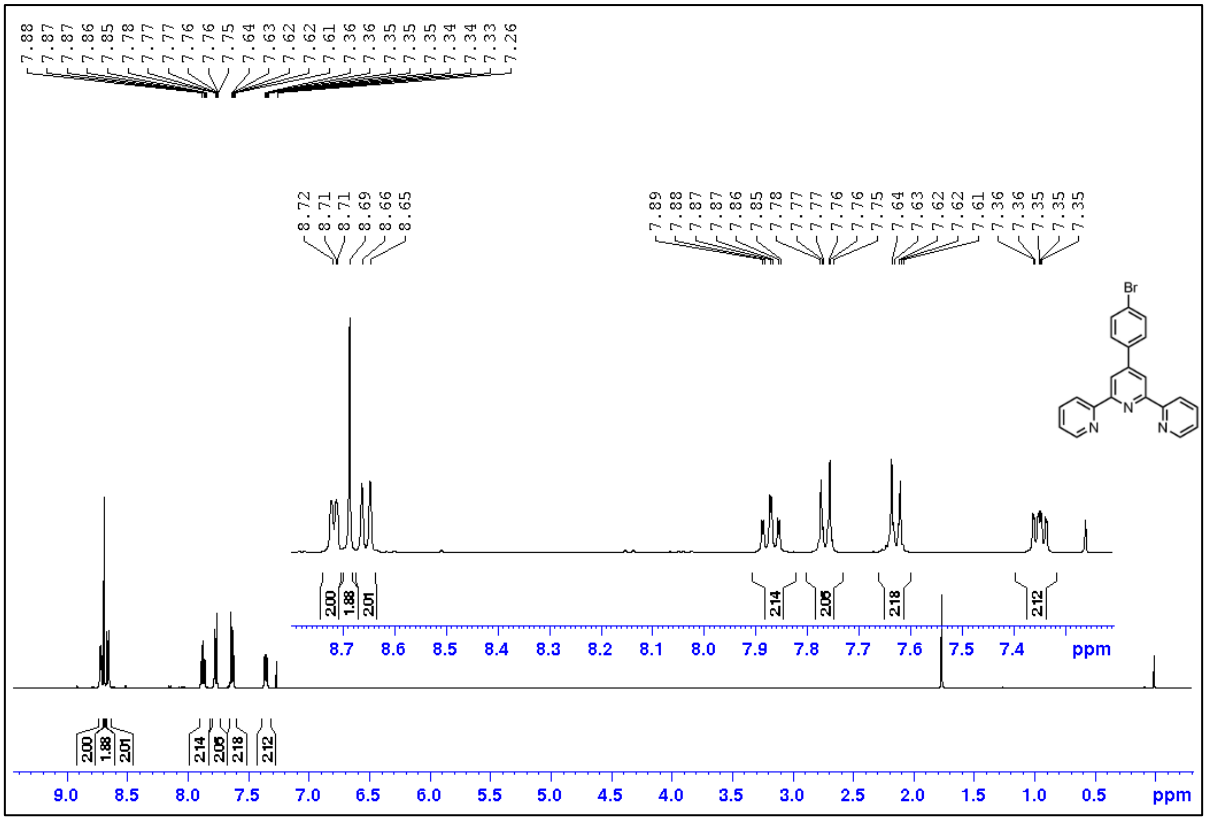

Figure S3a: *^{1}H NMR spectrum of **L4** (500 MHz, $CDCl_3$)* (water peak at 1.6 ppm).

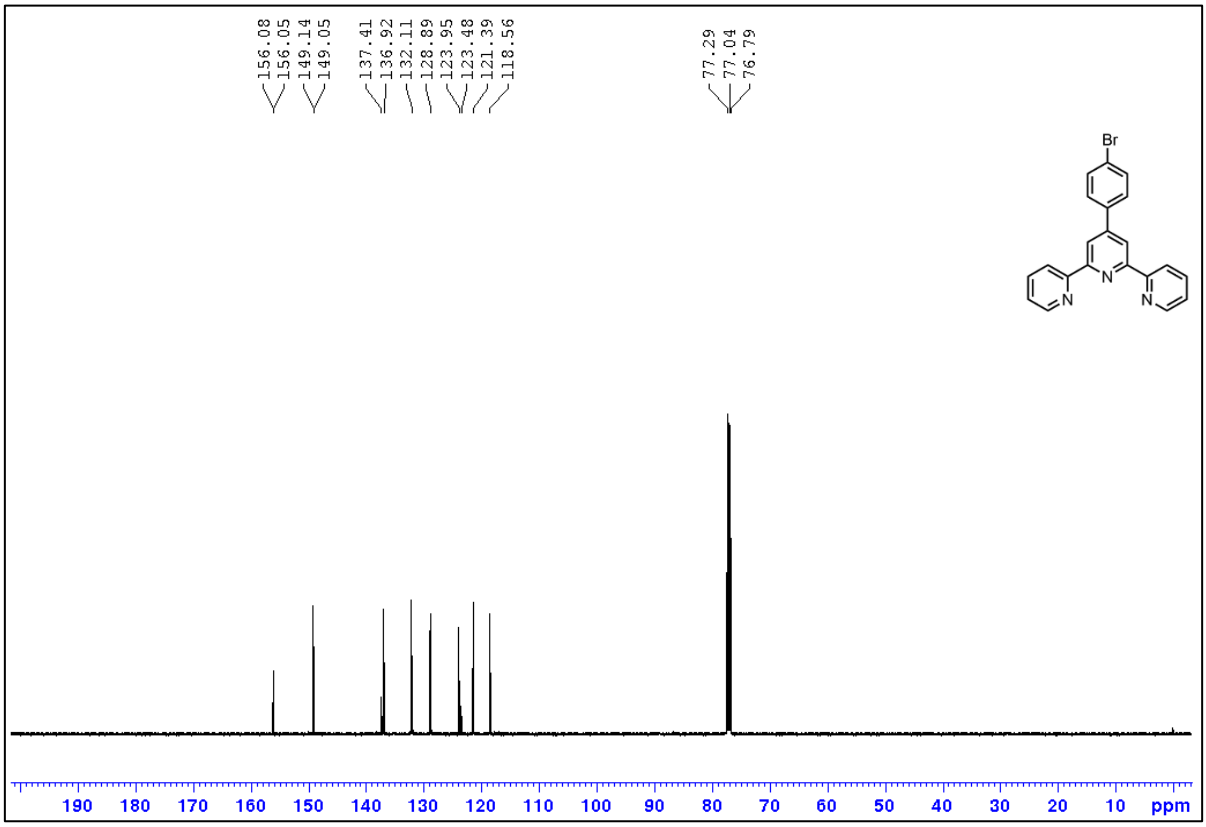

Figure S3b: *$^{13}C\{^{1}H\}$ NMR spectrum of **L4** (125 MHz, $CDCl_3$).*

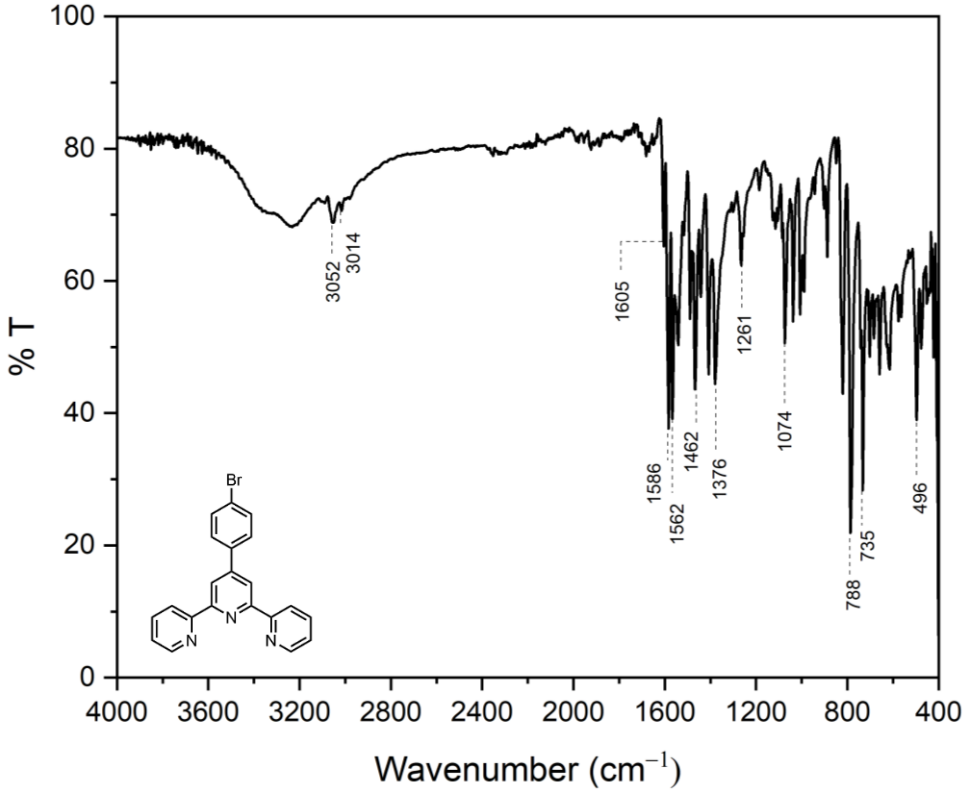

Figure S3c: *ATR–IR spectrum of* ***L4****.*

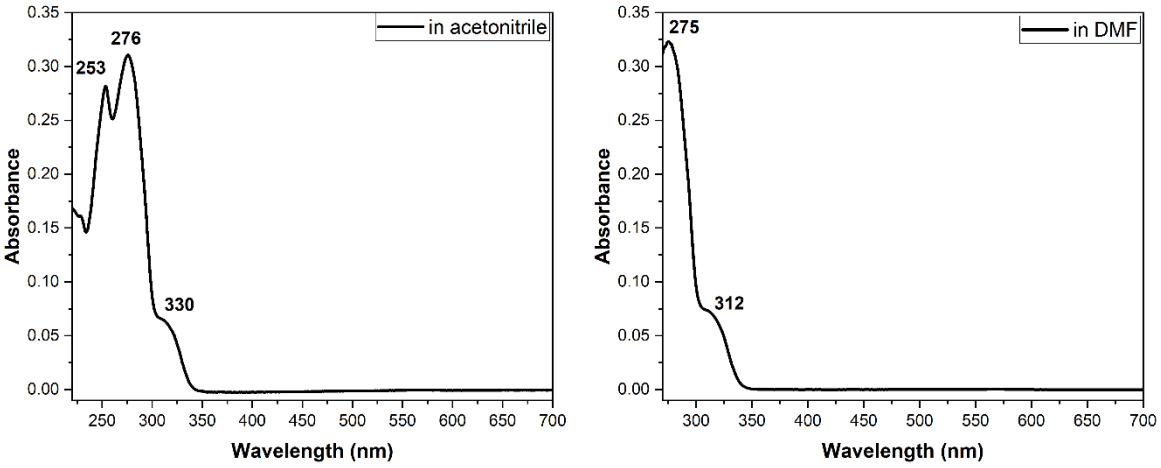

Figure S3d: *Absorbance spectra of* ***L4*** *(0.01 mM) in acetonitrile and DMF.*

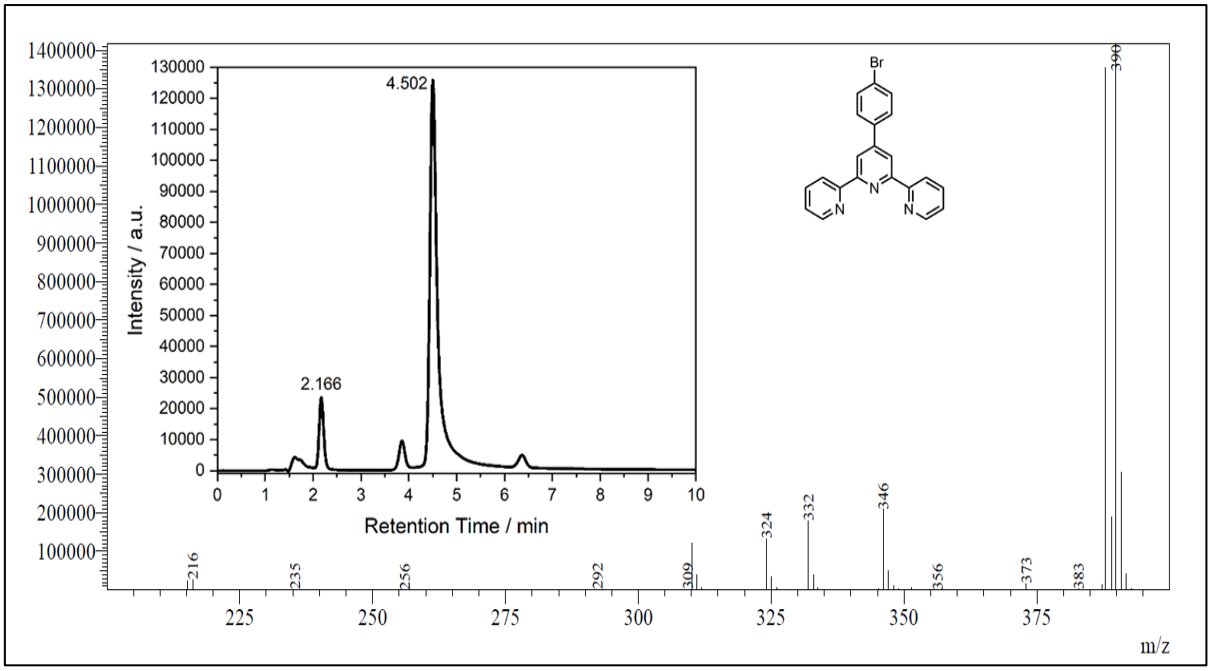

Figure S3e: *LC-MS spectrum of* ***L4****, mass values shown at 4.502 min; Mass fragmentation pattern for* ***L4*** *[$C_{21}H_{14}BrN_3$ = M]; m/z = 388 $[M+H]^+$ ($C_{21}H_{15}{}^{79}BrN_3$); m/z = 390 $[M+H]^+$ ($C_{21}H_{15}{}^{81}BrN_3$).*

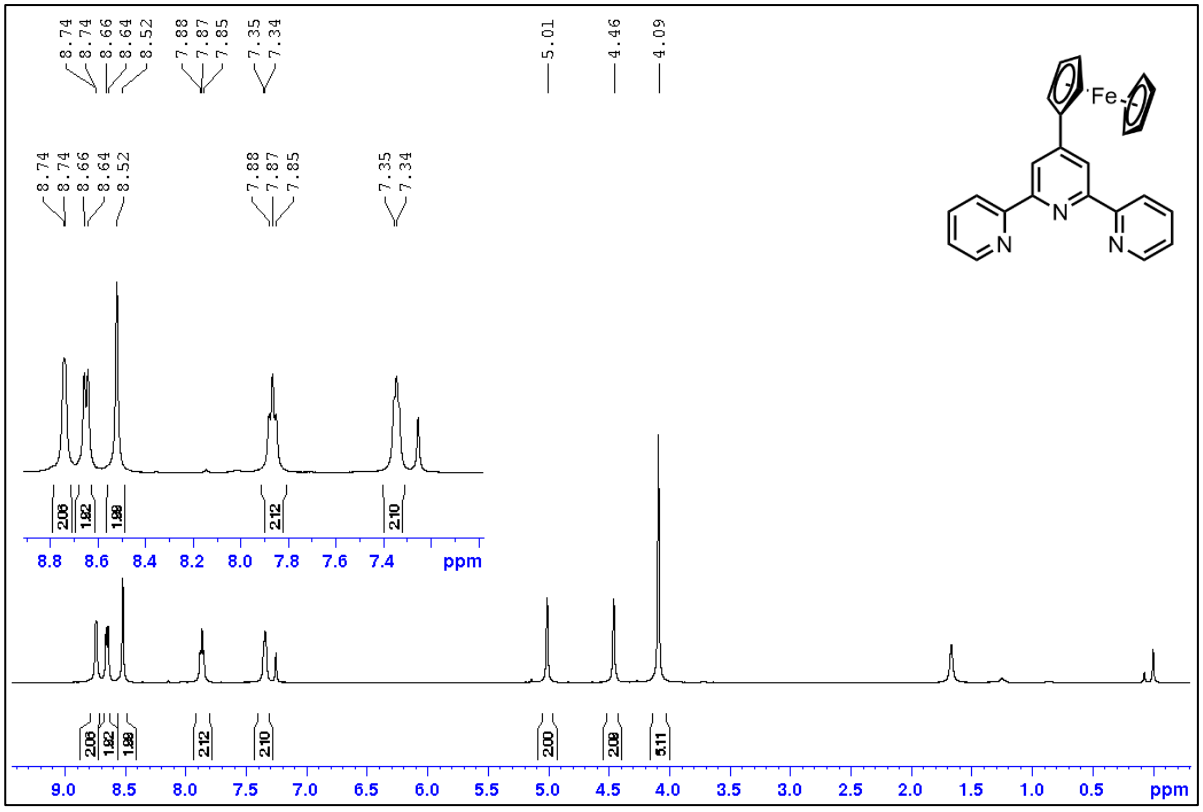

Figure S4a: *^{1}H NMR spectrum of* ***L5*** *(500 MHz, $CDCl_3$)* (water peak at 1.6 ppm).

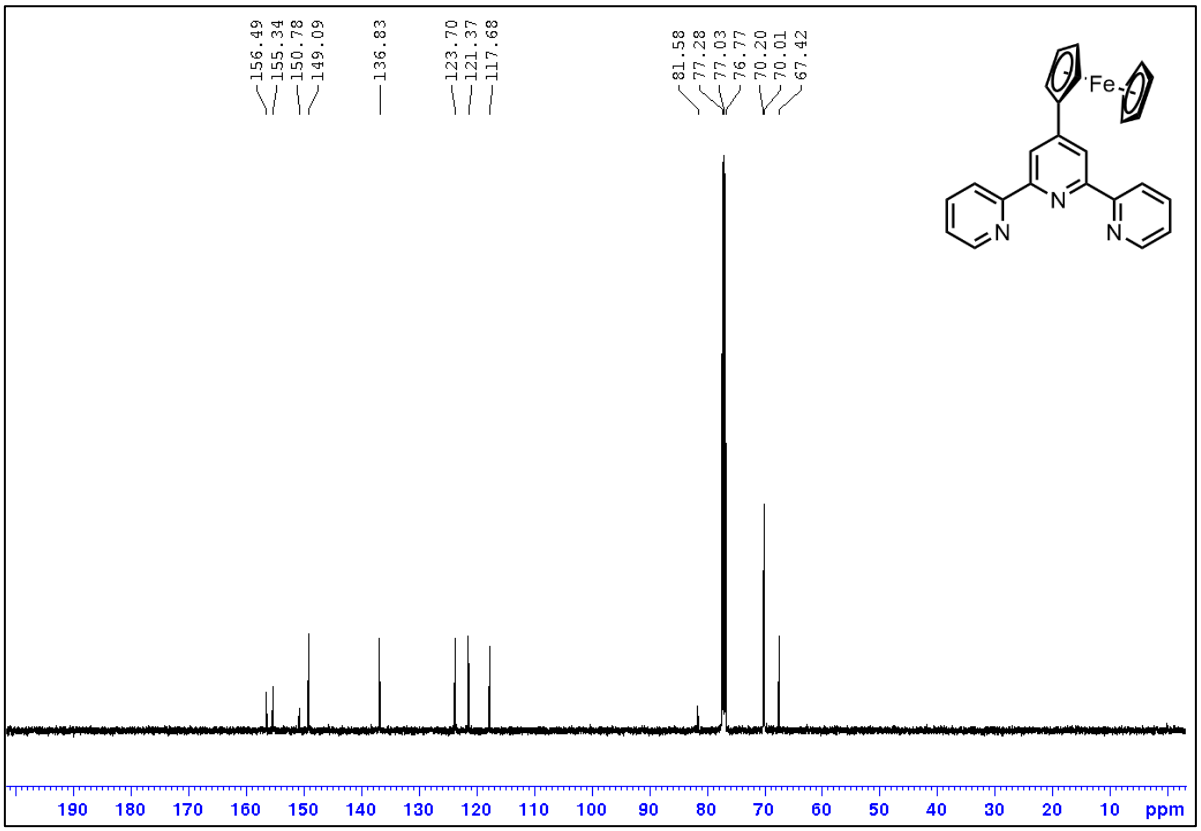

Figure S4b: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***L5*** *(125 MHz, $CDCl_3$).*

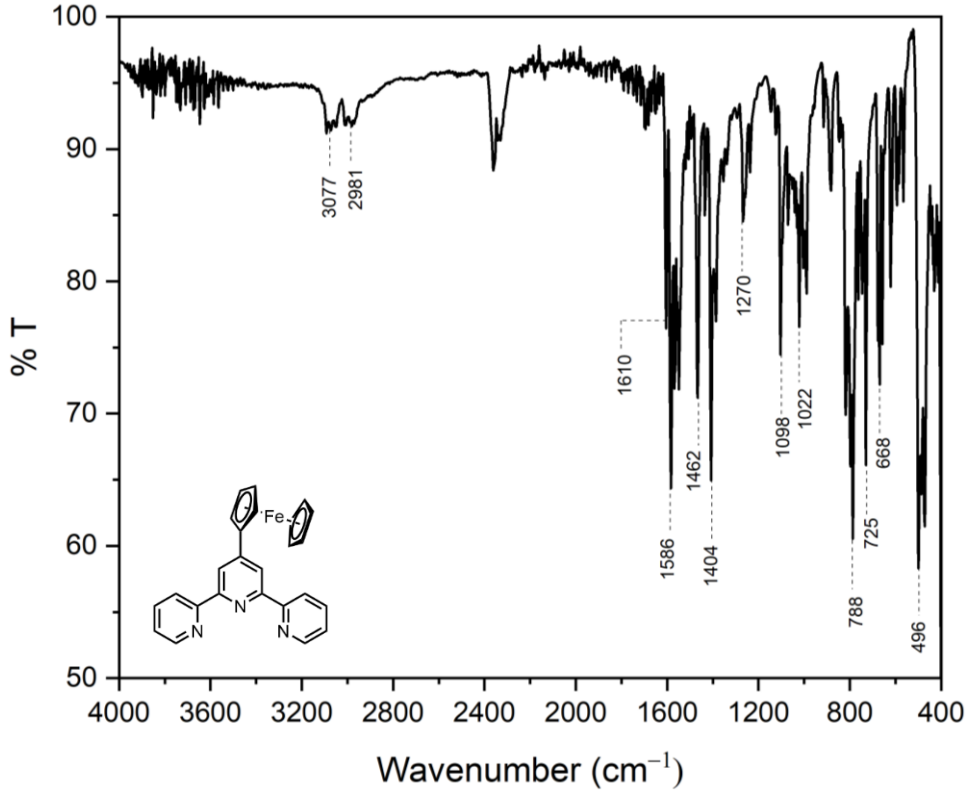

Figure S4c: *ATR–IR spectrum of* ***L5****.*

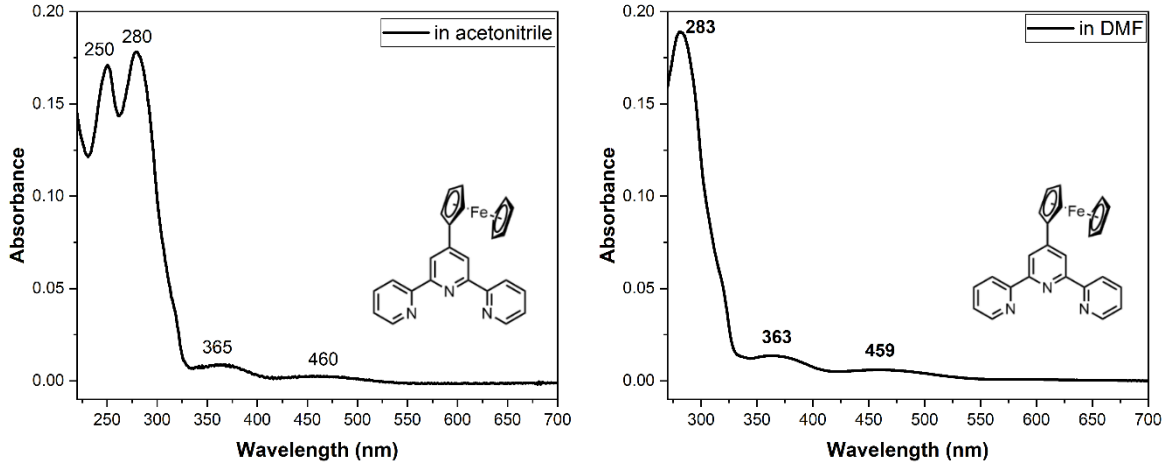

Figure S4d: *Absorbance spectra of* ***L5*** *(0.01 mM) in acetonitrile and DMF.*

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: L5		
Sample ID	: L5		
Data Filename	: L5_25-03-2023.lcd		
Method Filename	: C_95_D_5_10_min_0.2ml_min.lcm		
Batch Filename	: 25032023.lcb		
Vial #	: 1-91	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 3/25/2023 12:42:27 PM	Acquired by	: IIT GOA
Date Processed	: 3/25/2023 12:58:21 PM	Processed by	: IIT GOA

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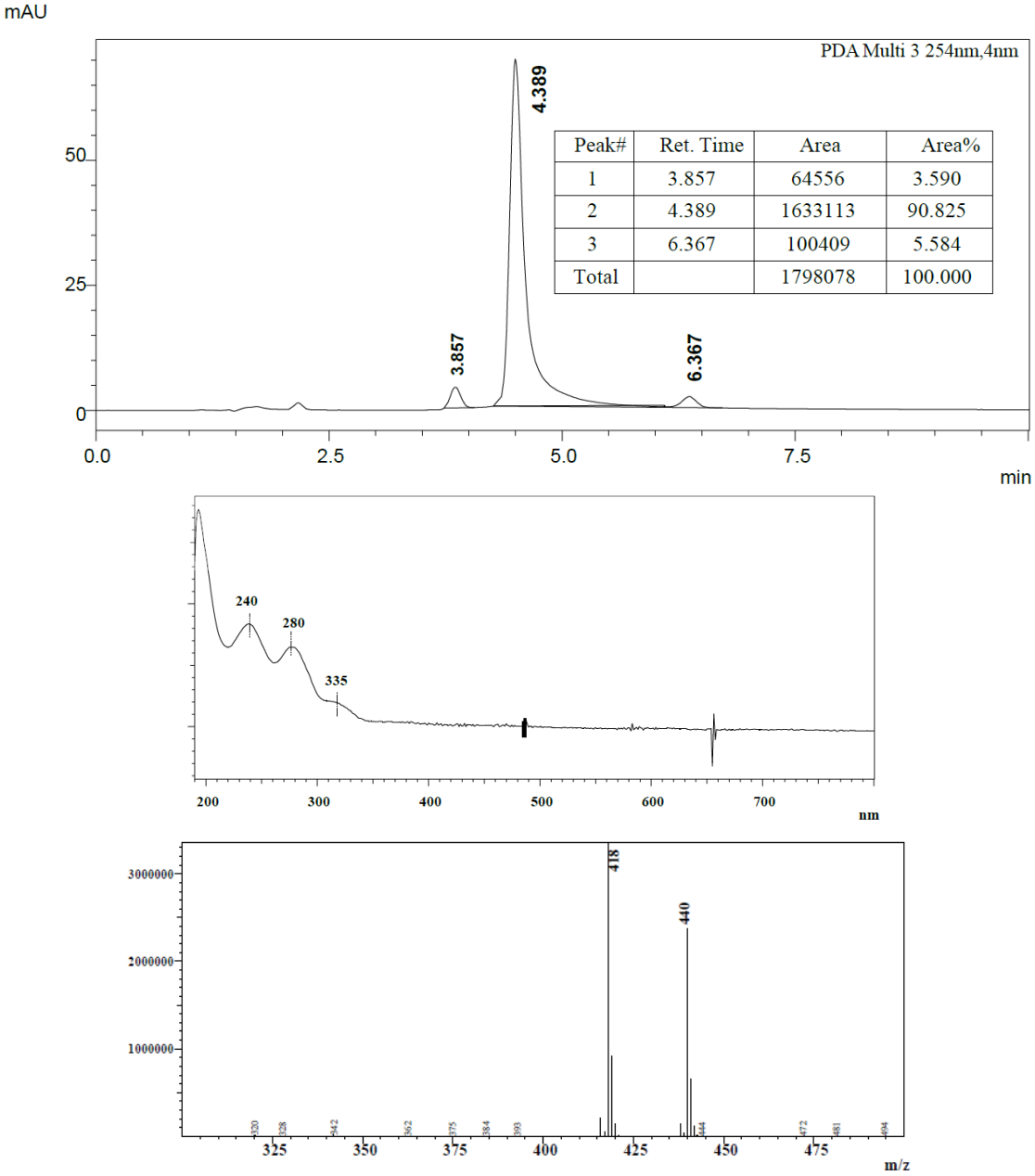

Peak#	Ret. Time	Area	Area%
1	3.857	64556	3.590
2	4.389	1633113	90.825
3	6.367	100409	5.584
Total		1798078	100.000

Figure S4e: *RP-HPLC-MS and corresponding UV-Vis spectra of* ***L5*** *at* t_R *= 4.389 min; HPLC purity 90%; m/z values for* t_R *= 3.857, 4.389 & 6.367 min shows same m/z: fragmentation pattern at 4.389 min* [$C_{25}H_{19}FeN_3$ *= M]; m/z = 418* $[M+H]^+$ ($C_{25}H_{20}FeN_3^+$), *m/z = 440* $[M+Na]^+$ ($C_{25}H_{20}FeN_3Na^+$).

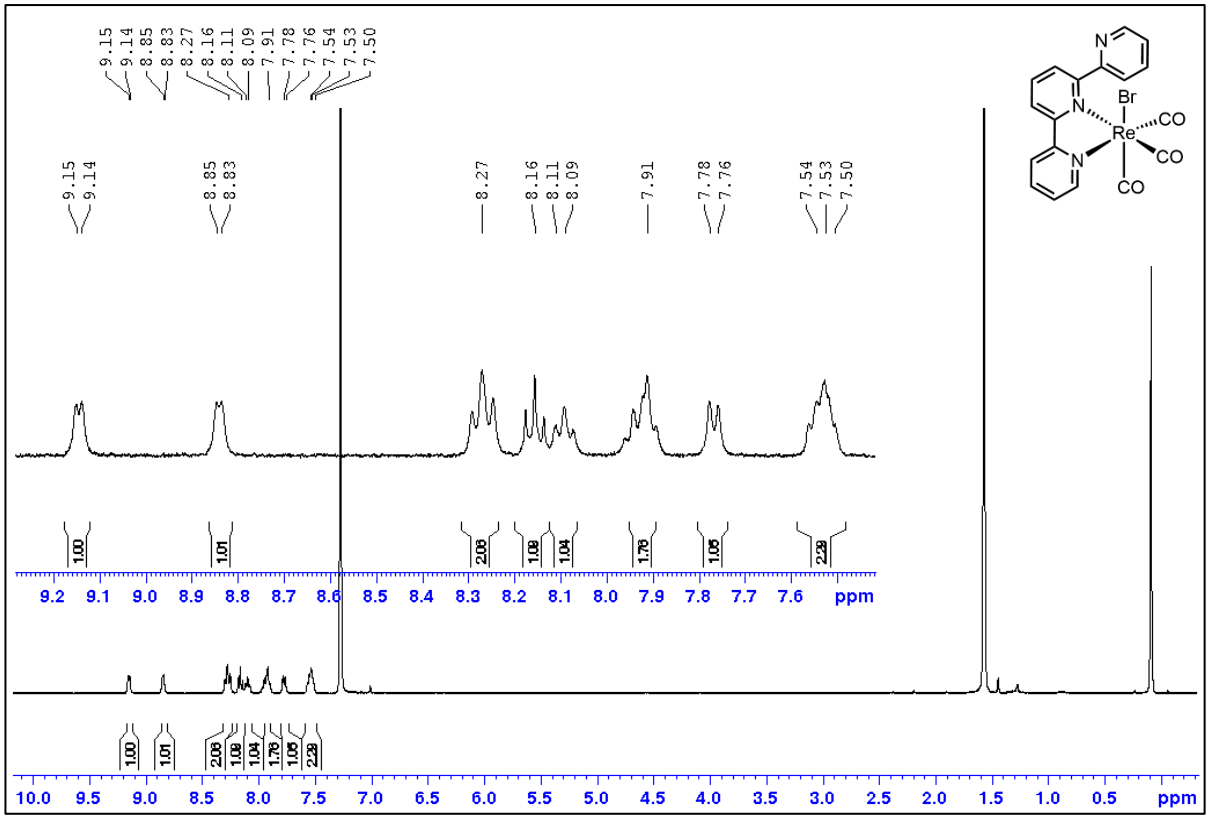

Figure S5a: *^{1}H NMR spectrum of* ***Re1*** *(400 MHz, $CDCl_3$)* (water peak at 1.6 ppm).

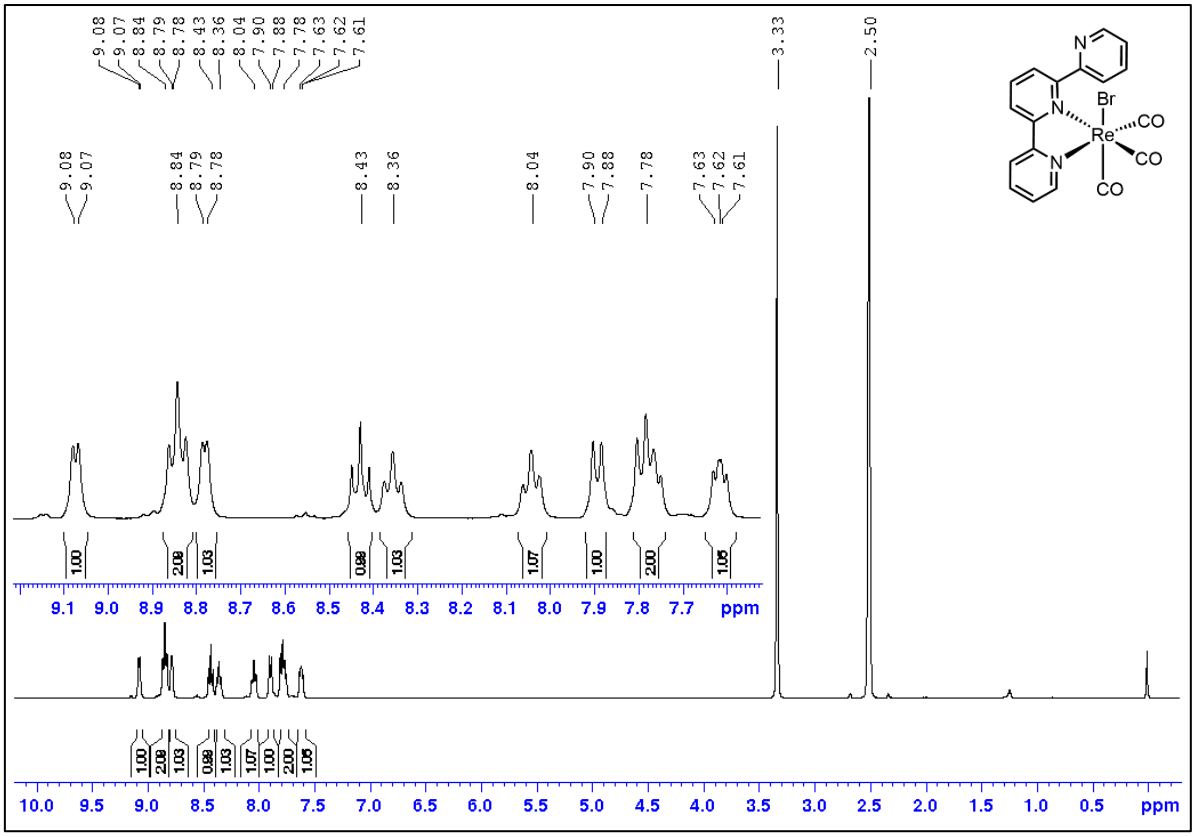

Figure S5b: *^{1}H NMR spectrum of* ***Re1*** *(400 MHz, DMSO-d_6)* (water peak at 3.33 ppm).

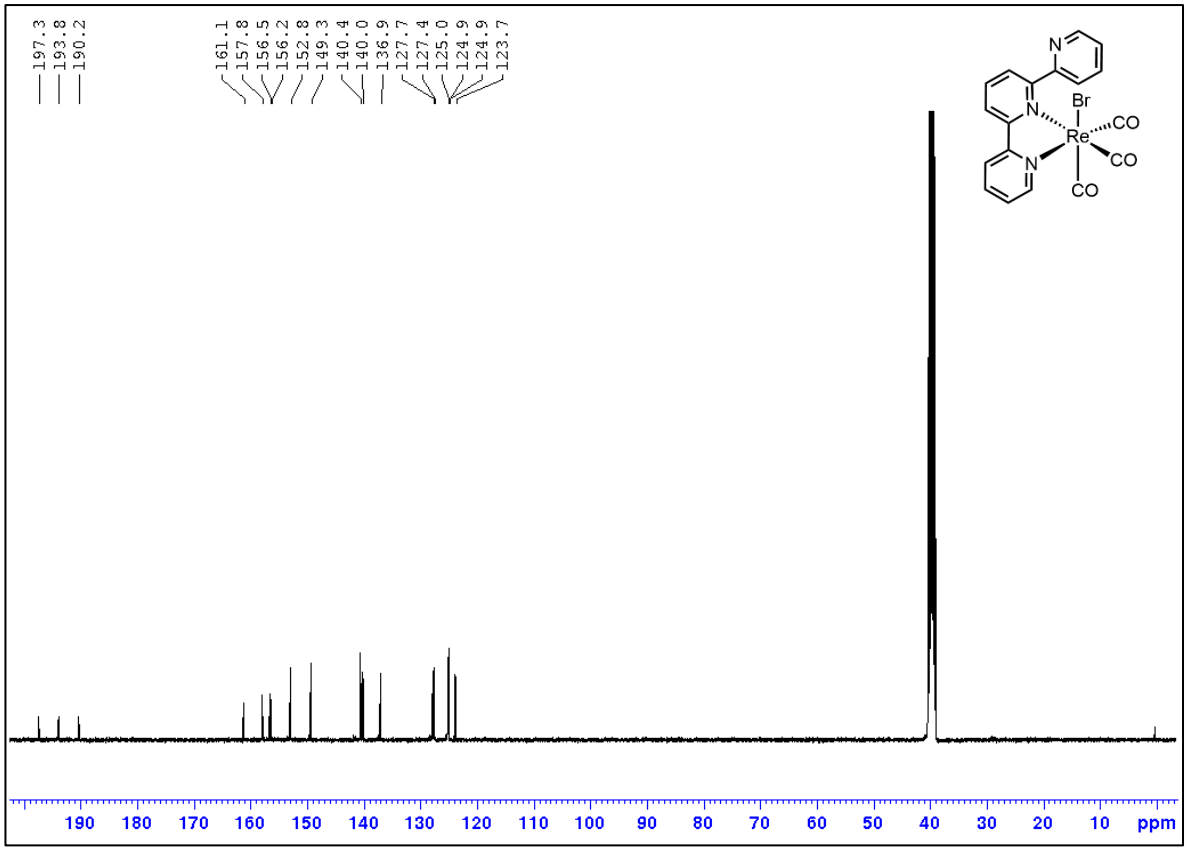

Figure S5c: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***Re1*** *(101 MHz, DMSO-d_6) with 16405 scans.*

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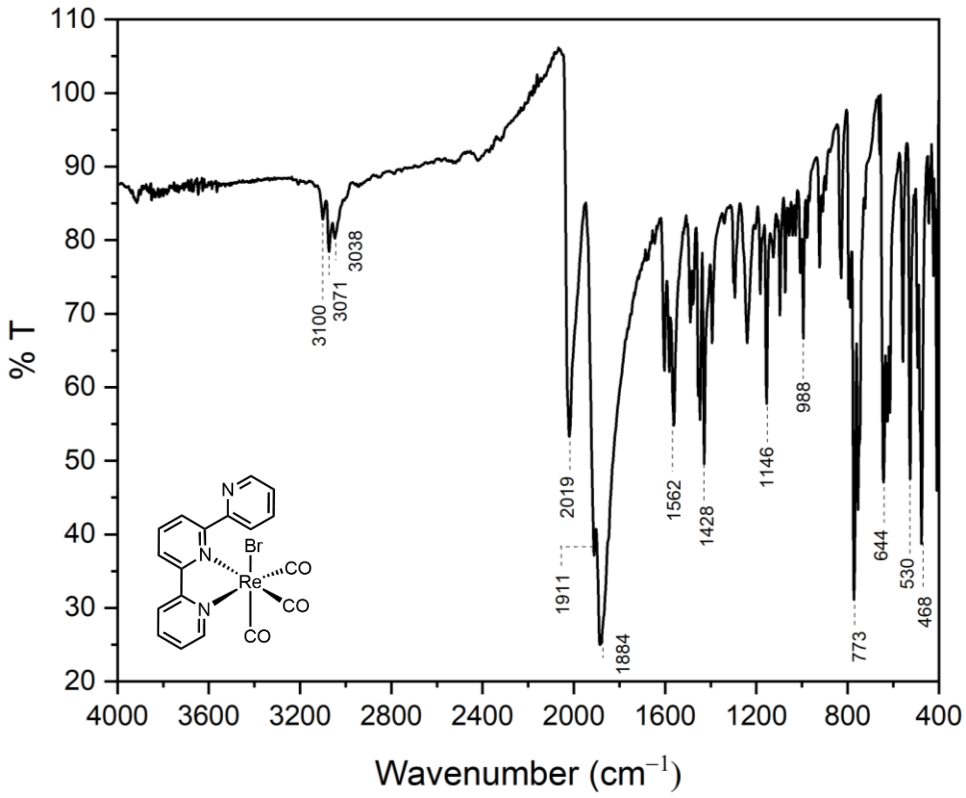


Figure S5d: *ATR–IR spectrum of* ***Re1****.*

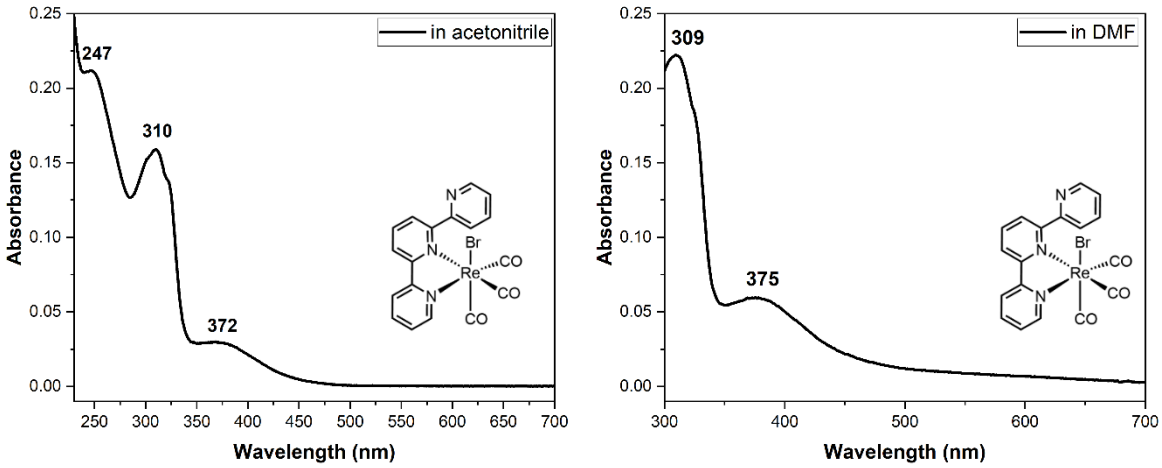


Figure S5e: *Absorbance spectra of* ***Re1*** *(0.01 mM) in acetonitrile and DMF.*

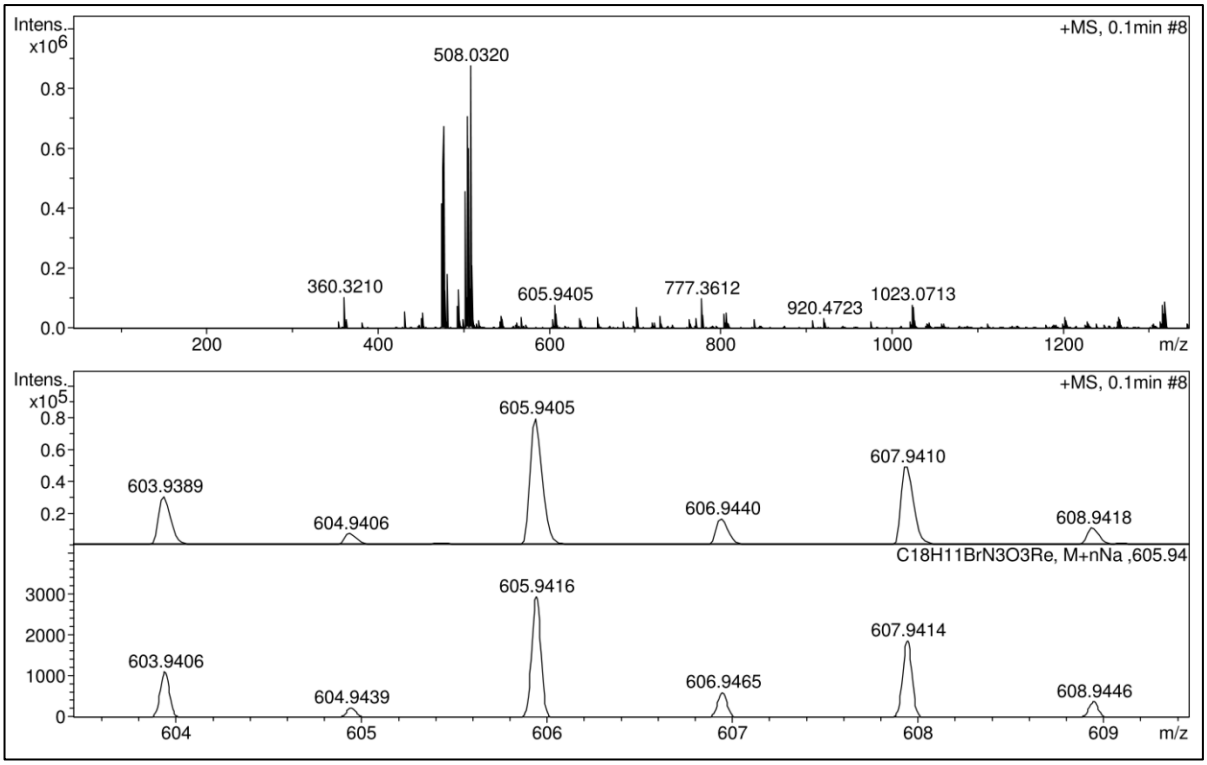


Figure S5e: *HRMS for* ***Re1*** *[$C_{18}H_{11}BrN_3O_3Re$ = M]* Calcd for [M+Na^+] *m/z* 605.9416 found *m/z* 605.9405; Calcd for [(M–CO–Br)$^+$+MeOH] *m/z* 508.0631 found *m/z 508.0320.*

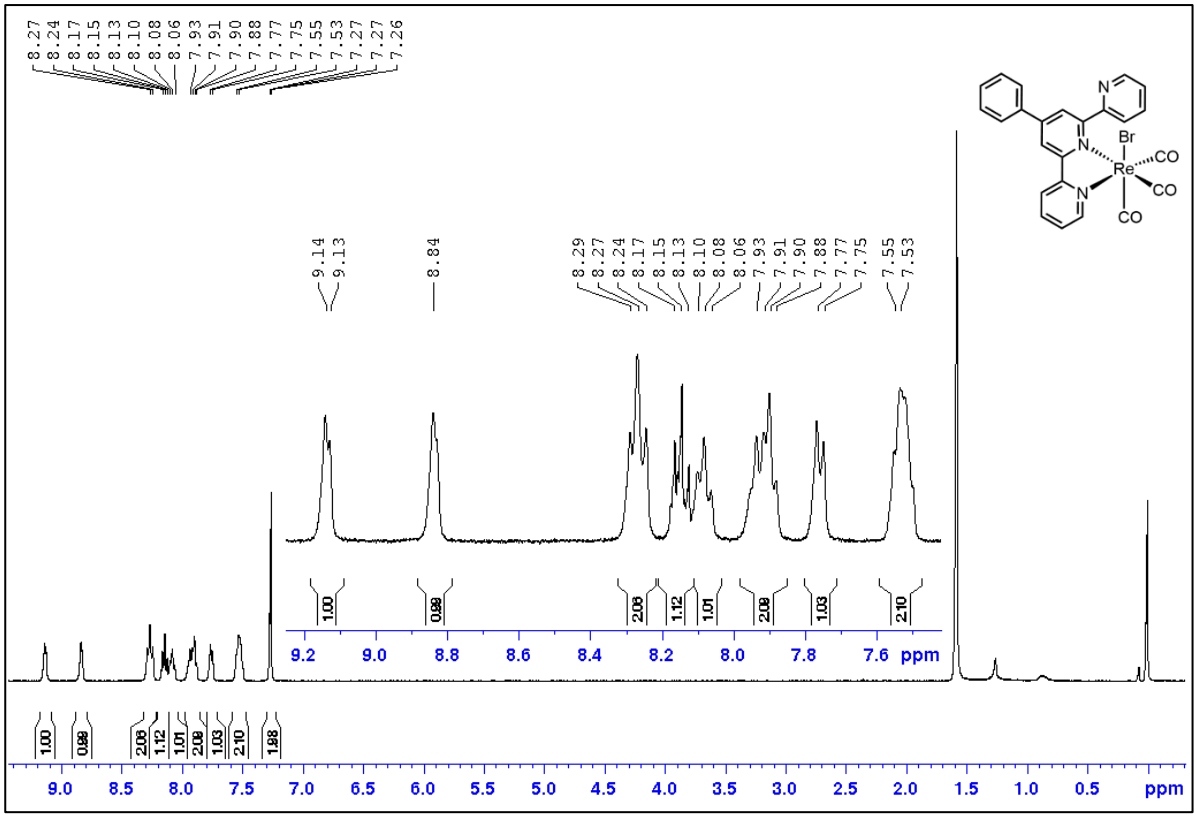


Figure S6a: *^{1}H NMR spectrum of* ***Re2*** *(500 MHz, $CDCl_3$)* (water peak at 1.6 ppm).

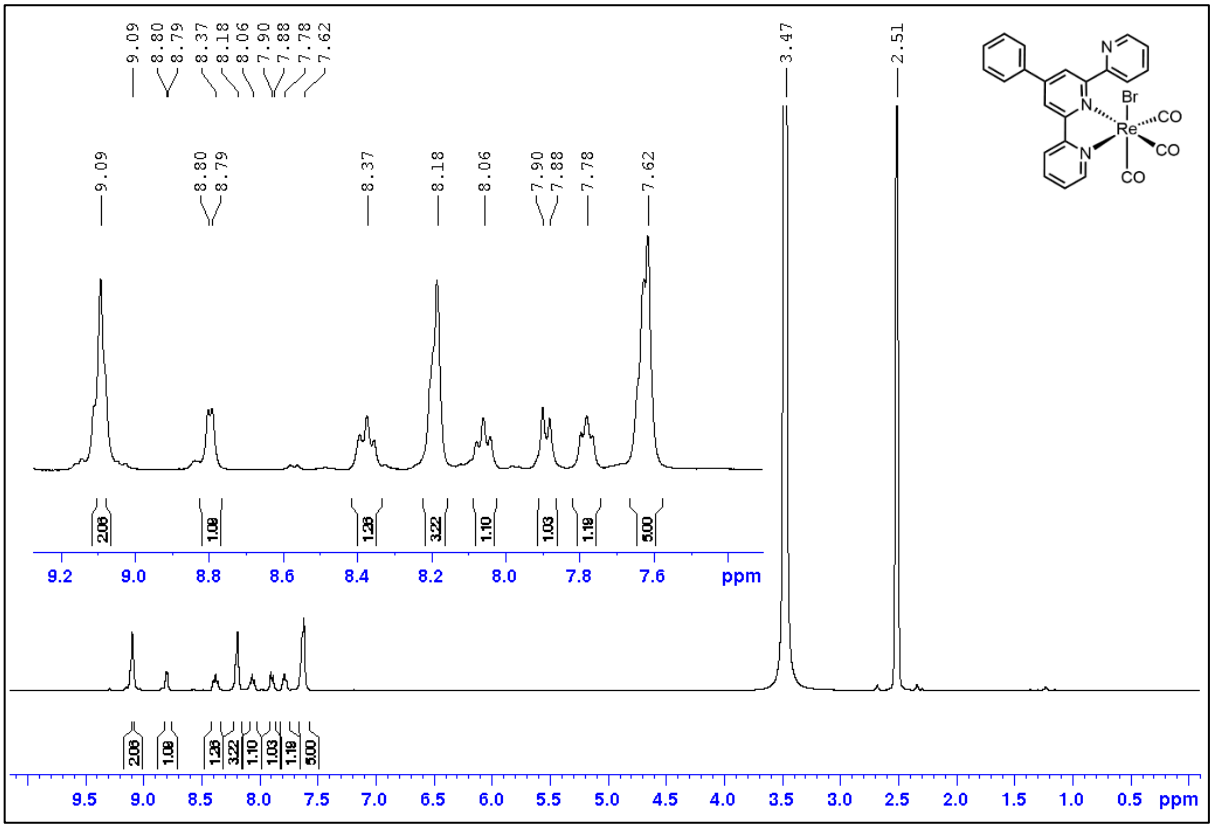


Figure S6b: *^{1}H NMR spectrum of* ***Re2*** *(400 MHz, DMSO-d_6)* (water peak at 3.47 ppm).

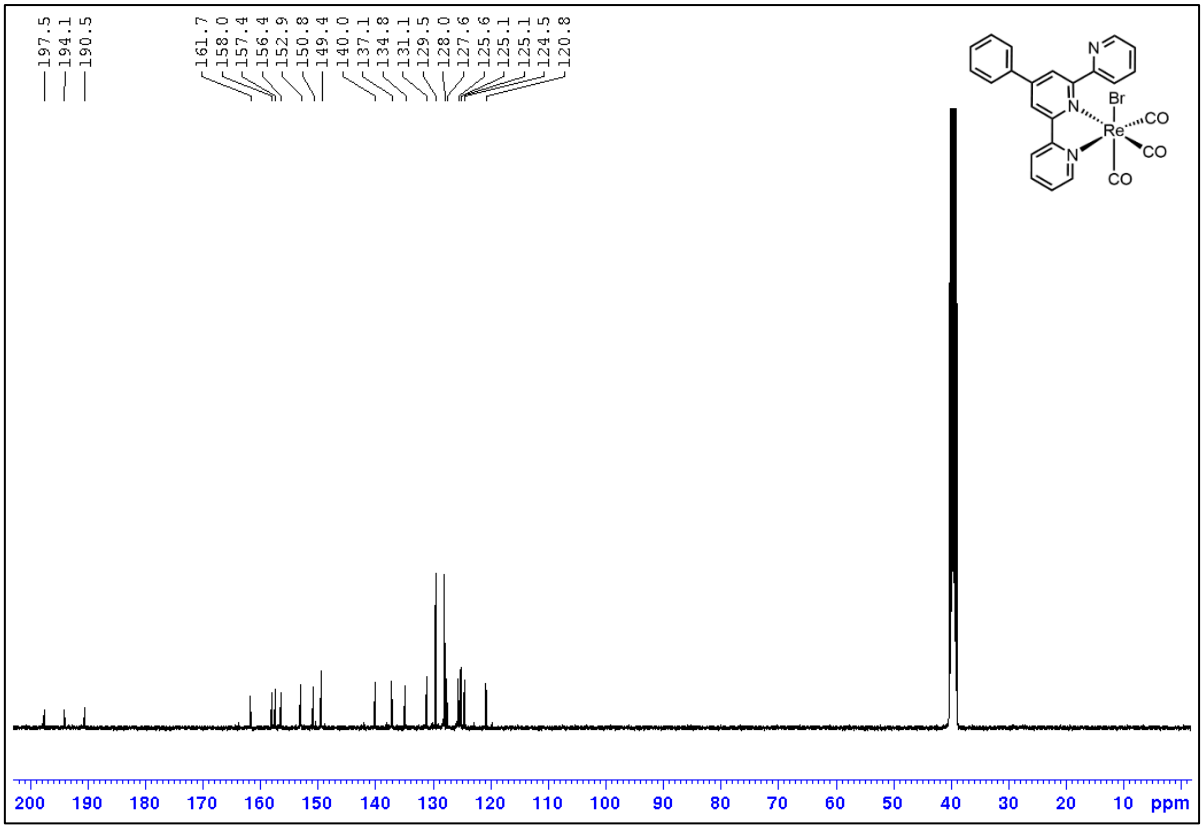


Figure S6c: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***Re2*** *(101 MHz, DMSO-d_6) with 13678 scans.*

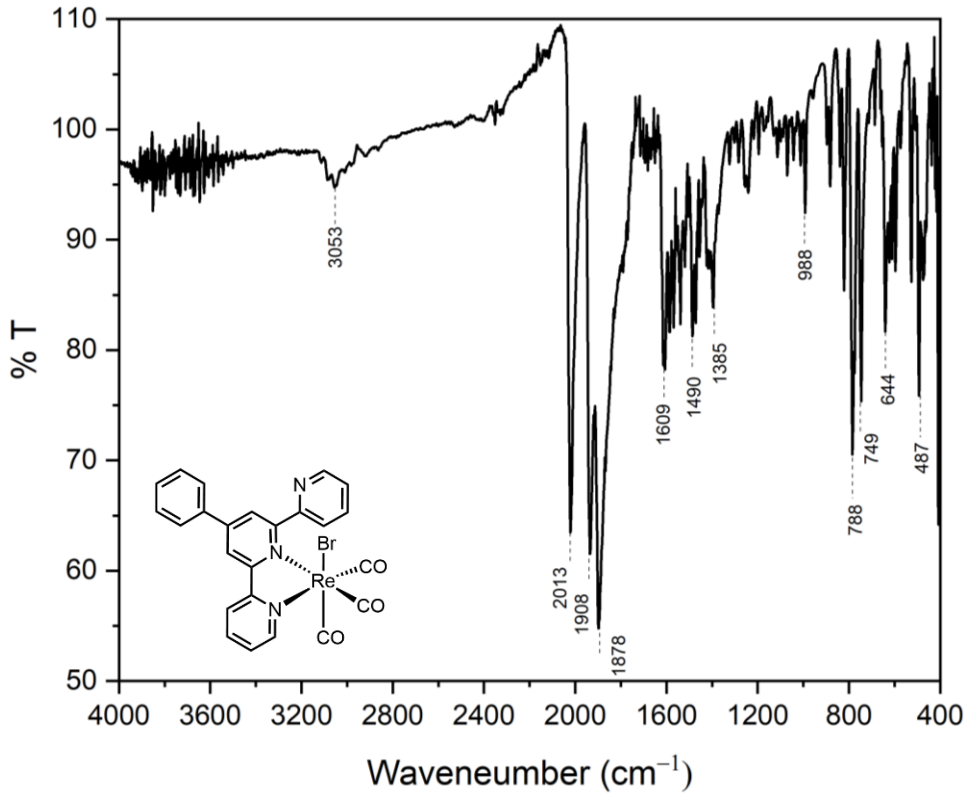


Figure S6d: *ATR–IR spectrum of* ***Re2****.*

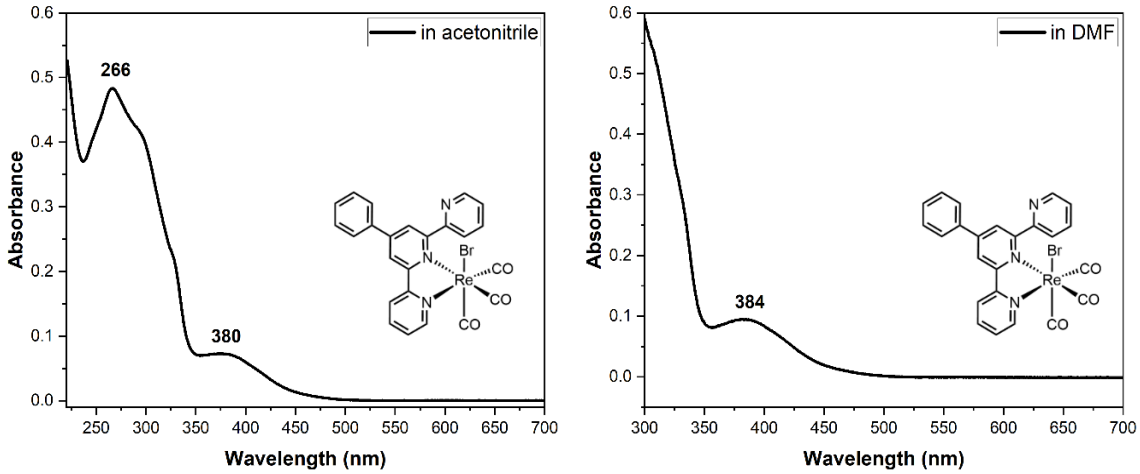


Figure S6e: *Absorbance spectra of* ***Re2*** *(0.01 mM) in acetonitrile and DMF.*

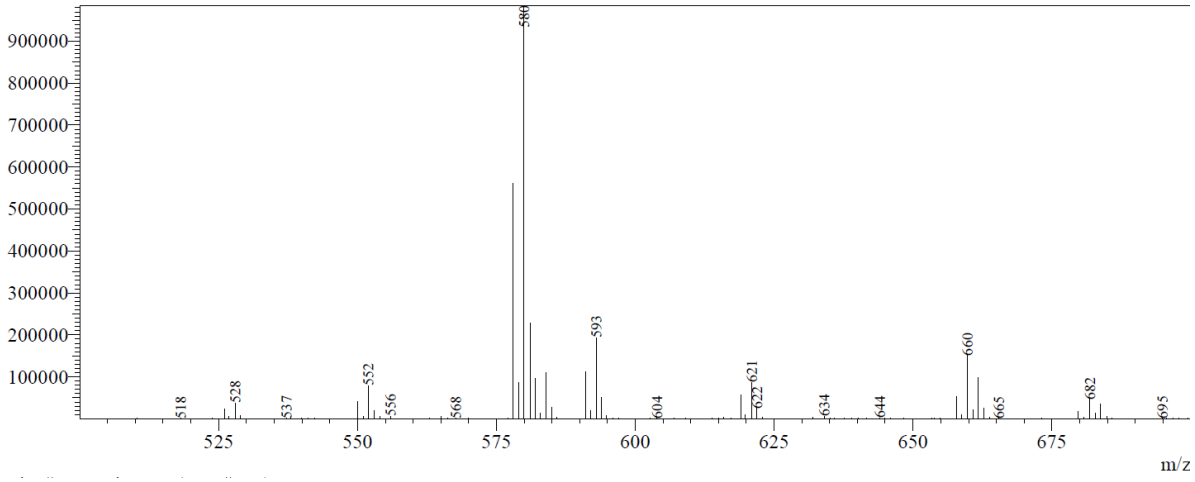


Figure S6f: *Mass fragmentation pattern and isotopic distribution for* ***Re2*** *[$C_{24}H_{15}BrN_3O_3Re$ = M]; m/z = 660 $[M+H]^+$ ($C_{24}H_{16}BrN_3O_3Re$);m/z = 580 $[M-Br]^+$ ($C_{24}H_{16}N_3O_3Re$).*

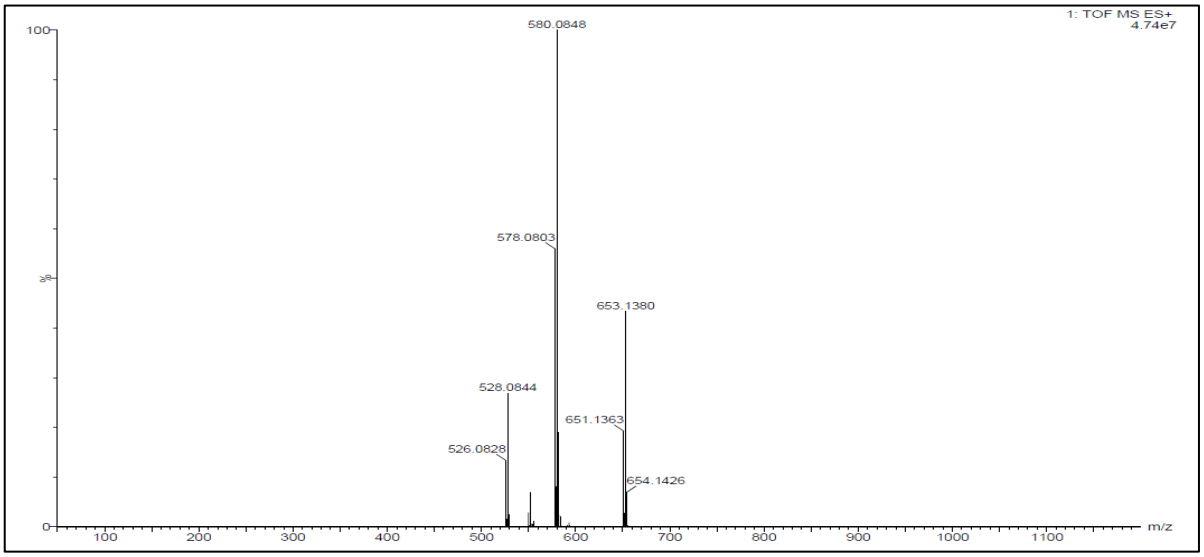


Figure S6g: *HRMS for* ***Re2*** *[$C_{24}H_{15}BrN_3O_3Re$ = M]; Calcd for $[M–CO+Na]^+$ m/z 653.9775 found m/z 653.1380; Calcd for $[(M–Br)^+]$ m/z 580.0643 found m/z 580.0848.*

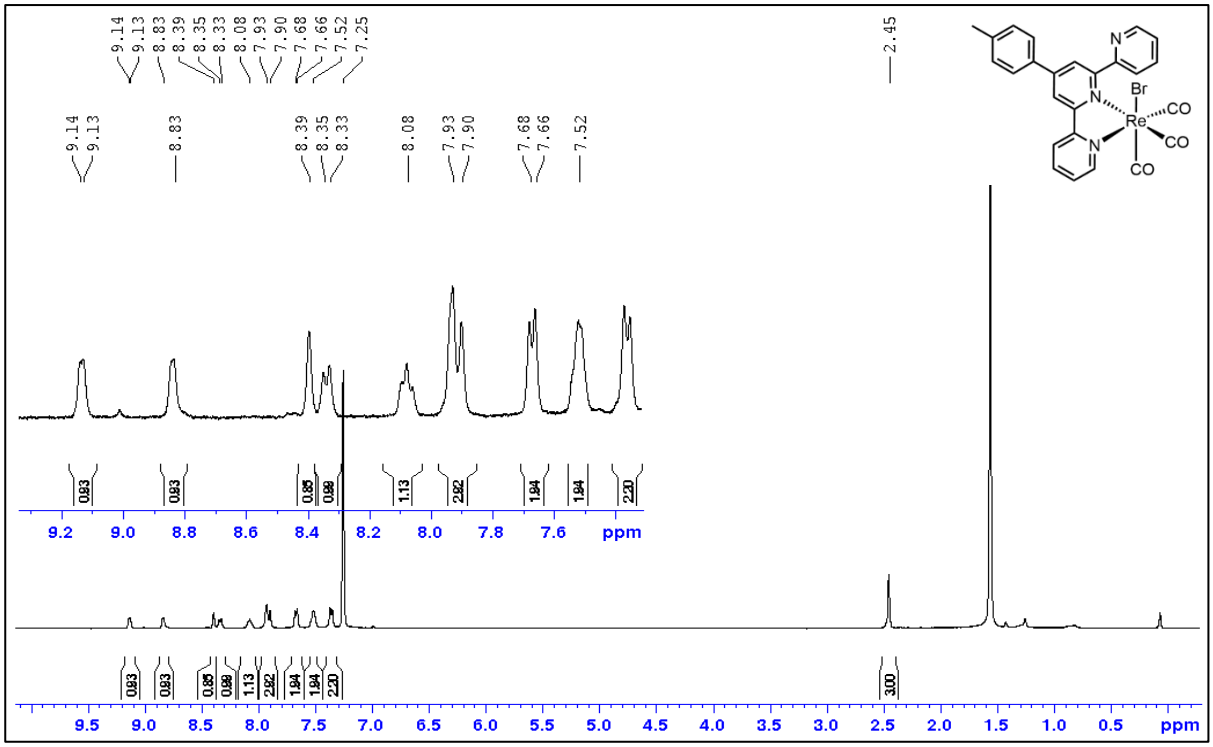


Figure S7a: *^{1}H NMR spectrum of* ***Re3*** *(400 MHz, $CDCl_3$)* (water peak at 1.6 ppm).

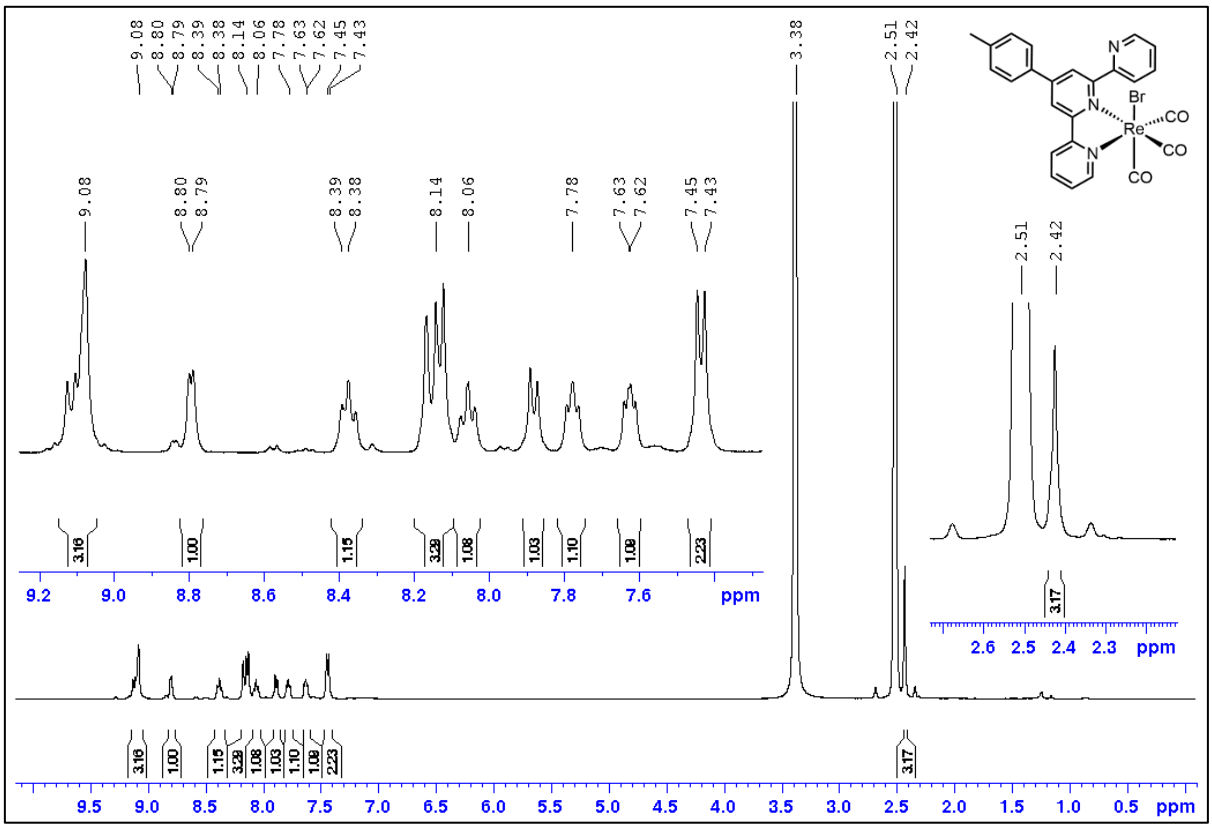


Figure S7b: *^{1}H NMR spectrum of* ***Re3*** *(400 MHz, DMSO-d_6)* (water peak at 3.38 ppm).

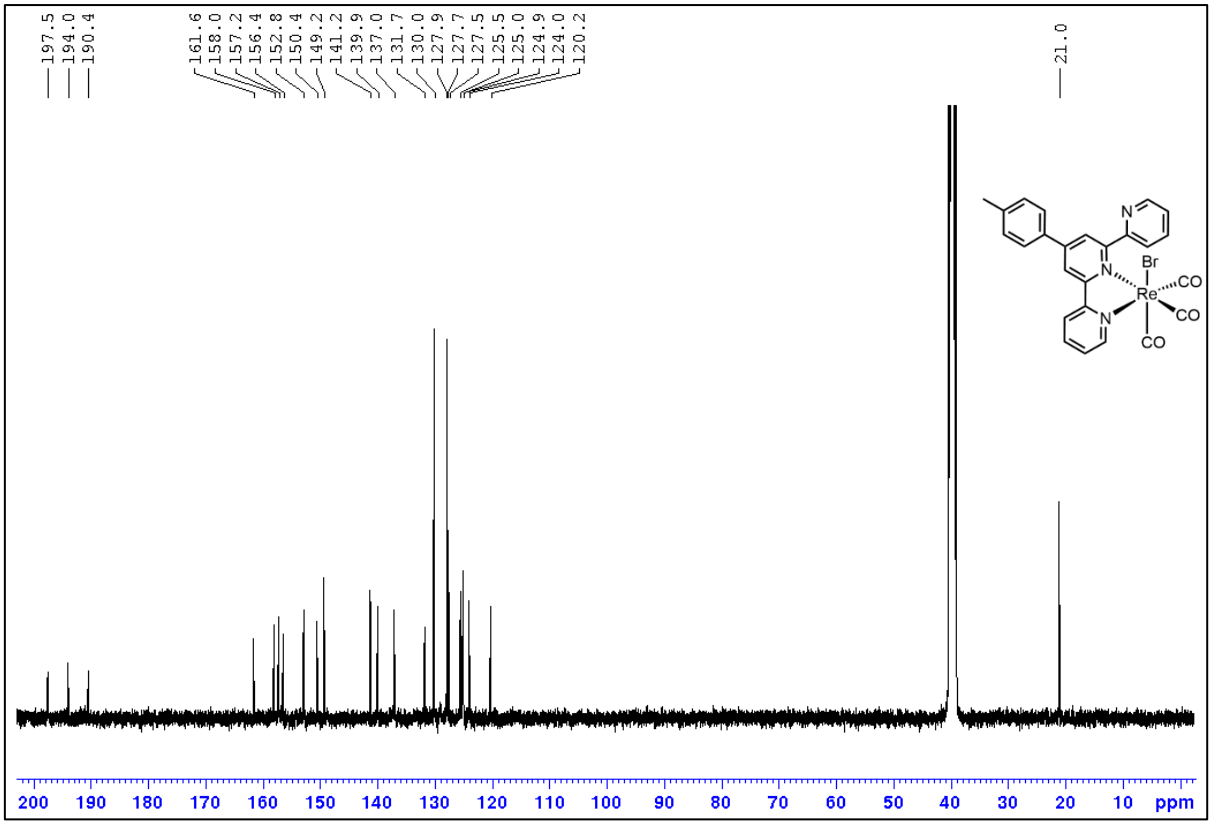


Figure S7c: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***Re3*** *(101 MHz, DMSO-d_6) with 13643 scans.*

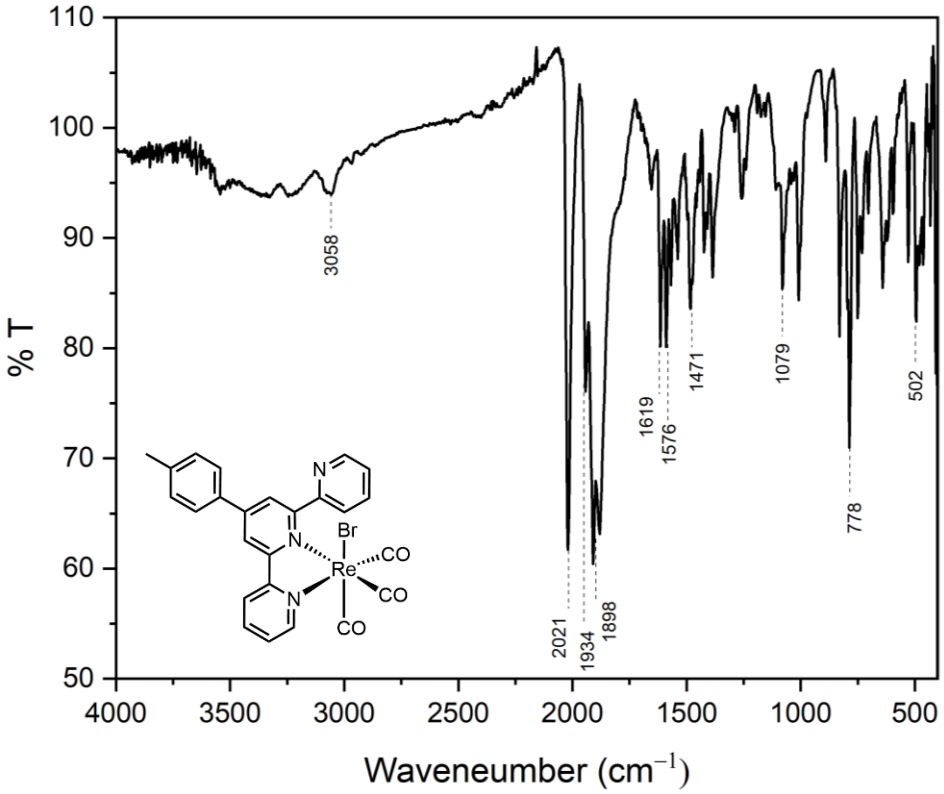


Figure S7d: *ATR–IR spectrum of* ***Re3****.*

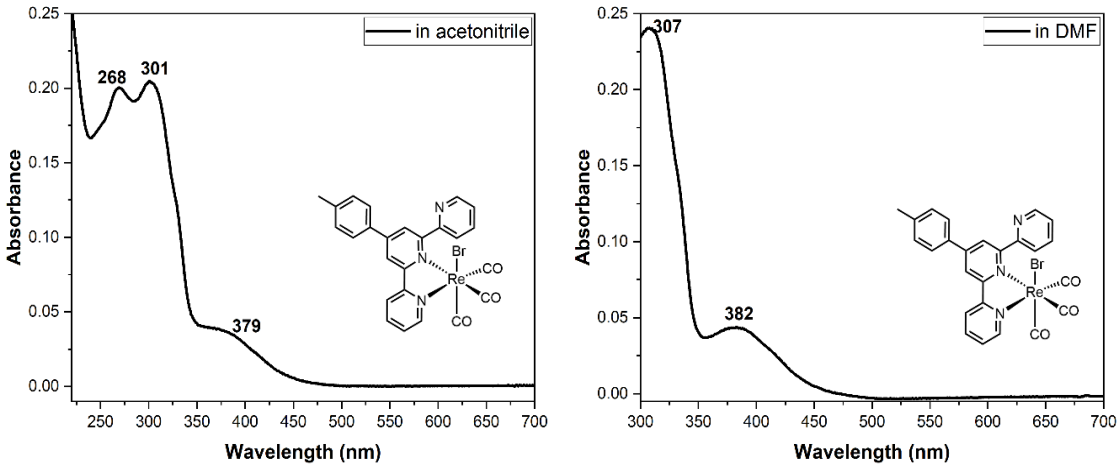


Figure S7e: *Absorbance spectra of* ***Re3*** *(0.01 mM) in acetonitrile and DMF.*

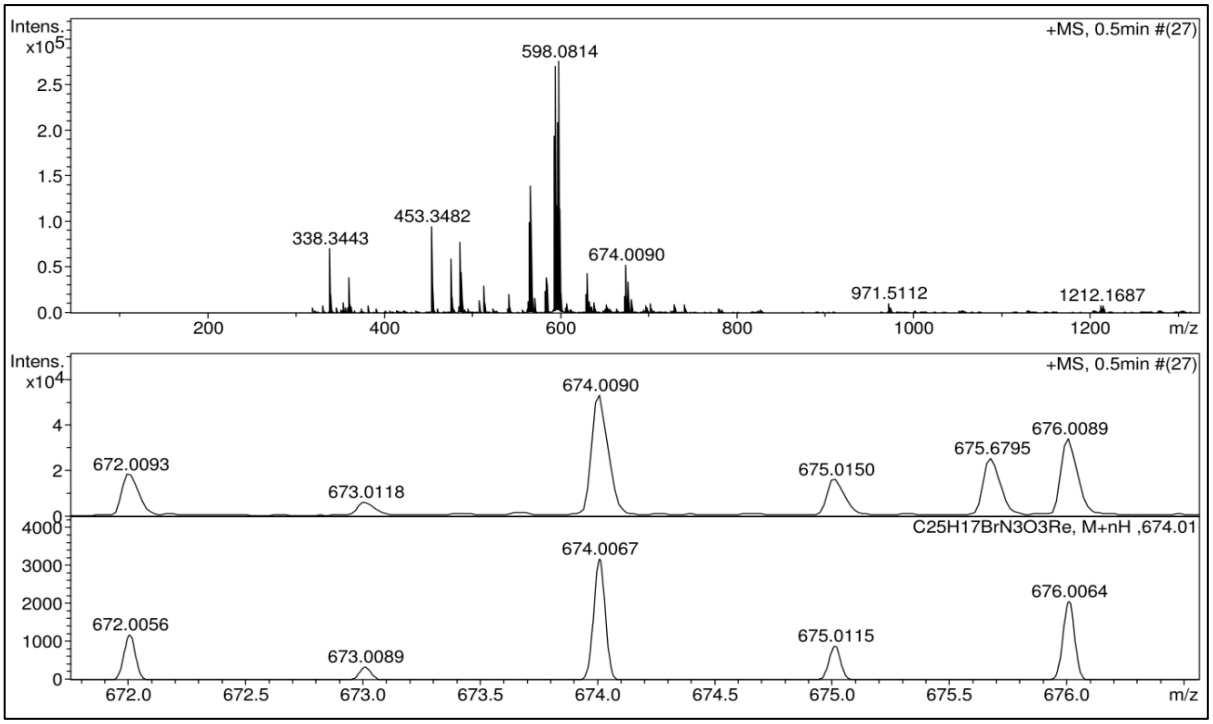


Figure S7f: *HRMS for* ***Re3*** *[$C_{25}H_{17}BrN_3O_3Re$ = M];* Calcd for $[M+H]^+$ *m/z = 674.0055 ($C_{25}H_{18}{}^{79}BrN_3O_3Re$)* found *m/z = 674.0090;* Calcd for $[(M–CO–Br)^+$+MeOH] *m/z = 598.1112* found *m/z =598.0814.*

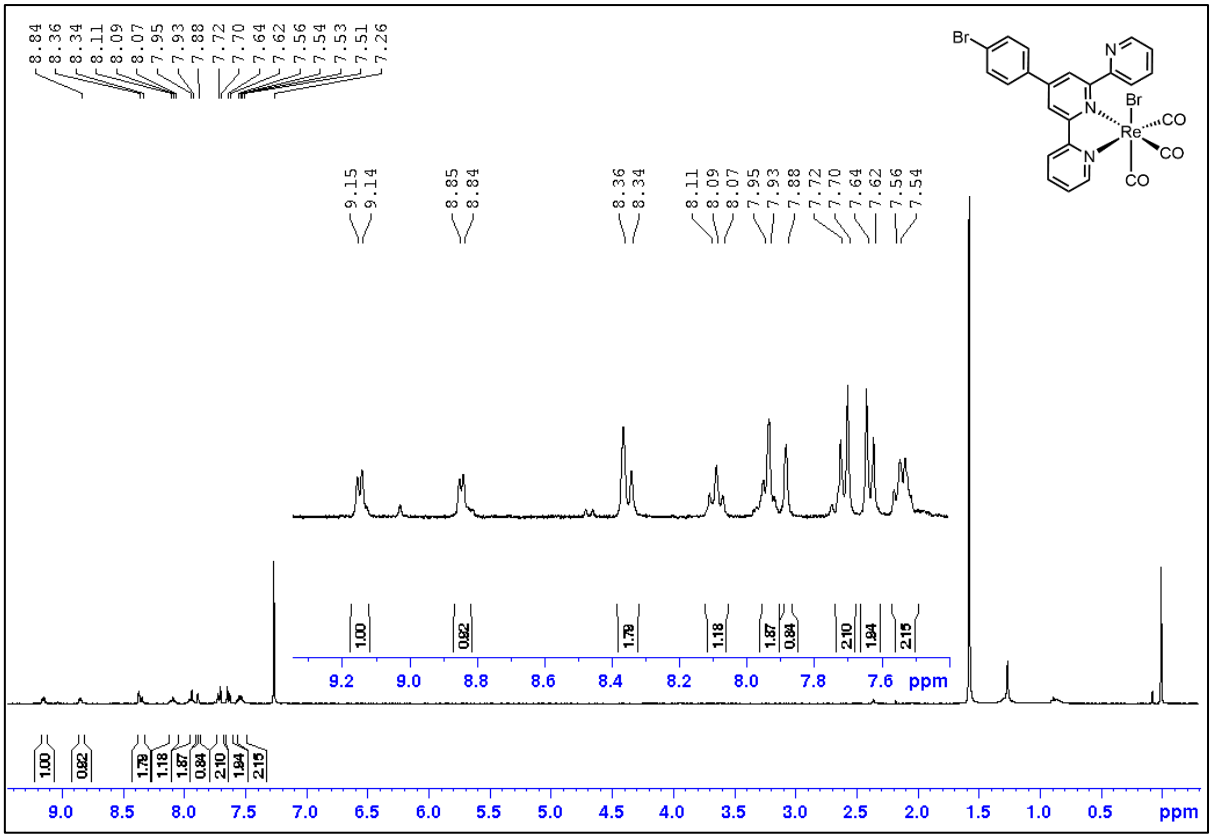


Figure S8a: *^{1}H NMR spectrum of* ***Re4*** *(500 MHz, $CDCl_3$)* (water peak at 1.6 ppm).

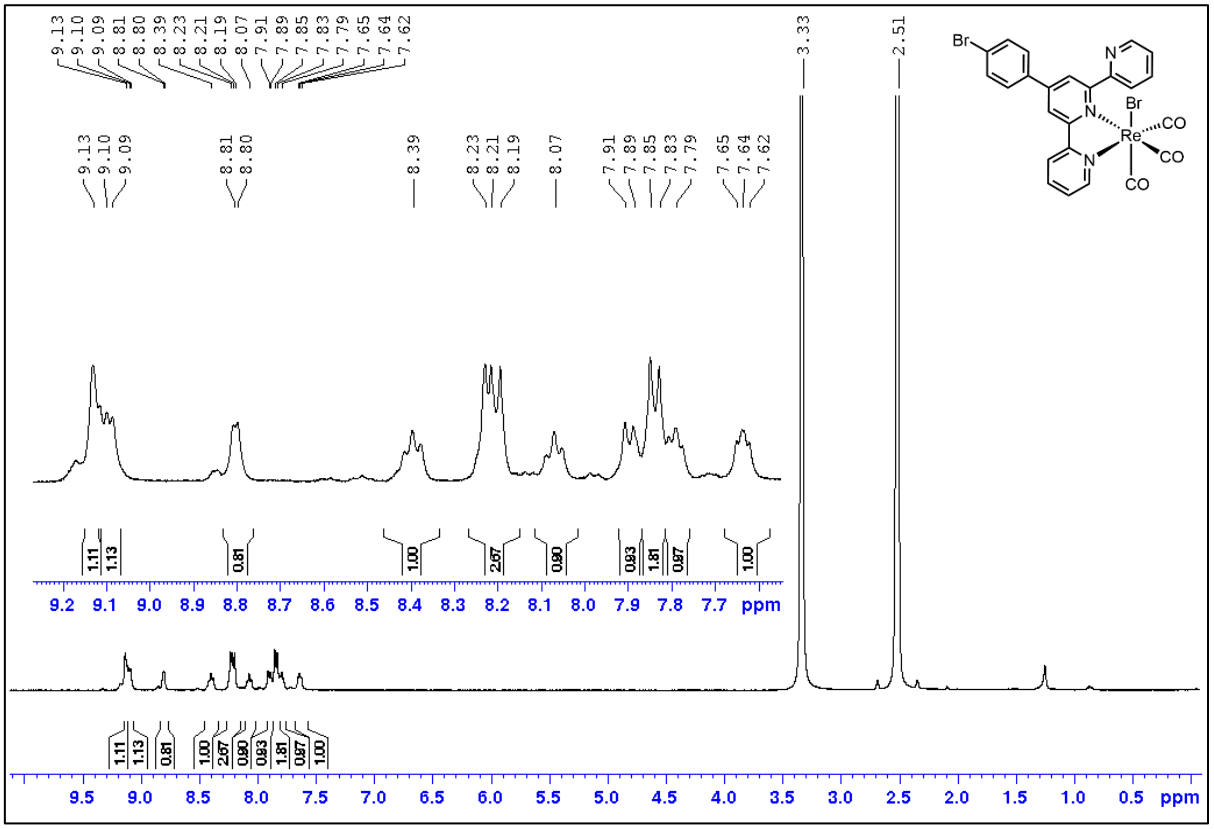


Figure S8b: *^{1}H NMR spectrum of* ***Re4*** *(400 MHz, DMSO-d_6)* (water peak at 3.33 ppm).

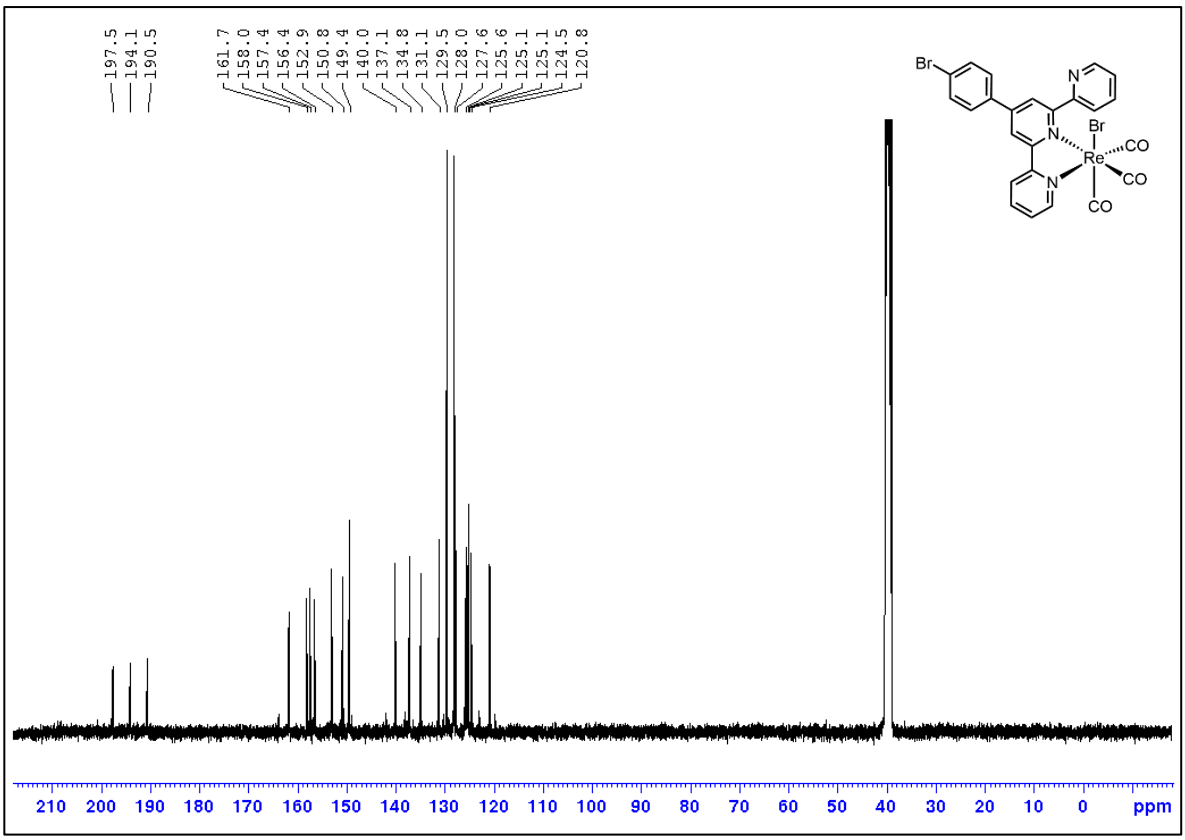


Figure S8c: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***Re4*** *(101 MHz, DMSO-d_6) with 11100 scans.*

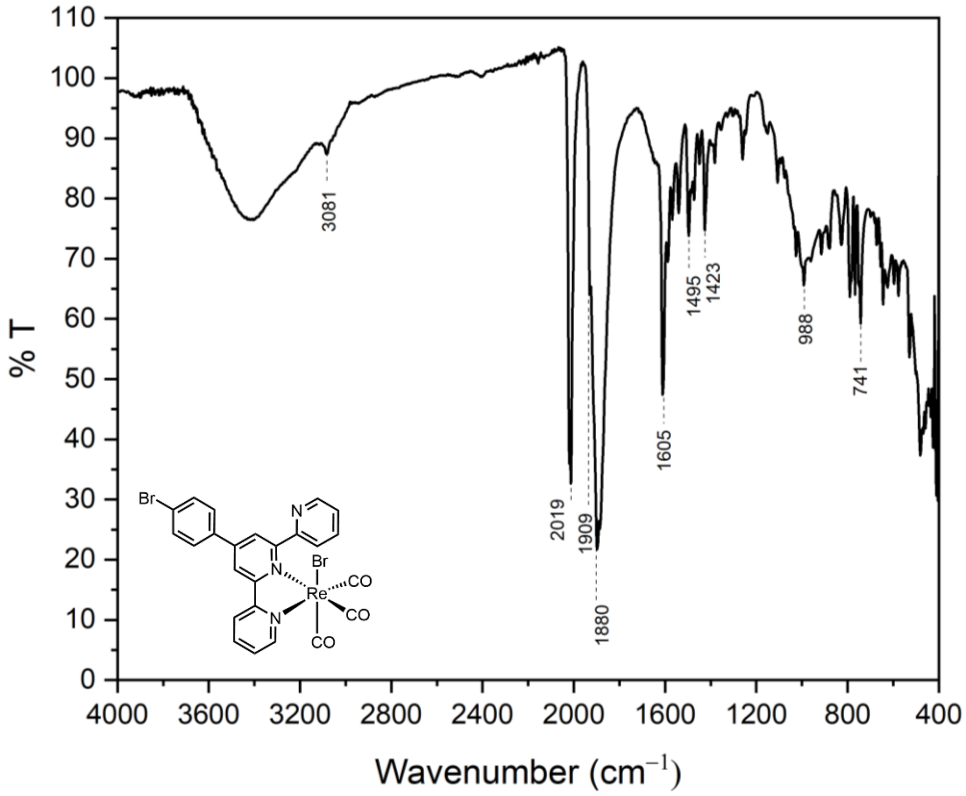


Figure S8d: *ATR–IR spectrum of* ***Re4****.*

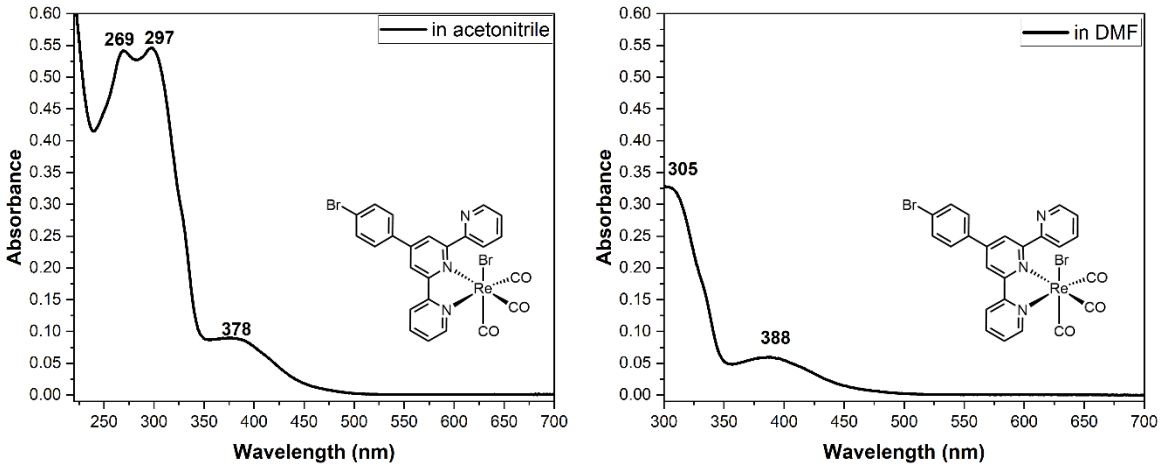


Figure S8e: *Absorbance spectra of* ***Re4*** *(0.01 mM) in acetonitrile and DMF.*

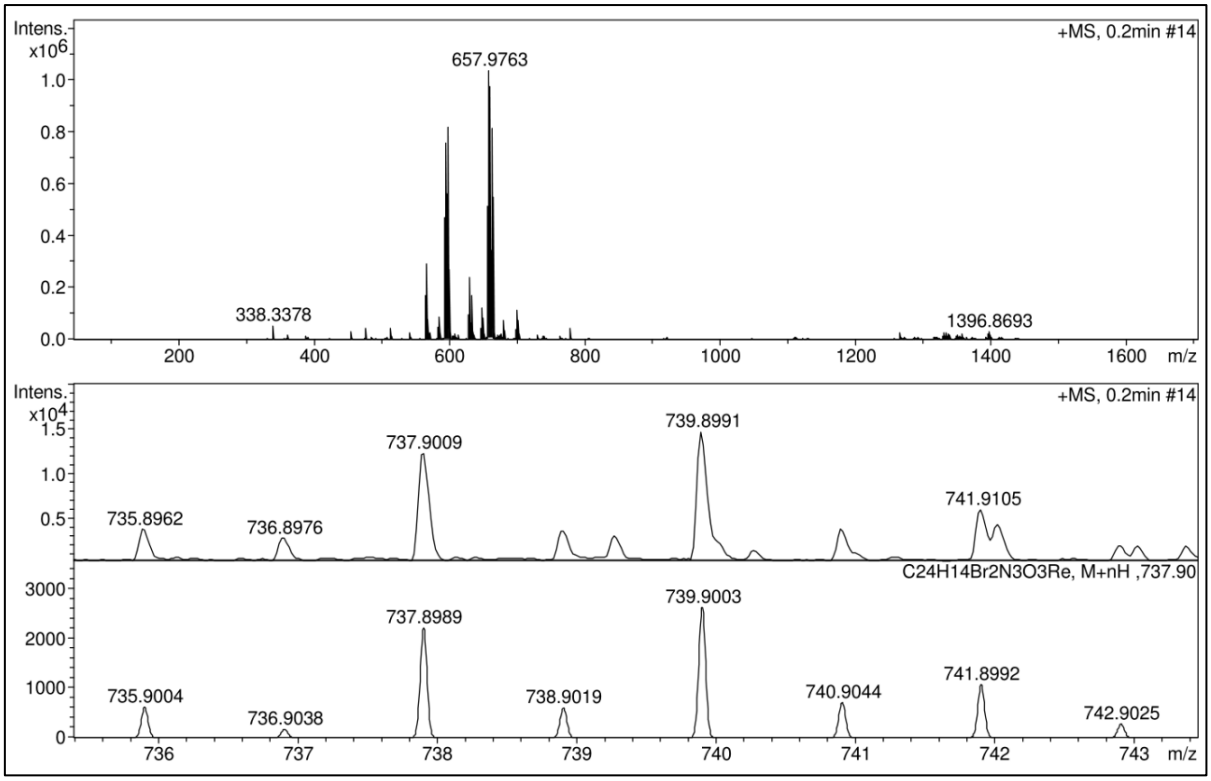


Figure S8f: *HRMS for* ***Re4*** *[$C_{24}H_{14}Br_2N_3O_3Re$ = M]* Calcd for $[M+H]^+$ *m/z = 739.9004 (*$C_{25}H_{18}{}^{81}Br_2N_3O_3Re$*)* found *m/z = 739.8991;* Calcd for $[(M–Br)^+]$ *m/z = 657.9748* found *m/z =657.9763.*

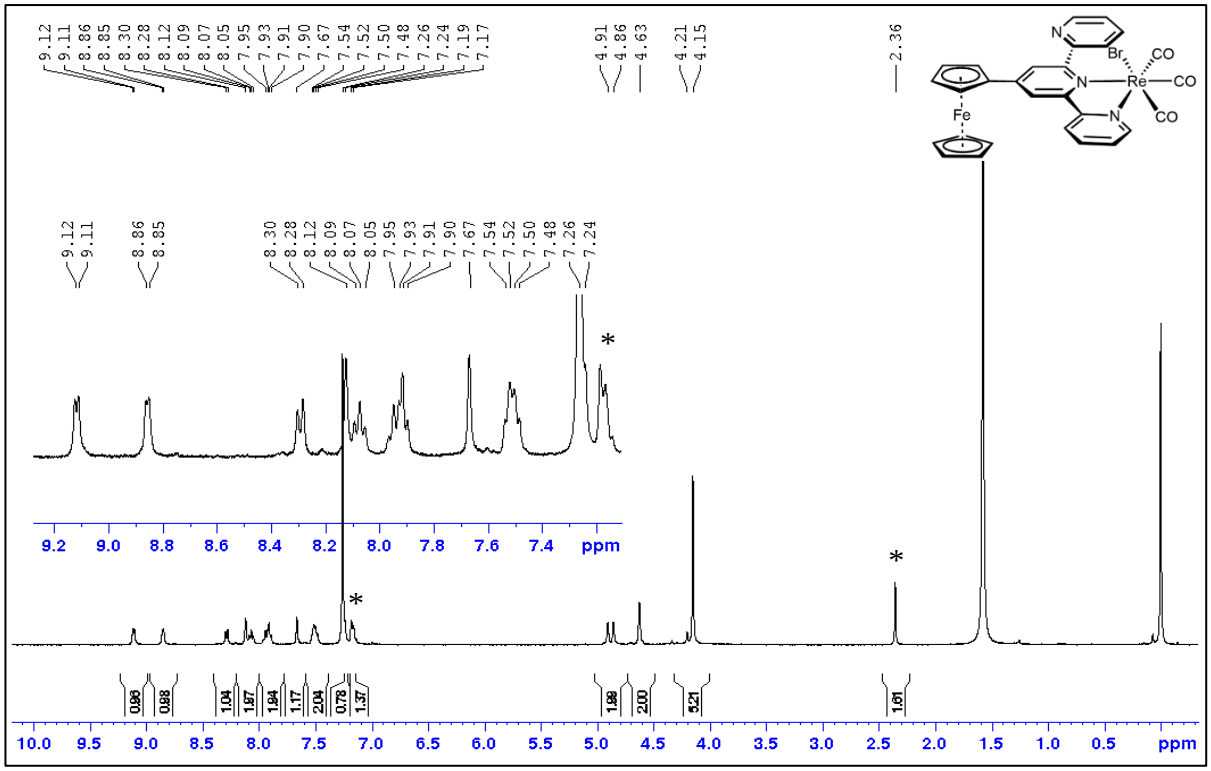


Figure S9a: *^{1}H NMR spectrum of* ***Re5*** *(400 MHz, $CDCl_3$)* (water peak at 1.6 ppm) *toluene peaks marked with *; observed at 7.24, 7.18 & 2.36 ppm; reported[3] at 7.25, 7.17 & 2.36 ppm.*

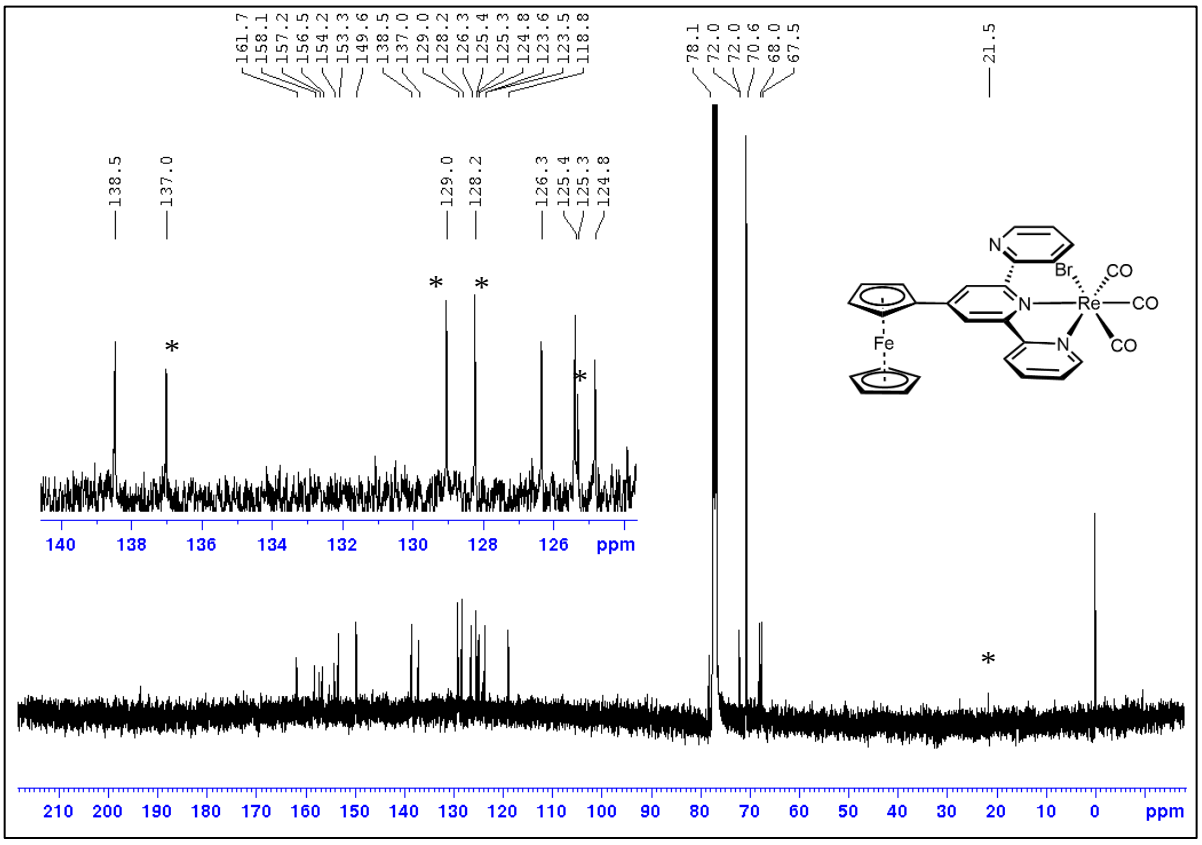


Figure S9b.: *$^{13}C\{^{1}H\}$ NMR spectrum of* ***Re5*** *(101 MHz, $CDCl_3$), with 15879 scans. The ^{13}C peaks for CO were not observed even with longer scans; toluene peaks marked with *; observed at 137.9, 129.1, 128.3, 125.3 & 21.5 ppm; reported[3] at 137.0, 129.0, 128.2, 125.3 & 21.5 ppm.*

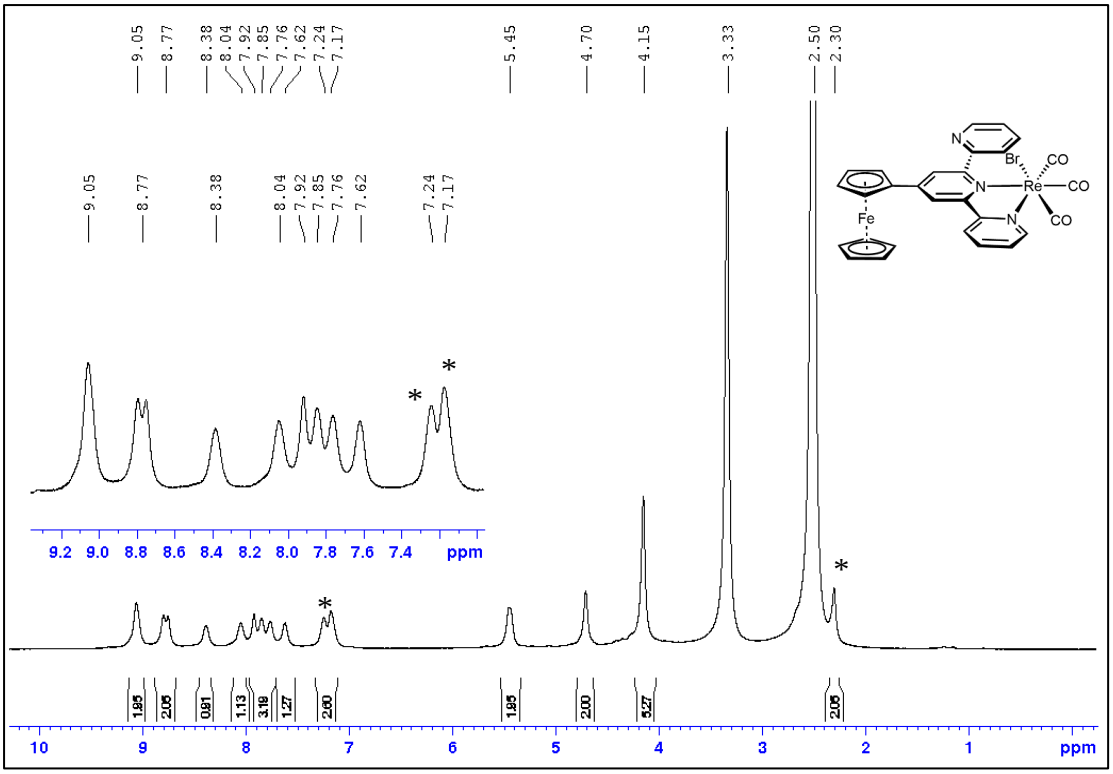


Figure S9c: *^{1}H NMR spectrum of **Re5** (400 MHz, DMSO-d_6) (water peak at 3.33 ppm); toluene peaks marked with *; observed at 7.24, 7.17 & 2.30 ppm; reported[3] at 7.25, 7.18 & 2.30 ppm.*

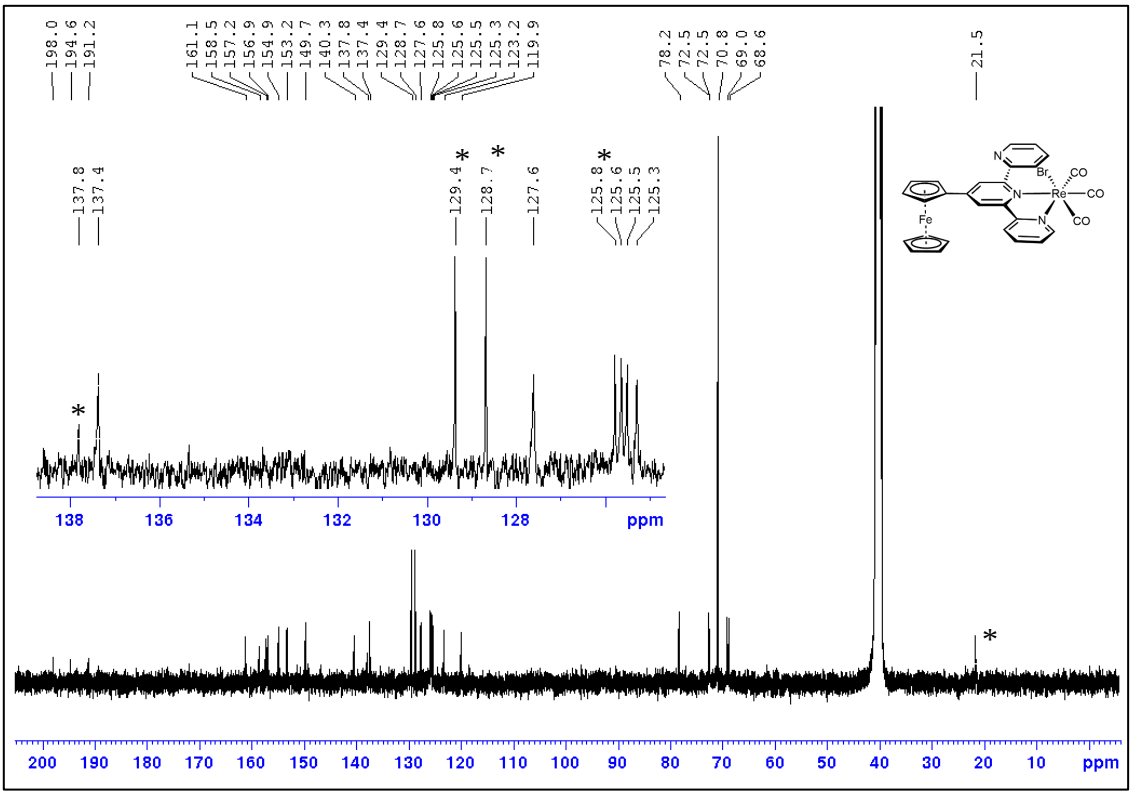


Figure S9d: *$^{13}C\{^{1}H\}$ NMR spectrum of **Re5** (101 MHz, DMSO-d_6)with 1024 scans; toluene peaks marked with *; observed at 137.8, 129.4, 128.7, 125.8 & 21.5 ppm; reported[3] at 137.4, 128.9, 128.2, 125.3 & 21.0 ppm.*

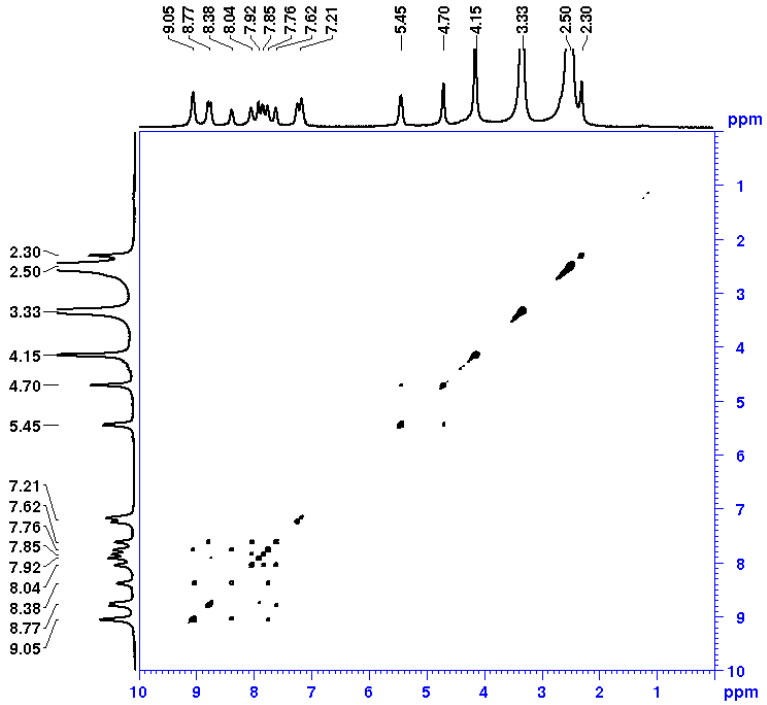


Figure S9e: *COSY spectra of* ***Re5*** *(DMSO-d_6).*

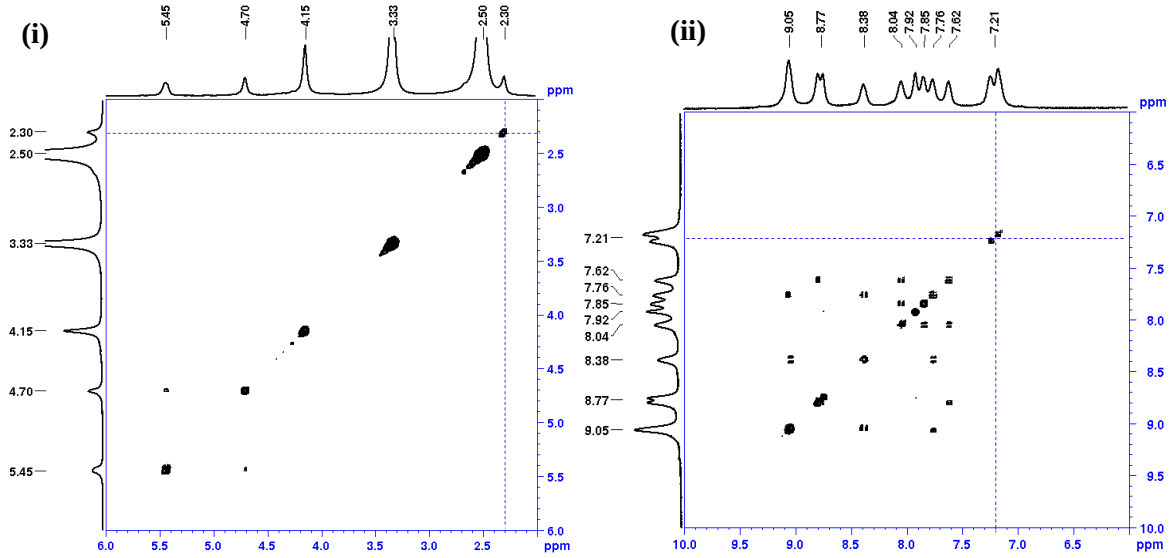


Figure S9f: *(i)Section of COSY spectra (0-6 ppm) shows the -CH_3 peak of toluene, with no correlation to any other protons; (ii) Section of COSY spectra (6-10 ppm) shows the aromatic protons of toluene, having no correlation with any other aromatic peaks of the complex.*

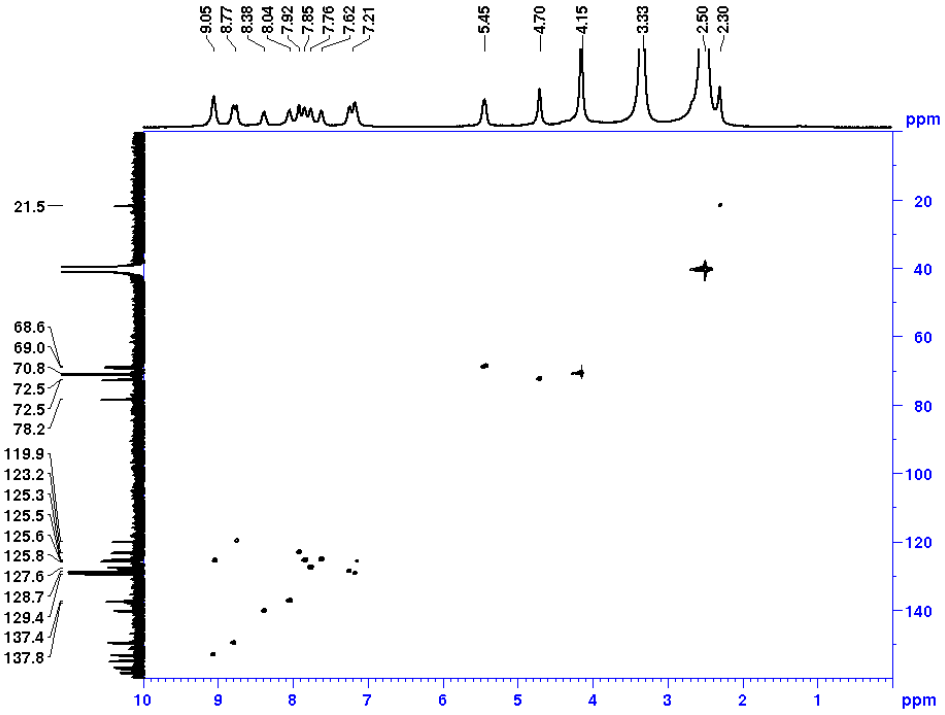


Figure S9g: *HSQC spectra of* ***Re5*** *(DMSO-d_6).*

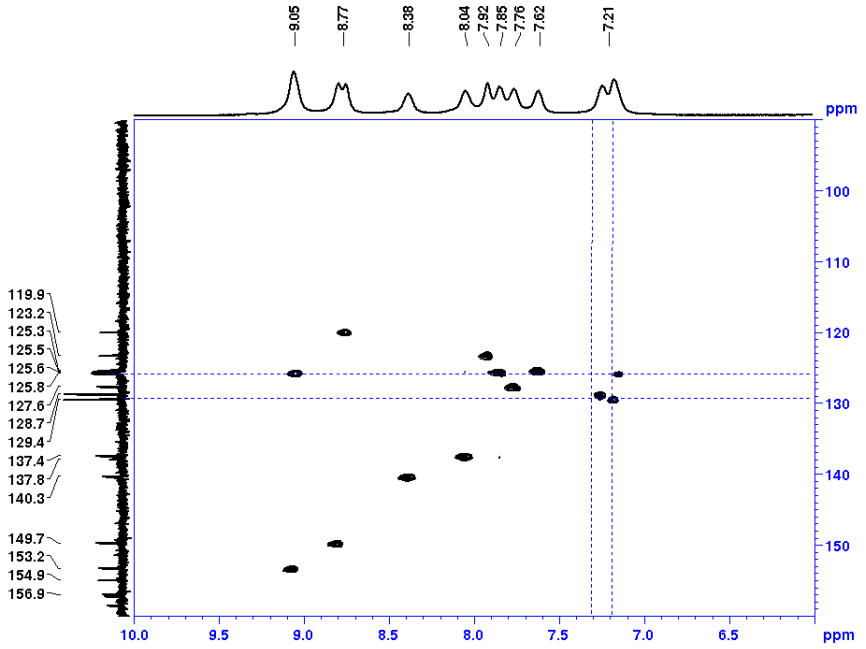


Figure S9h: *HSQC spectra of the aromatic region shows three ^{13}C correlated with the protons at 7.21 ppm, which are characteristic of toluene*[3].

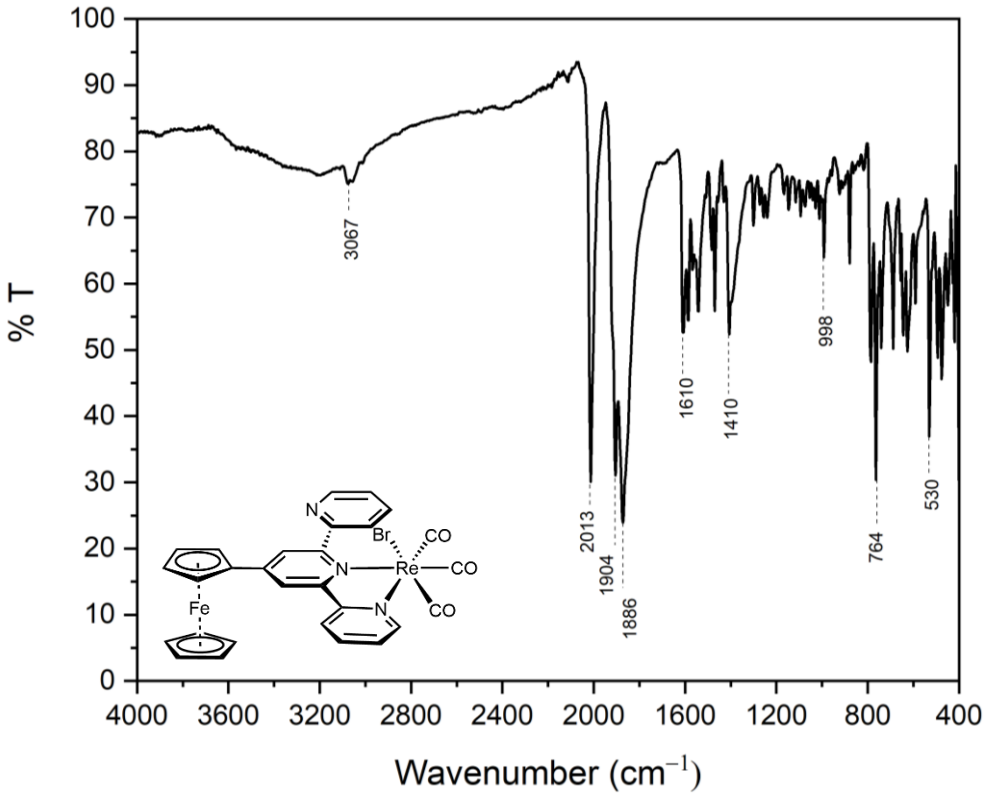


Figure S9i: *ATR–IR spectrum of* ***Re5****.*

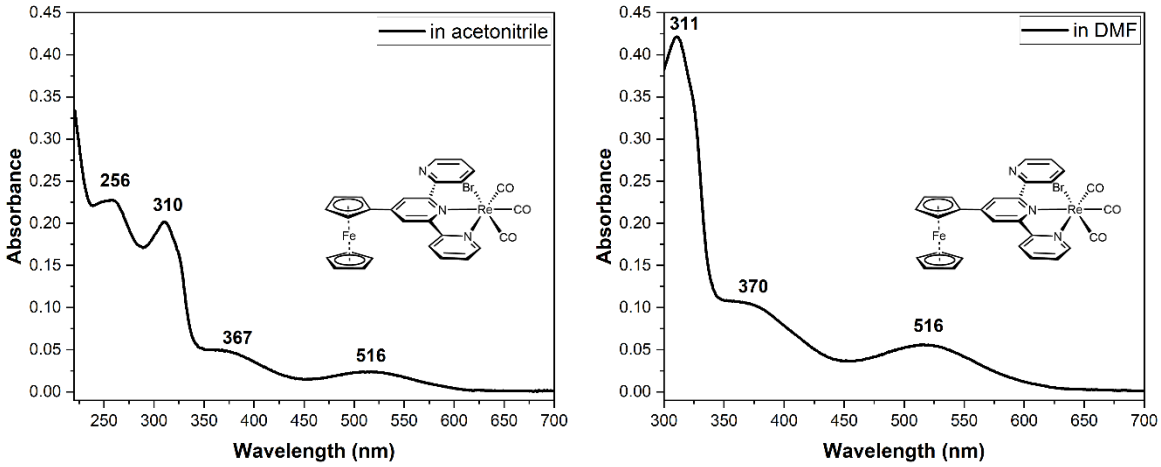


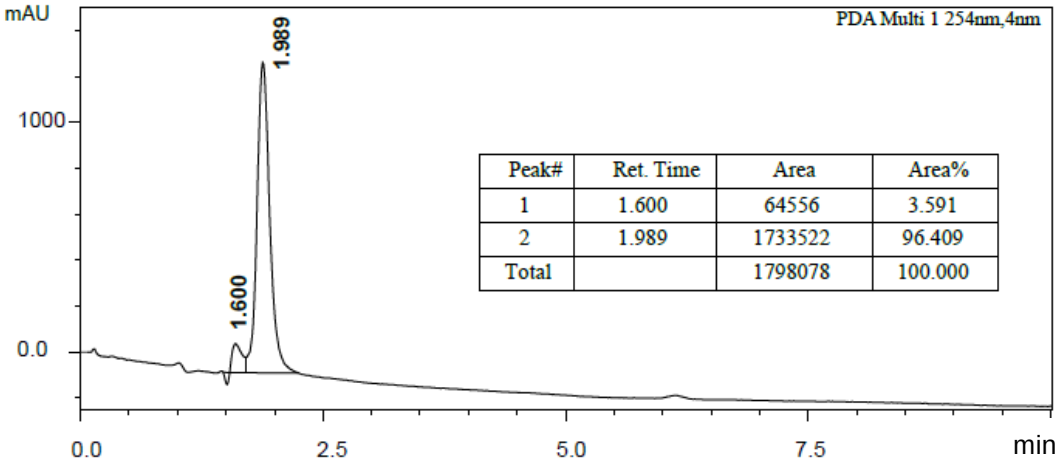
Figure S9j: *Absorbance spectra of* ***Re5*** *(0.01 mM) in acetonitrile and DMF.*

SHIMADZU LabSolutions **Analysis Report**

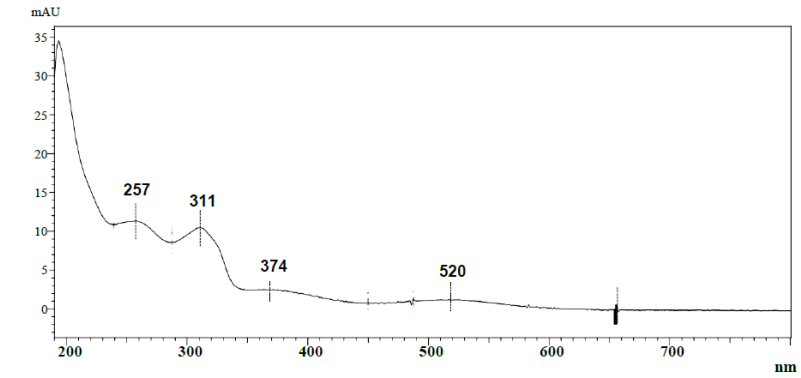
<Sample Information>

Sample Name	: Re5		
Sample ID	: Re5		
Data Filename	: Re5_27-03-2023_003.lcd		
Method Filename	: C_95_D_5_10_min_0.2ml_min.lcm		
Batch Filename	: 27032023.lcb		
Vial #	: 1-93	Sample Type	: Unknown
Injection Volume	: 0.5 uL		
Date Acquired	: 3/27/2023 10:22:05 AM	Acquired by	: IIT GOA
Date Processed	: 3/27/2023 10:32:10 AM	Processed by	: IIT GOA

<Chromatogram>



Peak#	Ret. Time	Area	Area%
1	1.600	64556	3.591
2	1.989	1733522	96.409
Total		1798078	100.000



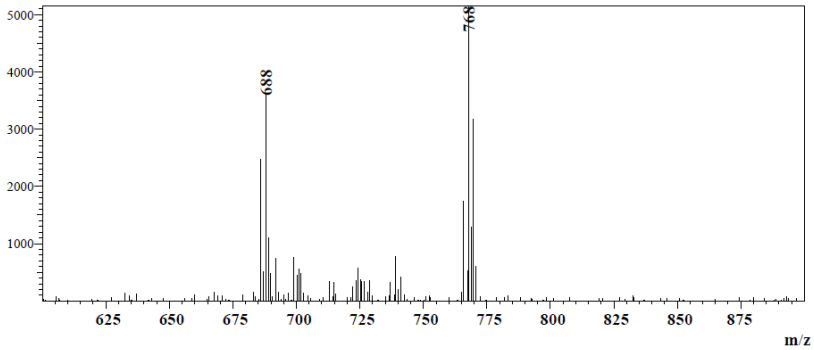


Figure S9k: *RP-HPLC-MS and corresponding UV-Vis spectra of* ***Re5*** *at t_R = 1.989 min; HPLC purity 96.4%; m/z values for t_R = for 1.600 & 1.989 min shows same m/z; Mass fragmentation pattern at 1.989 min [$C_{28}H_{19}BrFeN_3O_3Re$ = M], m/z = 768 $[M+H]^+$ ($C_{28}H_{20}BrFeN_3O_3Re$), m/z = 688 $[M-Br]^+$ ($C_{28}H_{19}N_3O_3Re$).*

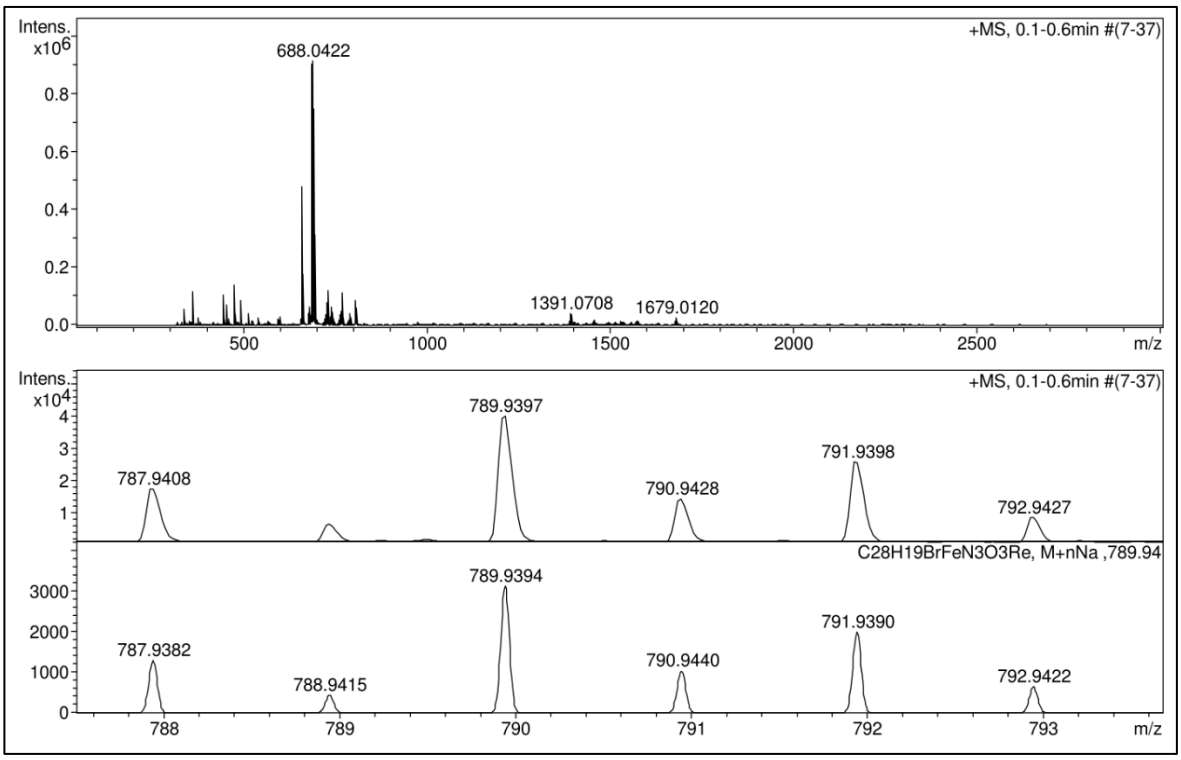
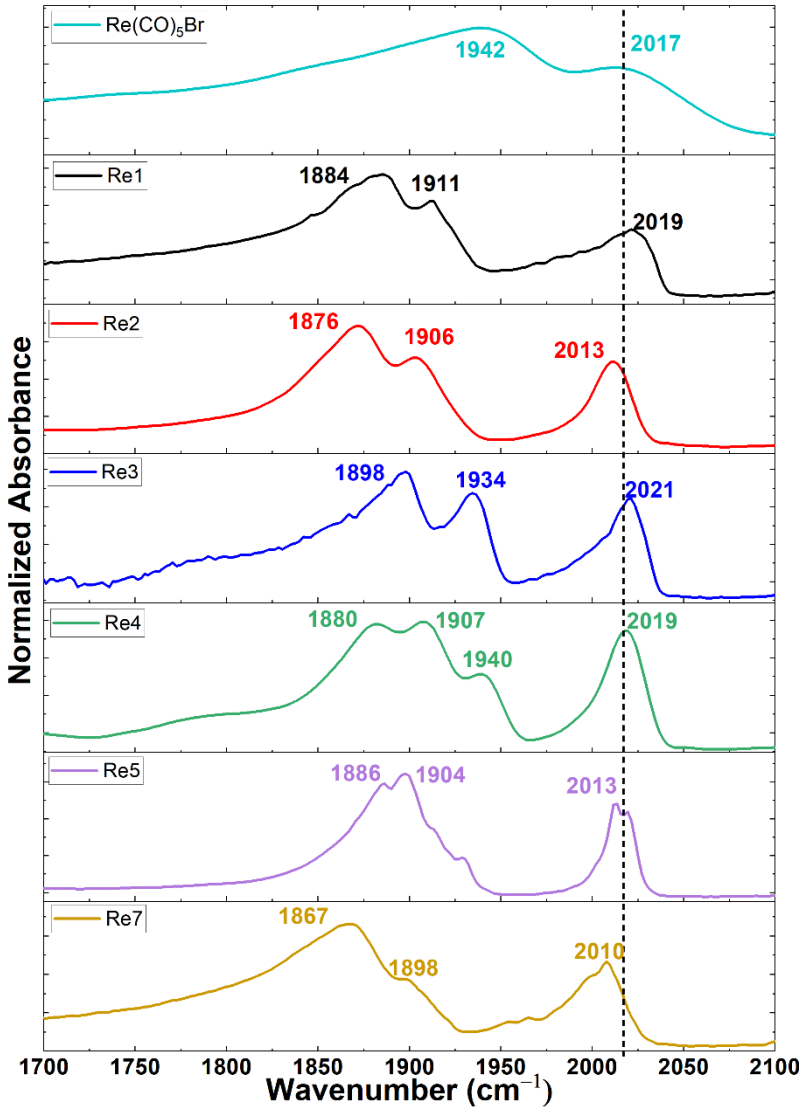


Figure S9i: *HRMS for* ***Re5*** *[$C_{28}H_{19}BrFeN_3O_3Re$ = M] Calcd for $[M+Na]^+$ m/z = 789.9394 ($C_{28}H_{19}{}^{79}BrFeN_3O_3ReNa$) found m/z = 789.9397 $[M+Na]^+$; Calcd for $[(M–Br)^+]$ m/z = 688.0352 found m/z =688.0422.*



Re(I) complexes	$\upsilon_{str(C=O)}$ ***(cm^{-1})***		
Re(CO)$_5$Br	*2017*	*1942*	
Re1	*2019*	*1911*	*1884*
Re2	*2013 (2018)*[1]	*1906 (1909)*	*1876 (1878)*
Re3	*2021*	*1934*	*1898*
Re4	*2019*	*1940 & 1907*	*1880*
Re5	*2013*	*1904*	*1886*
Re(bpy)(CO)$_3$Br/Re7	*2010(2011)*[2]	*1898 (1903)*	*1867 (1880)*

Figure S10: *Comparisons of infrared spectra for all Re(I) complexes and Re(CO)$_5$Br, the starting precursor. In the parenthesis, previously reported values are shown.*

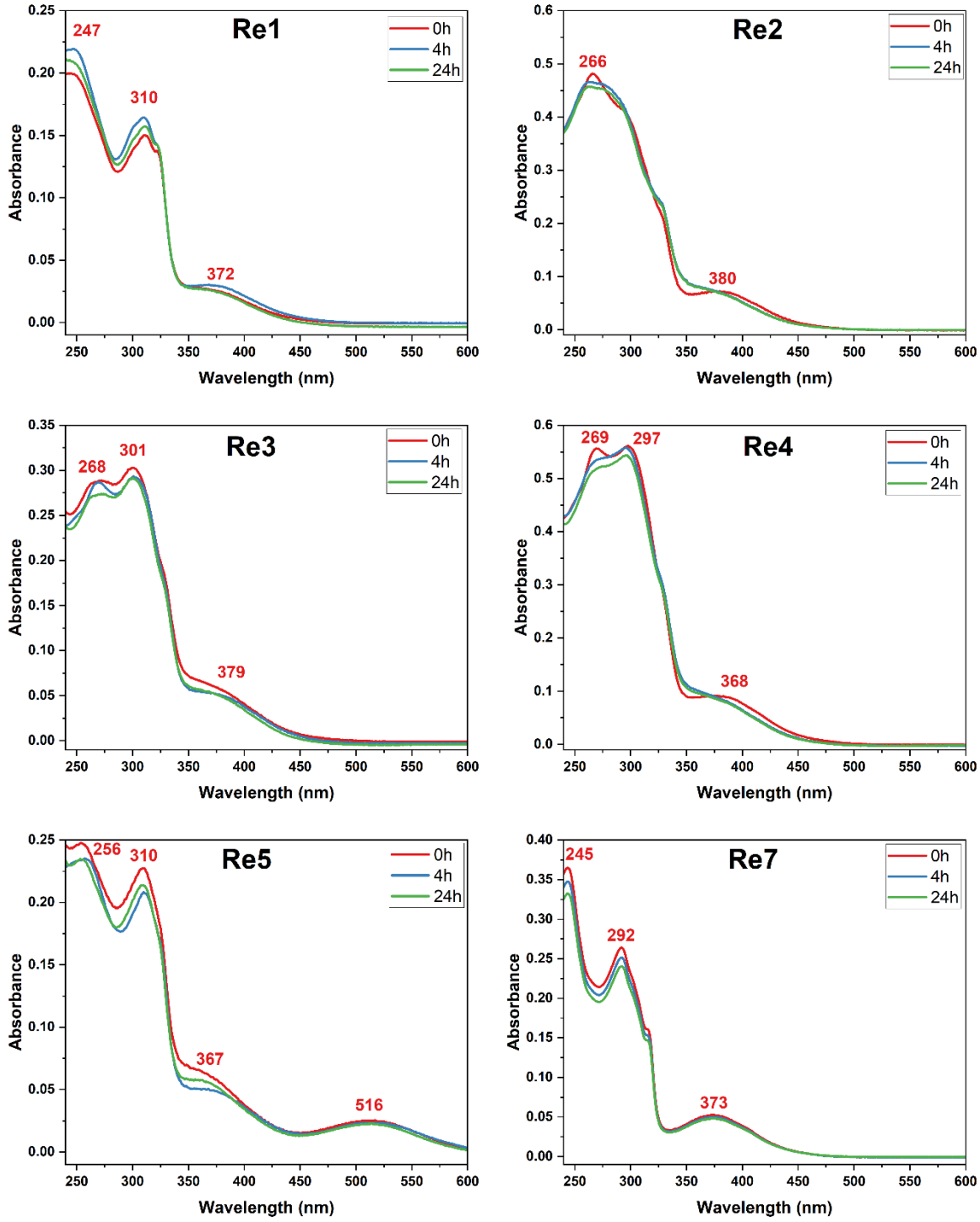
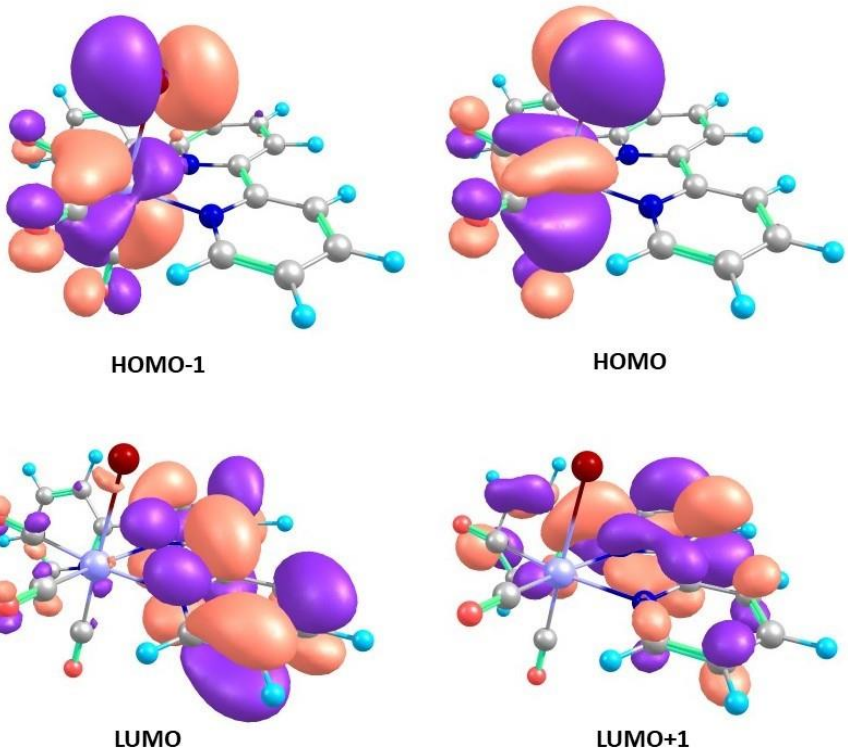


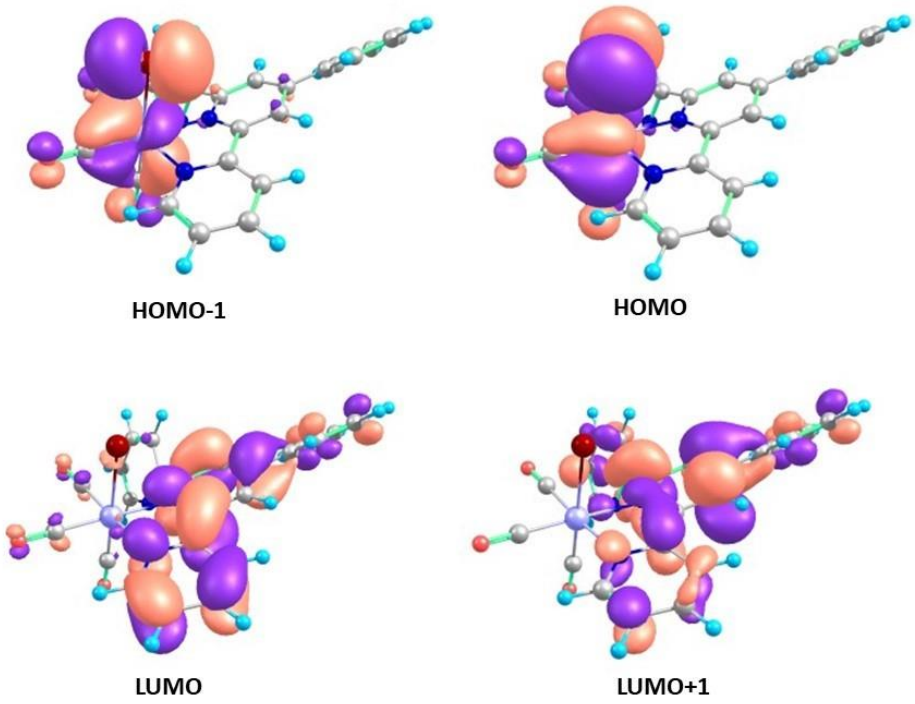
Figure S11.: *UV-Vis spectral changes in Re(I) complexes (0.01 mM in acetonitrile, obtained from diluting a stock solution of 0.3 mM in acetonitrile) shown at certain time intervals 0 h, 4 h and 24 h. The sample was kept at ambient condition.*



Transition Wavelength(nm)	***Oscillator Strength***	***Excitations***	***Nature***
249	*0.180*	*π (tpy) → π*(tpy)* *p_x (Br) → π*(tpy)*	*ILCT*
256	*0.146*	*π (tpy) → π*(tpy)* *p_y (Br) → π*(tpy)*	*ILCT*
303	*0.393*	*π(tpy) → π*(tpy)* *π_{yz}(Re-Br) → π*(tpy)*	*Combination of MLCT and ILCT*
431	*0.056*	*$5d_{yz}$ (Re), $4p_y$(Br) →π*(tpy)*	*MLCT*

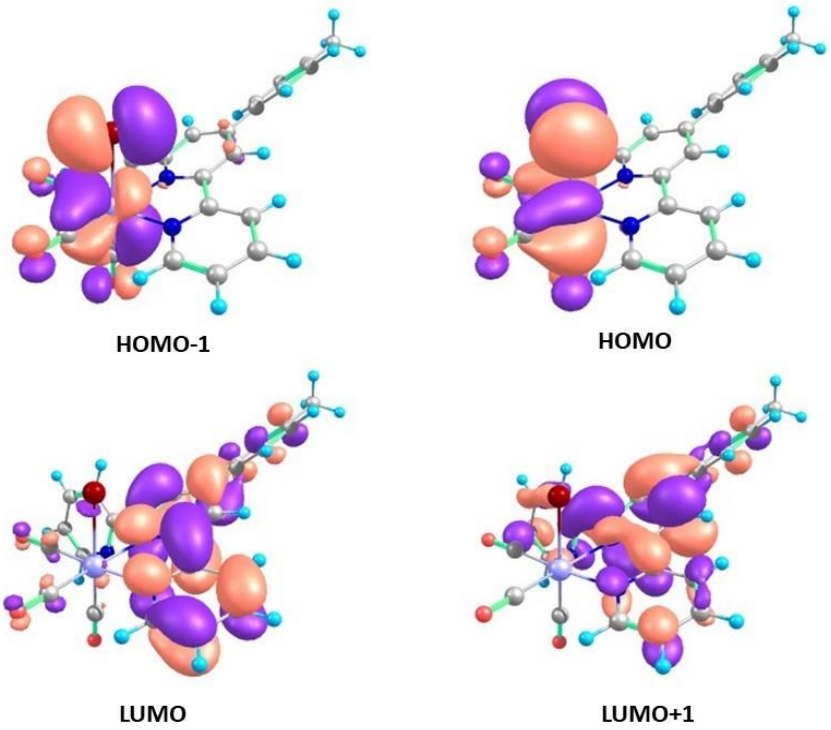
tpy=terpyridine

Figure S12*: Frontier Molecular Orbitals of complex* ***Re1****; with TDDFT data calculated at B3LYP/Def2-TZVP level of theory using acetonitrile as implicit solvent.*



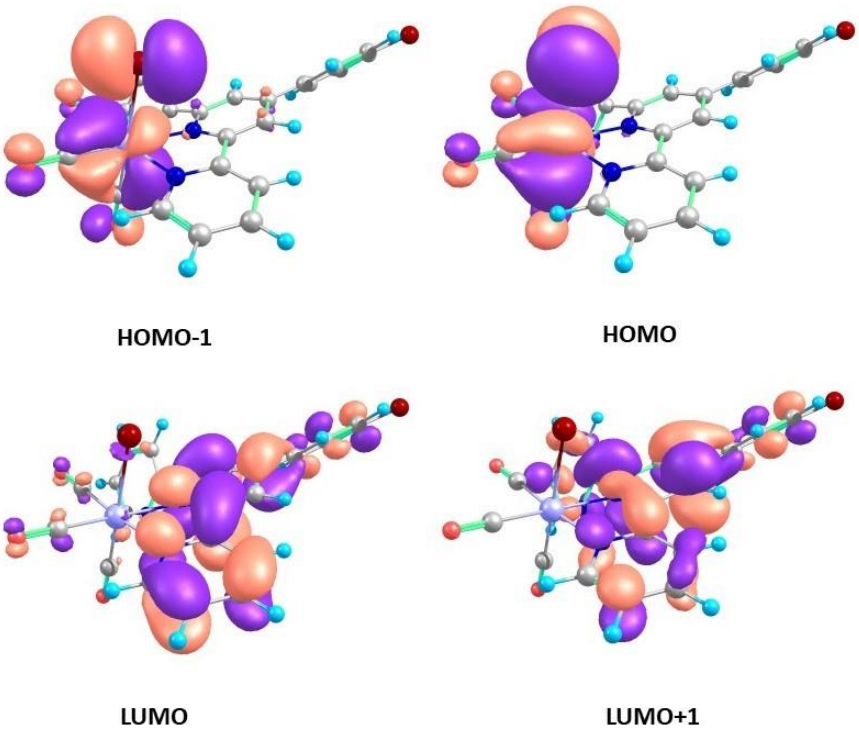
Transition Wavelength(nm)	***Oscillator Strength***	***Excitations***	***Nature***
281	*0.355*	*π (tpy) → π*(tpy)* *p_y (Br) → π*(tpy)*	*ILCT*
309	*0.287*	*π(tpy) → π*(tpy)* *π_{yz}(Re-Br) → π*(tpy)*	*Combination of MLCT and ILCT*
438	*0.088*	*$5d_{yz}$ (Re), $4p_y$(Br) →π*(tpy)*	*MLCT*

Figure S13*: Frontier Molecular Orbitals of complex* ***Re2****; with TDDFT data calculated at B3LYP/Def2-TZVP level of theory using acetonitrile as implicit solvent.*



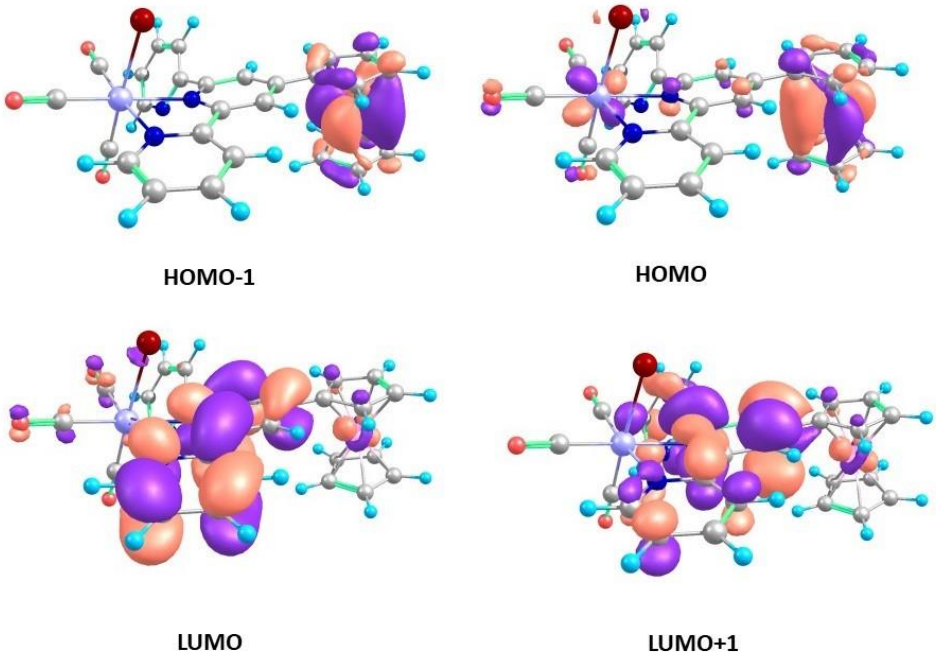
Transition Wavelength(nm)	***Oscillator Strength***	***Excitations***	***Nature***
287	*0.328*	*π (tpy) → π*(tpy)* *p_y (Br) → π*(tpy)*	*ILCT*
309	*0.227*	*π(tpy) → π*(tpy)* *π_{yz}(Re-Br) → π*(tpy)*	*Combination of MLCT and ILCT*
436	*0.098*	*$5d_{yz}$ (Re), $4p_y$(Br) →π*(tpy)*	*MLCT*

***Figure S14**: Frontier Molecular Orbitals of complex **Re3**; with TDDFT data calculated at B3LYP/Def2-TZVP level of theory using acetonitrile as implicit solvent.*



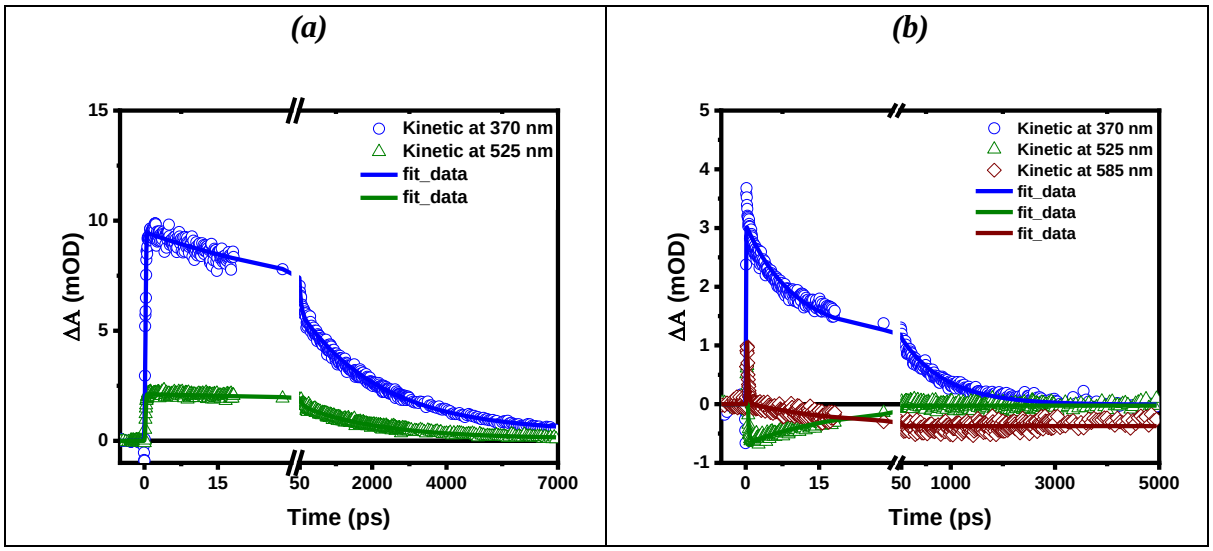
Transition Wavelength(nm)	***Oscillator Strength***	***Excitations***	***Nature***
285	*0.437*	*π (tpy) → π*(tpy)* *p_y (Br) → π*(tpy)*	*ILCT*
310	*0.211*	*π(tpy) → π*(tpy)* *π_{yz}(Re-Br) → π*(tpy)*	*Combination of MLCT and ILCT*
441	*0.095*	*$5d_{yz}$ (Re), $4p_y$(Br) →π*(tpy)*	*MLCT*

Figure S15*: Frontier Molecular Orbitals of complex* ***Re4****; with TDDFT data calculated at B3LYP/Def2-TZVP level of theory using acetonitrile as implicit solvent.*



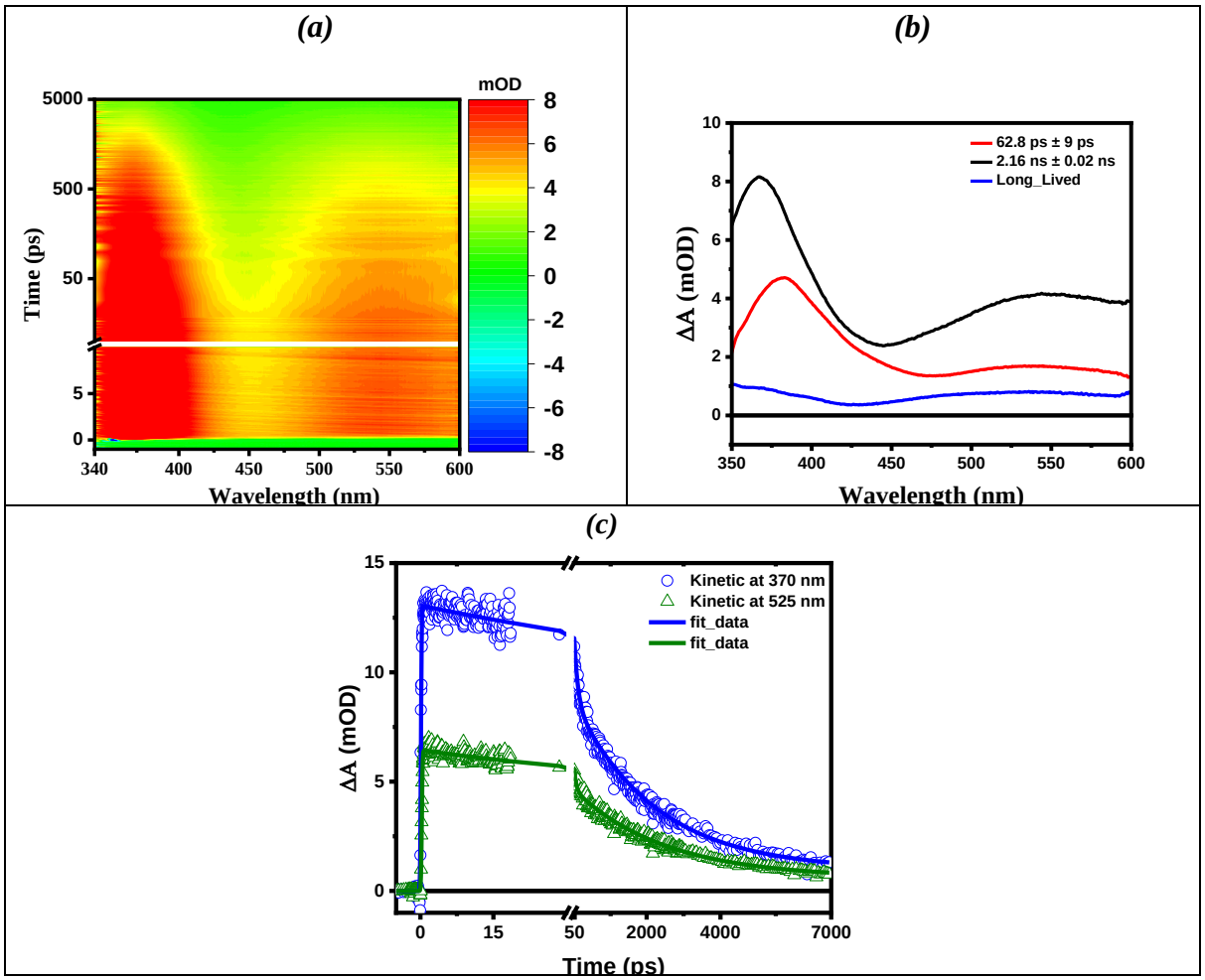
Transition Wavelength(nm)	***Oscillator Strength***	***Excitations***	***Nature***
282	*0.260*	*π (tpy) → π*(tpy)* *p_y (Br) → π*(tpy)*	*ILCT*
309	*0.197*	*π(tpy) → π*(tpy)* *π_{yz}(Re-Br) → π*(tpy)*	*Combination of MLCT and ILCT*
438	*0.098*	*$3d_{xy}$ (Fe) →π*(tpy)* *$5d_{yz}$ (Re), $4p_y$(Br) →π*(tpy)*	*MLCT*
516	*0.008*	*$3d_{x2-y2}$ (Fe), → $3d_{xz}$ (Fe)* *$3d_{z2}$ (Fe)→ $3d_{yz}$ (Fe)*	*d-d transition*
602	*0.013*	*$3d_{x2-y2}$ (Fe) → $3d_{xz}$ (Fe)* *$3d_{xy}$ (Fe) → $3d_{yz}$ (Fe)*	*d-d transition*

Figure S16*: Frontier Molecular Orbitals of complex* ***Re5****; with TDDFT data calculated at B3LYP/Def2-TZVP level of theory using acetonitrile as implicit solvent.*



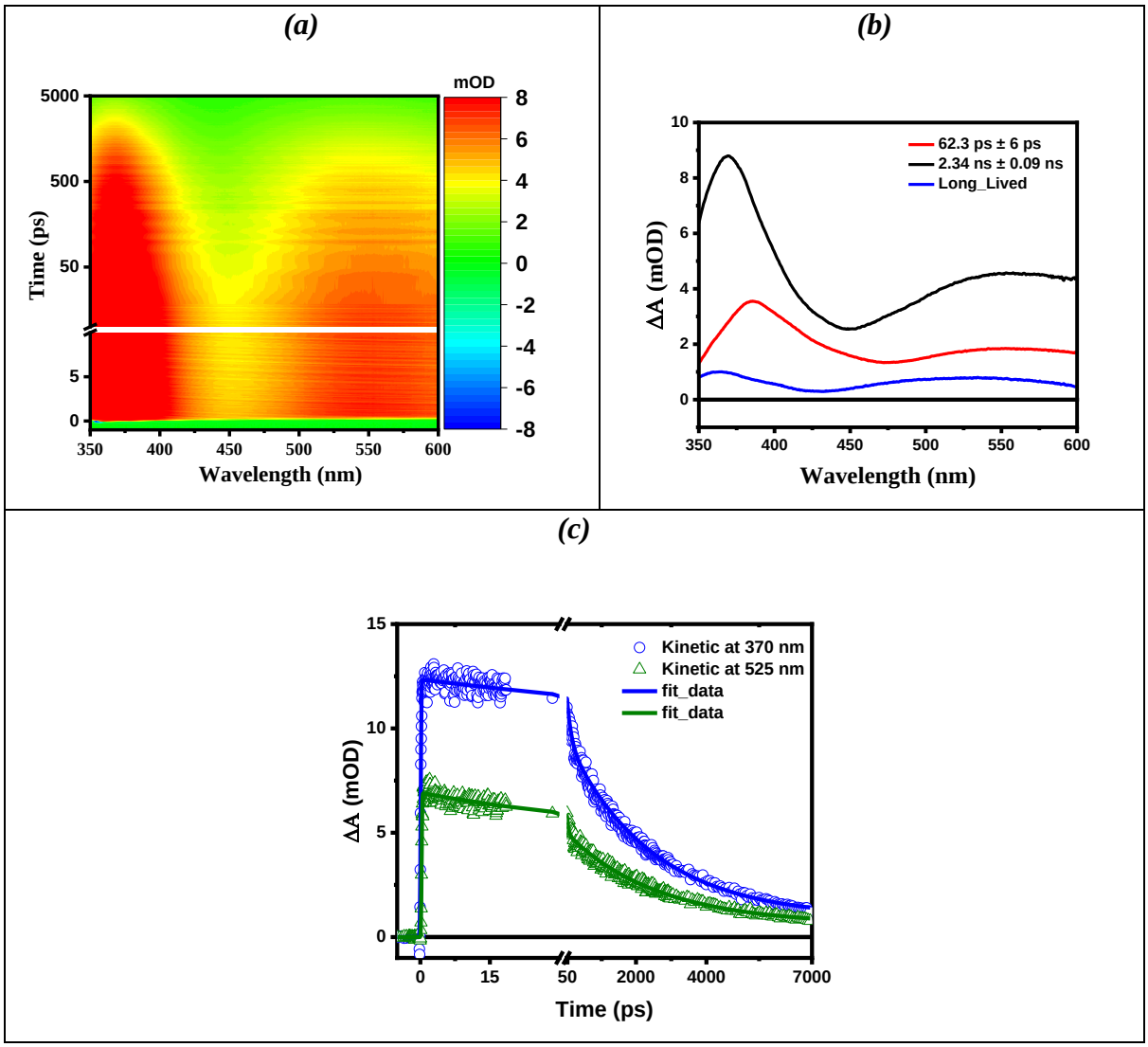
Compound	*Wavelength (nm)*	*τ_1 (ps)*	*τ_2 (ps)*	*Standard Deviation*
Re1	*370*	*46 ± 5* *(0.0034 ± 0.0001)* *0.38*	*2212 ± 149* *(0.0055 ± 0.0001)* *0.62*	*0.0002*
	525	*97 ± 25* *(0.0005 ± 0.00001)* *0.25*	*2212 ± 164* *(0.0015 ± 0.00003)* *0.75*	*0.0001*
Re5	*370 nm*	*10 ± 0.7* *0.0018 ± 0.00001* *0.60*	*855.0* *0.0012 ± 0.0001* *0.40*	*0.0001*
	525 nm		*19 ± 3* *-0.0006 ± 0.00003*	*0.00001*
	585 nm	-	*18 ± 3* *0.0003 ± 0.00002*	*0.00001*

***Figure S17**: Kinetic traces at 370 nm and 525 nm for **Re1 (a)** and 370 nm, 525nm, and 585 nm for **Re5 (b)**, with the kinetic fitting parameters in the table.*



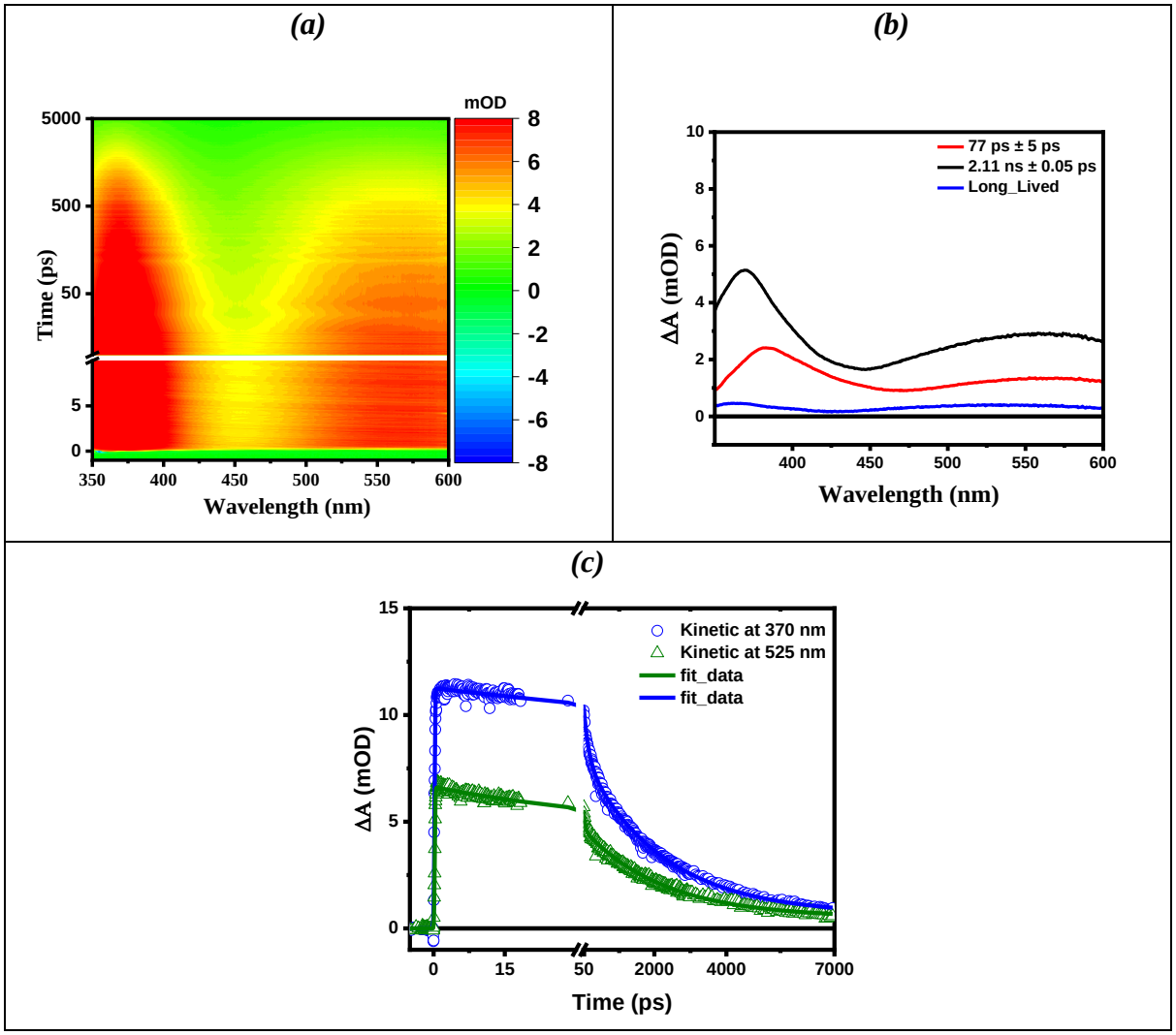
Compound	*Wavelength (nm)*	*τ_1 (ps)*	*τ_2 (ps)*	*Standard Deviation*
Re2	*370*	*100 ± 18* *(0.0042 ± 0.0002)* *0.37*	*2213 ± 210* *(0.007 ± 0.0002)* *0.63*	*0.0003*
	525	*58 ± 11* *(0.0020 ± 0.0001)* *0.29*	*2466 ± 200* *(0.0040 ± 0.0001)* *0.71*	*0.0002*

Figure S18: ***(a)*** *2D plots of* ***Re2****,* ***(b)*** *global lifetime analysis,* ***(c)*** *Kinetic traces at 370 nm and 525 nm; with the kinetic fitting parameters in the table.*



Compound	*Wavelength (nm)*	*τ_1 (ps)*	*τ_2 (ps)*	*Standard Deviation*
Re3	*370*	*118 ± 25* *(0.0028 ± 0.0002)* *0.19*	*2438 ± 180* *(0.0086 ± 0.0001)* *0.81*	*0.0002*
	525	*46 ± 8* *(0.0018 ± 0.0001)* *0.29*	*2585 ± 206* *(0.0044 ± 0.0001)* *0.71*	*0.0002*

Figure S19: ***(a)*** *2D plots of* ***Re3****,* ***(b)*** *global lifetime analysis,* ***(c)*** *Kinetic traces at 370 nm and 525 nm; with the kinetic fitting parameters in the table.*



Compound	*Wavelength (nm)*	*τ_1 (ps)*	*τ_2 (ps)*	*Standard Deviation*
Re4	*370*	*141 ± 19* *(0.0021 ± 0.0001)* *0.30*	*2210 ± 130* *(0.0049 ± 0.0001)* *0.70*	*0.0001*
	525	*45 ± 4* *(0.0012 ± 0.0001)* *0.30*	*2226 ± 95* *(0.0028 ± 0.0001)* *0.70*	*0.0001*

Figure S20: ***(a)*** *2D plots of* ***Re4****,* ***(b)*** *global lifetime analysis,* ***(c)*** *Kinetic traces at 370 nm and 525 nm; with the kinetic fitting parameters in the table.*

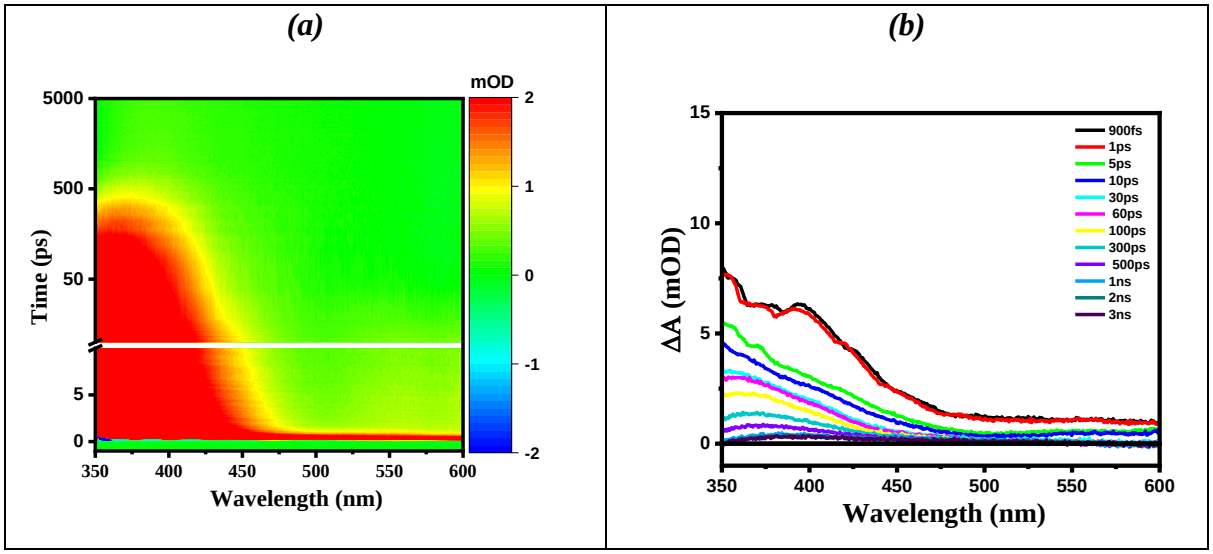


Figure S21: ***(a)*** *2D plots of* ***L5****,* ***(b)*** *transient absorption spectra at different delay times.*

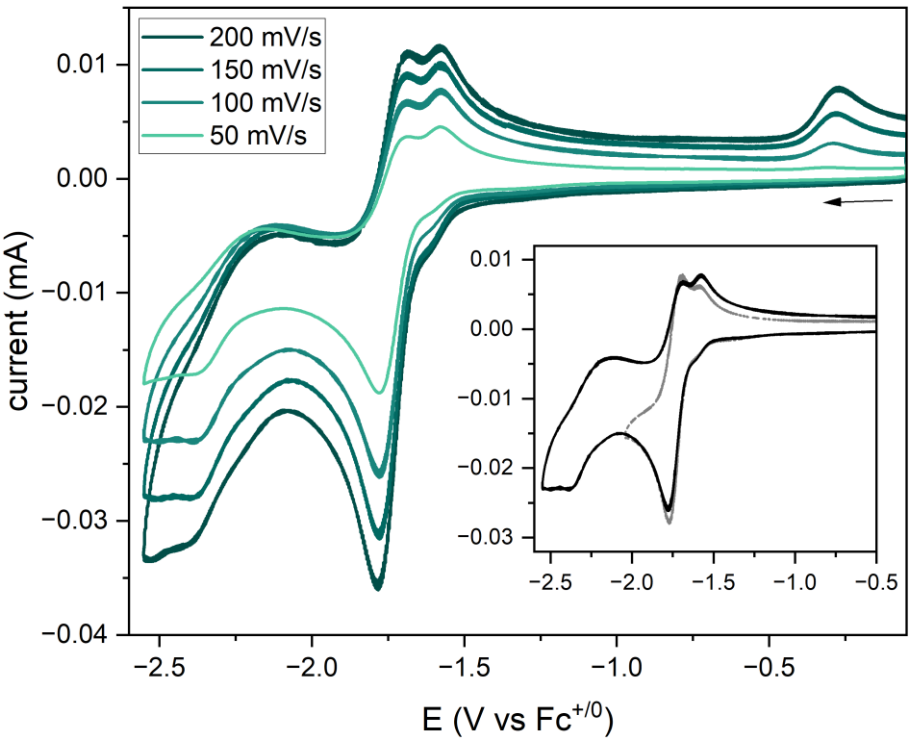


Figure S22: *Scan rate dependent cyclic voltammograms of 1 mM* ***Re1*** *in* N_2 *saturated acetonitrile containing 0.1 M n-*Bu_4NBF_4 *as the supporting electrolyte. The inset figure shows the voltammogram of* ***Re1*** *when the scan is reversed before the second reduction.*

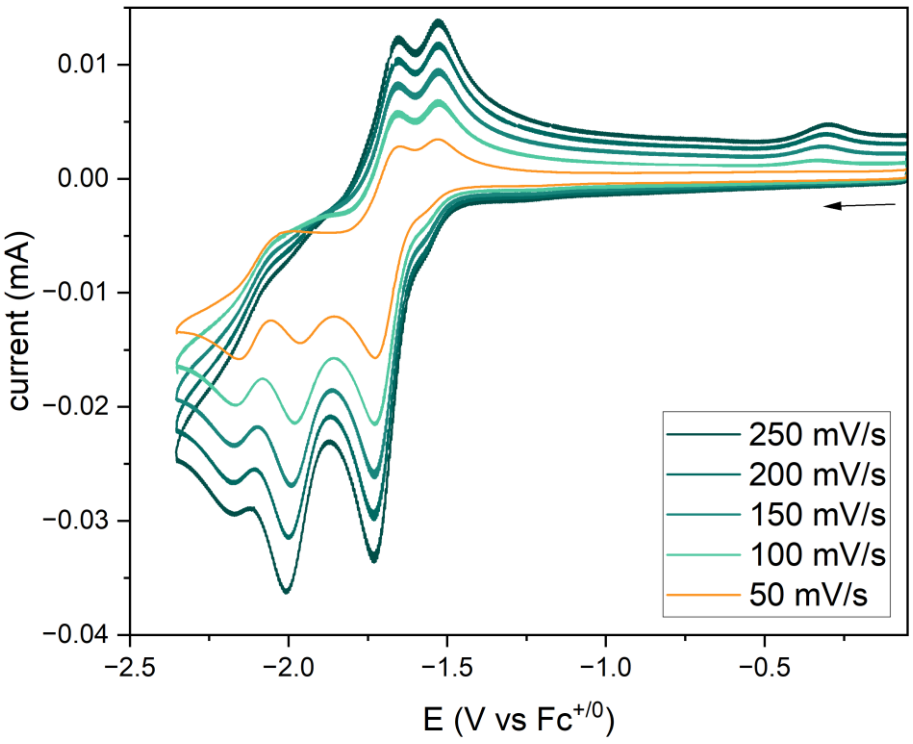


Figure S23: *Scan rate dependent cyclic voltammograms of 1 mM* ***Re2*** *in N_2 saturated acetonitrile containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte.*

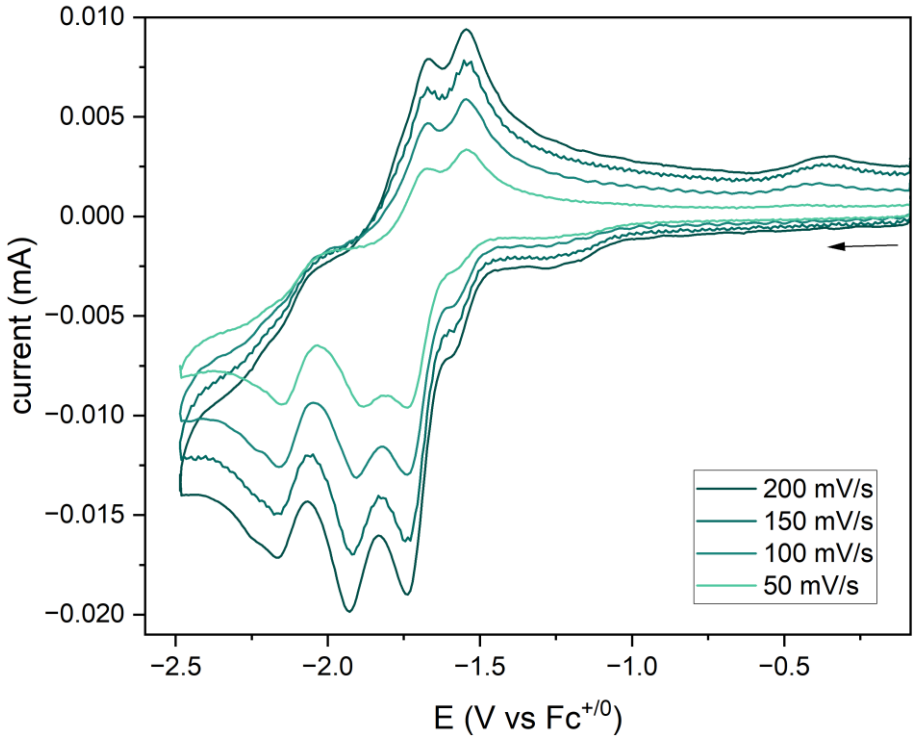


Figure S24: *Scan rate dependent cyclic voltammograms of 0.6 mM* ***Re3*** *in N_2 saturated acetonitrile containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte.*

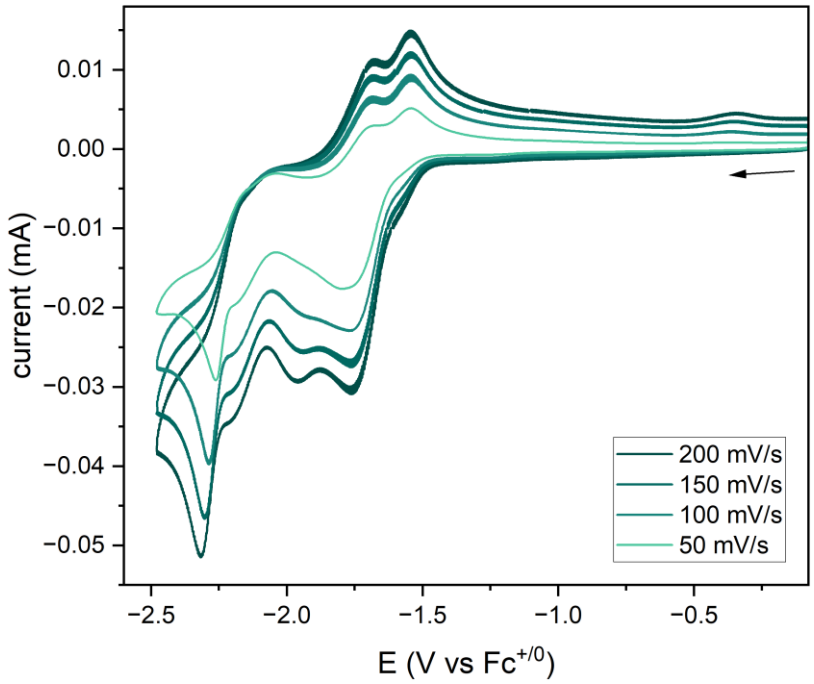


Figure S25: *Scan rate dependent cyclic voltammograms of 1 mM* ***Re4*** *in N_2 saturated acetonitrile containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte.*

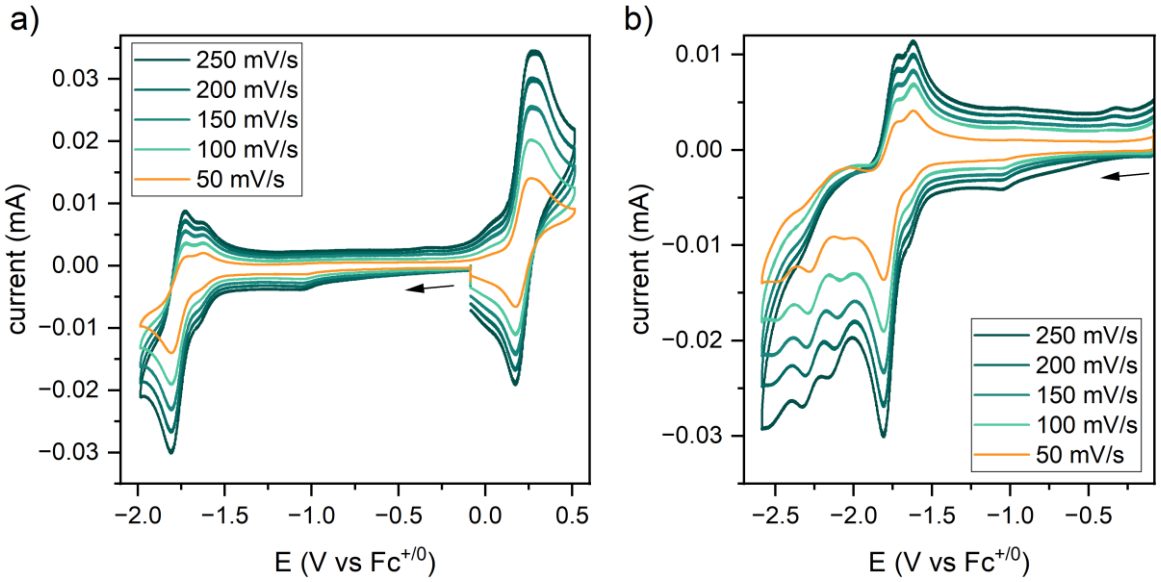


Figure S26: *Scan rate dependent cyclic voltammograms of 1 mM* ***Re5*** *in N_2 saturated acetonitrile containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte. Figure* ***(a)*** *shows oxidative event(s) and the first reduction event. Figure* ***(b)*** *shows the reduction processes occurring before –2.55 V.*

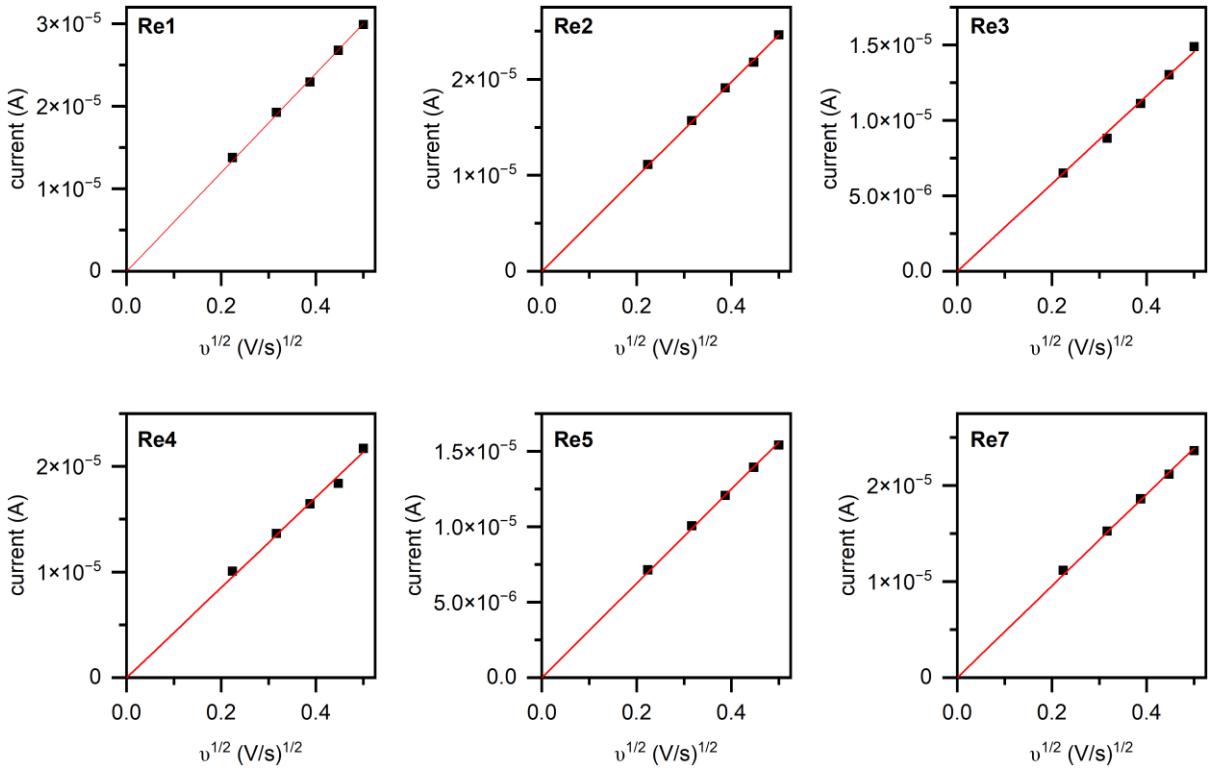


Figure S27: *Determination of diffusion coefficients from scan rate dependent CVs shown in* ***Figure S22-26****. Peak currents for the first reductive step (~ –1.8 V) vs the square root of the scan rate for* ***Re1-5*** *and* ***Re7****.*

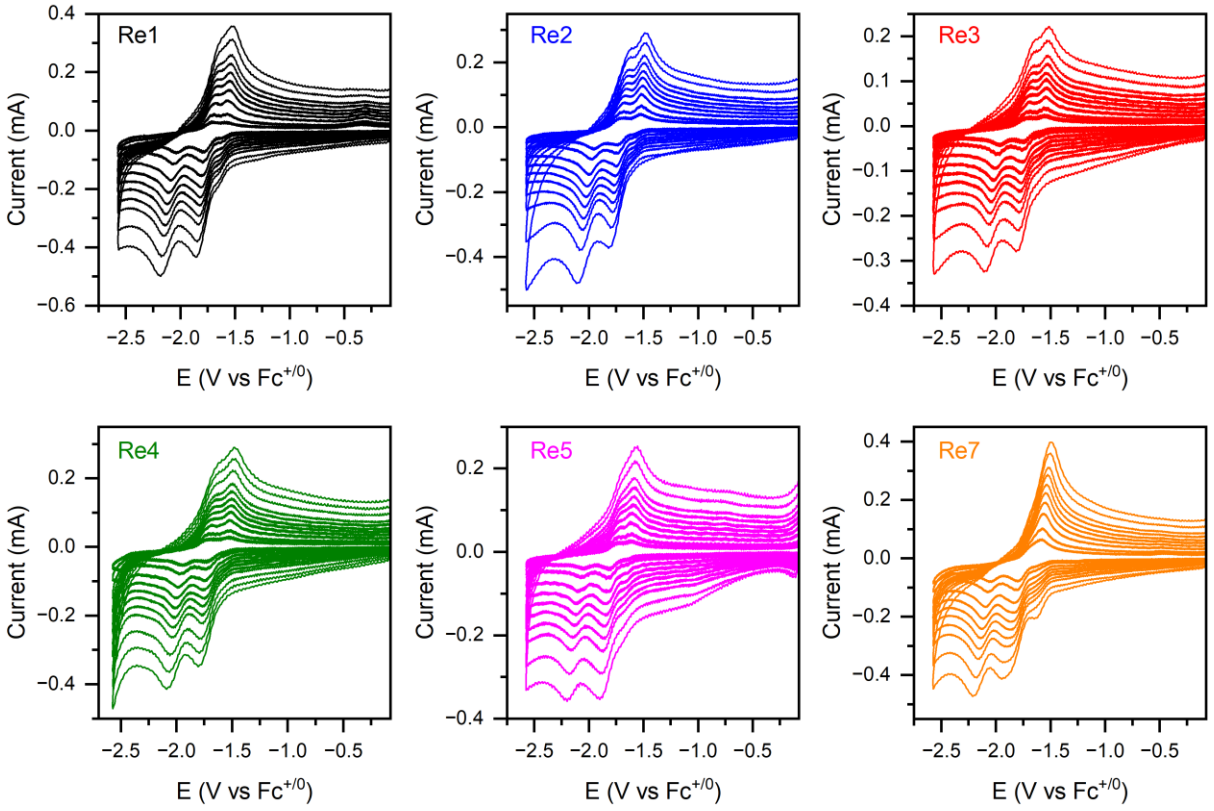


Figure S28: *Scan rate dependent cyclic voltammograms of Re1-5 and Re7 at fast scan rates (25, 20, 15, 12.5, 10, 8, 6, 4, 2, 1 V s^{-1}) in N_2 saturated acetonitrile containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte.*

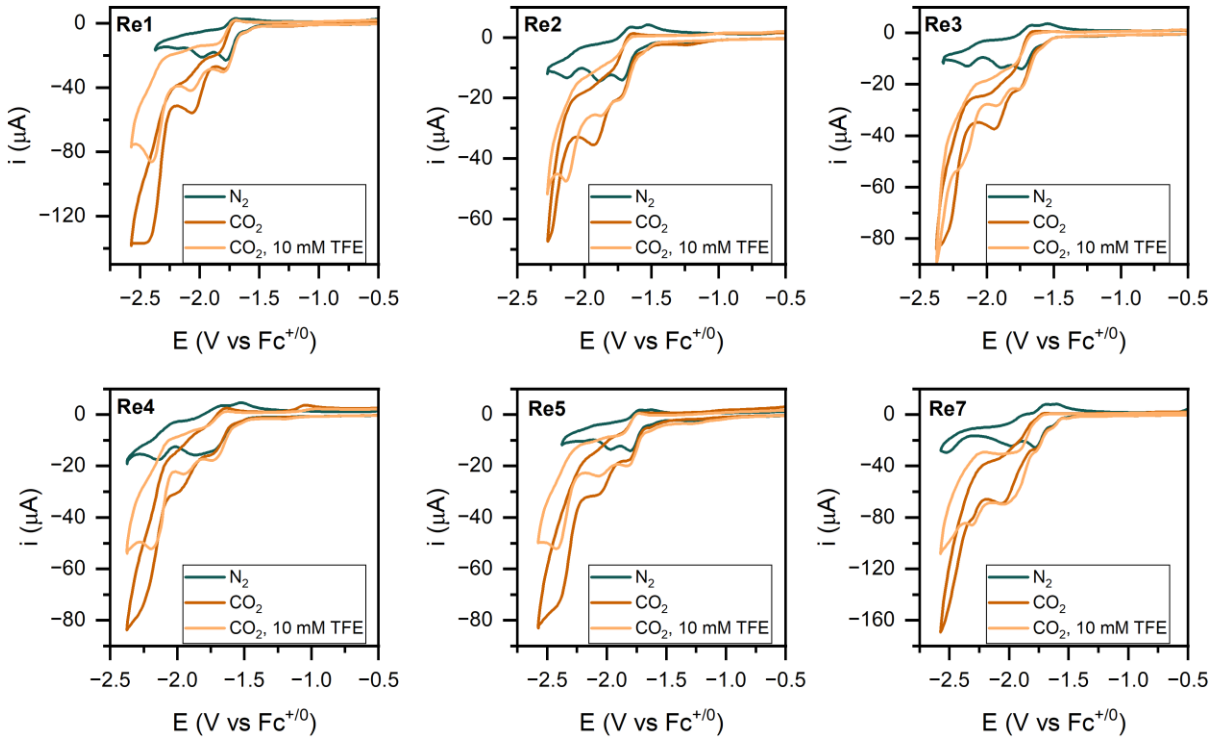


Figure S29: *Catalytic cyclic voltammograms of **Re1-5** and **Re7** recorded in acetonitrile under N_2 and CO_2 in the absence or presence of 10 mM trifluoroethanol (TFE). Voltammograms were recorded at 100 mV s^{-1} using 0.1 M n-Bu_4NBF_4 as the supporting electrolyte.*

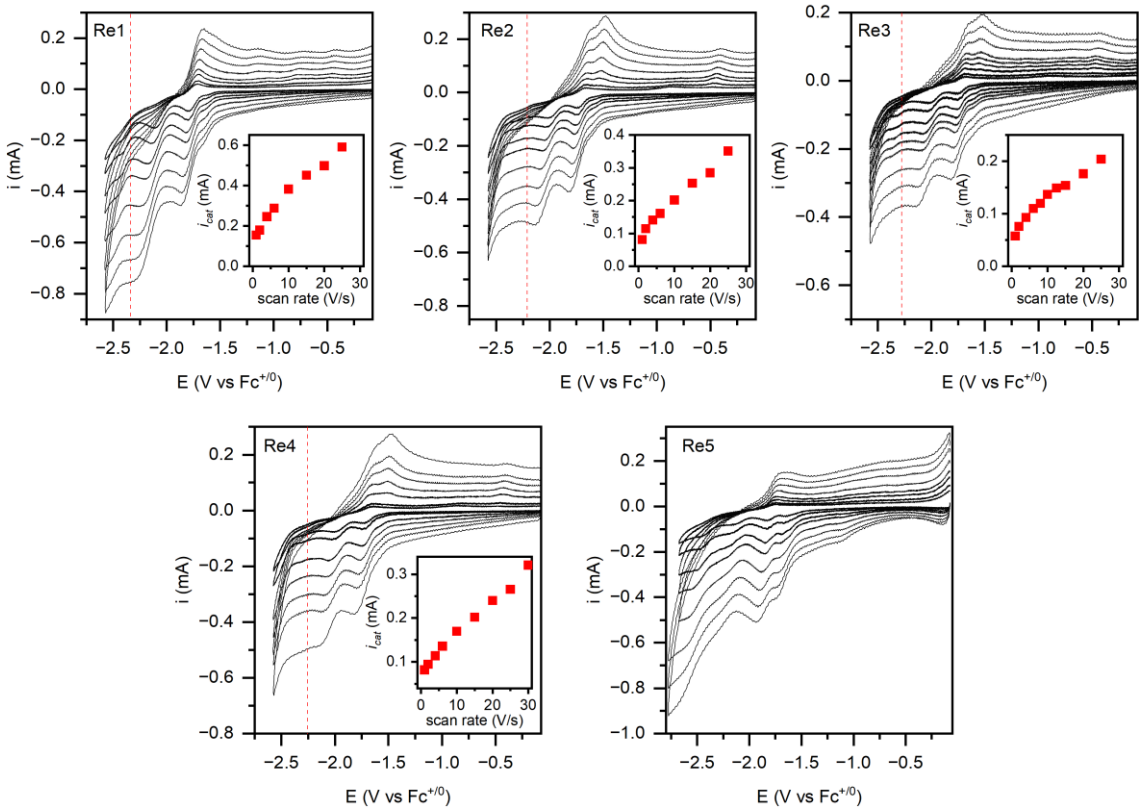


Figure S30: *Cyclic voltammograms of* ***Re1-5*** *at fast scan rates (25, 20, 15, 12.5, 10, 8, 6, 4, 2, 1 V s^{-1}) in CO_2 saturated acetonitrile containing 0.1 M n-Bu_4NBF_4 as the supporting electrolyte. The inset figures present the scan rate dependence of the plateau catalytic current (i_{cat}). The corresponding potential is shown by the red dashed line.*

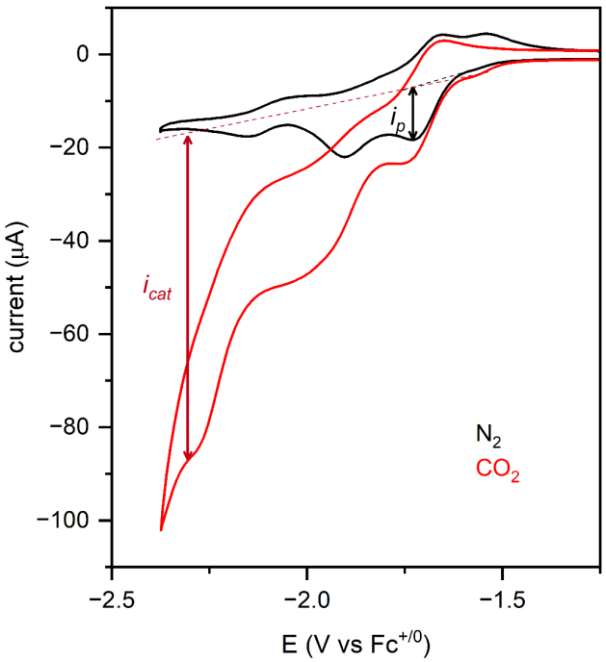


Figure S31: *Representative cyclic voltammograms of* ***Re2*** *(~1 mM) under N_2 and CO_2 saturated acetonitrile to demonstrate the determination of i_{cat} and i_p. Conditions: supporting electrolyte 0.1 M n-Bu_4NBF_4, scan rate 100 mV s^{-1}.*

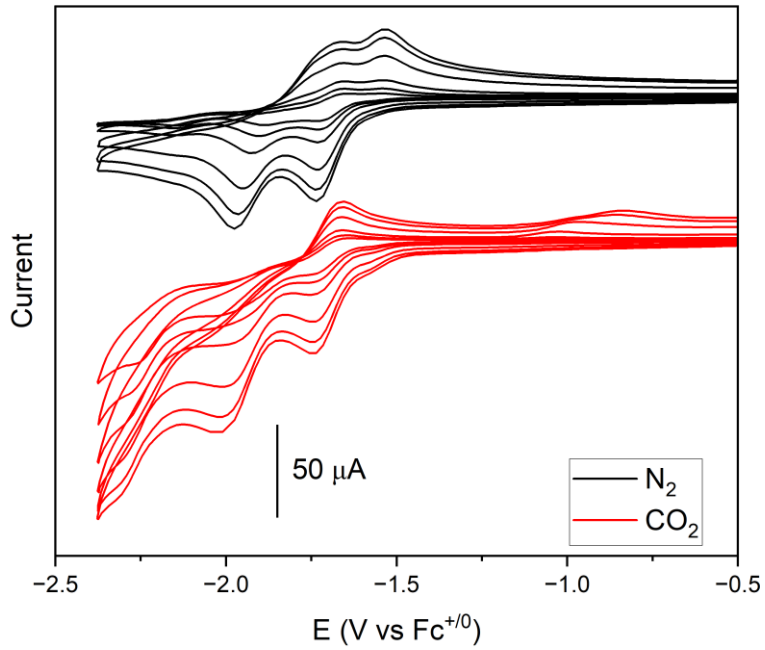


Figure S32: *Cyclic voltammograms of* ***Re2*** *(~1 mM) under N_2 and CO_2 saturated acetonitrile at different scan rates (1, 0.8, 0.5, 0.2, 0.1, 0.05 V s^{-1}). Conditions: supporting electrolyte 0.1 M n-Bu_4NBF_4.*

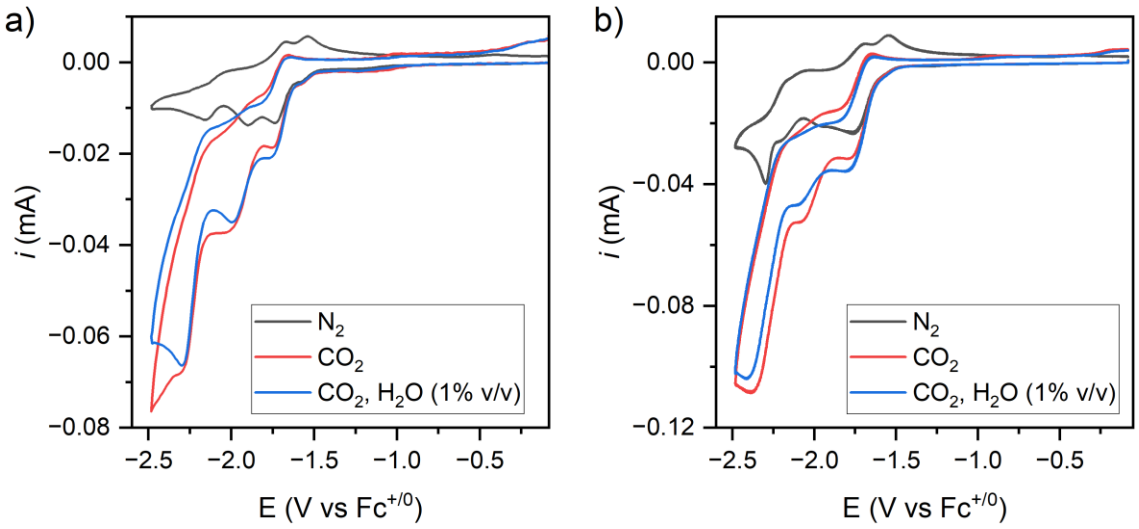


Figure S33: *Cyclic voltammograms of (a)* ***Re3*** *(0.6 mM) and (b)* ***Re4*** *(1 mM) under N_2 and CO_2 in neat acetonitrile and in acetonitrile/water mixture (99:1 v/v), demonstrating minimal effect of water on electrocatalysis. Condition: 0.1 M n-Bu_4NBF_4 supporting electrolyte, 0.1 V s^{-1} scan rate.*

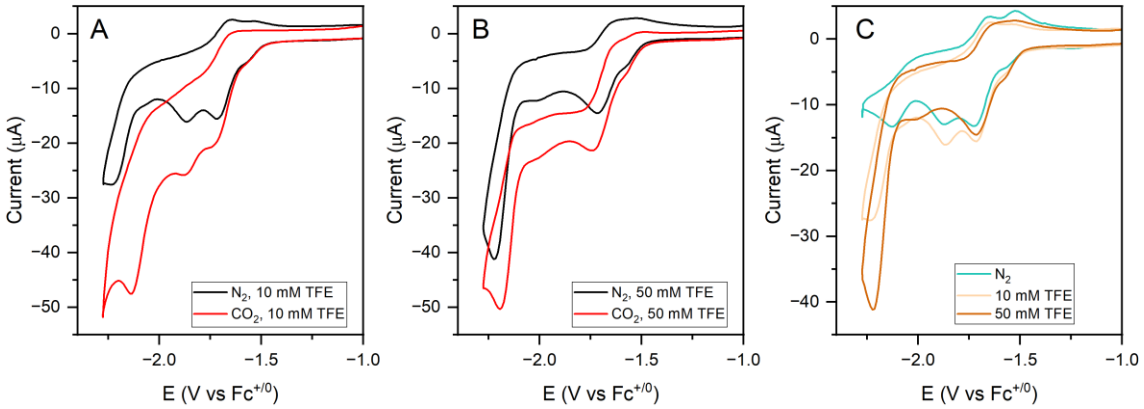


Figure S34: *Cyclic voltammograms of* ***Re2*** *under N_2 and CO_2 in the presence varying concentration of TFE. Figure A and B show the voltametric response in the presence of 10 mM and 50 mM TFE, respectively, under N_2 and CO_2. Figure C shows the difference in response under N_2 without TFE and in the presence of TFE (10 and 50 mM). Condition: 0.1 M n-Bu_4NBF_4 supporting electrolyte, 0.1 V s^{-1} scan rate.*

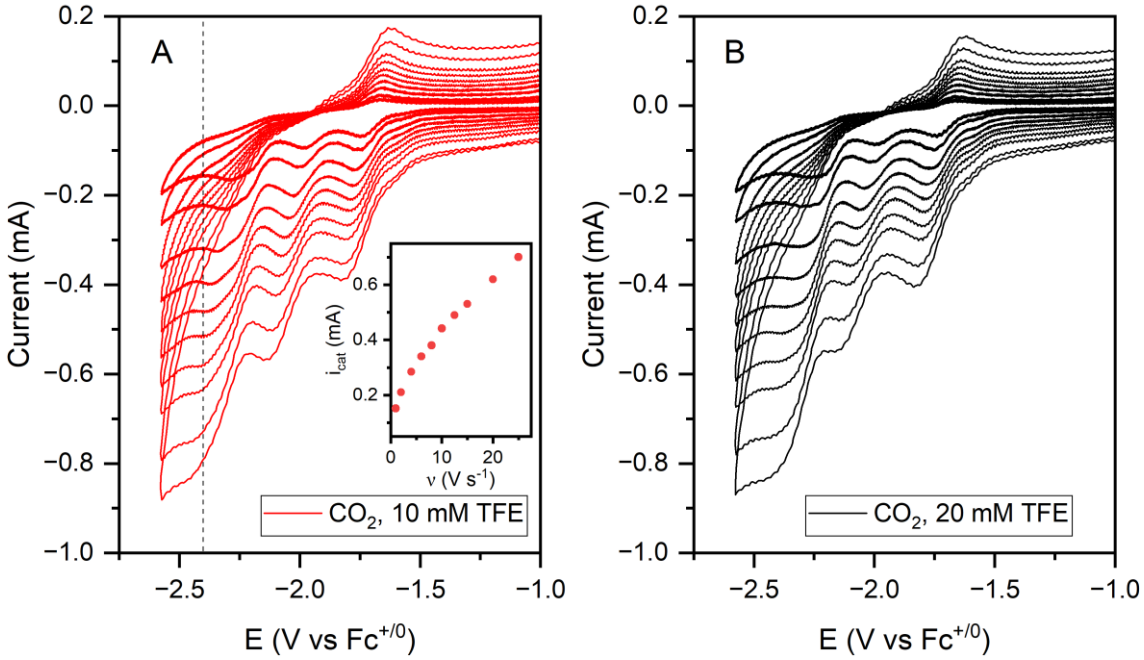


Figure S35*: Cyclic voltammograms of* ***Re2*** *(~0.6 mM) at fast scan rates (25, 20, 15, 12.5, 10, 8, 6, 4, 2, 1 V s^{-1}) in CO_2 saturated acetonitrile containing (A) 10 mM TFE and (B) 20 mM TFE. 0.1 M n-Bu_4NBF_4 was used as the supporting electrolyte. Inset figure (A) shows the dependence of i_{cat} on scan rate.*

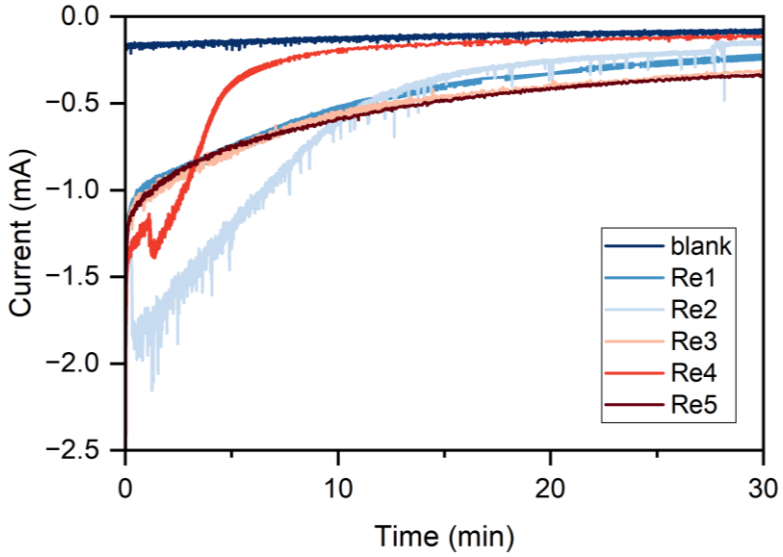


Figure S36: *Current versus time plots for controlled potential electrolyses of* ***Re1-5*** *in CO_2 saturated 0.5% (v/v) water/acetonitrile mixture –2.3 V vs $Fc^{+/0}$. Blank trace shows current in the absence of any catalyst. Electrolyses were performed using a glassy carbon plate working electrode (A ~ 2 cm^2) and 0.1 M n-Bu_4NBF_4 electrolyte.*

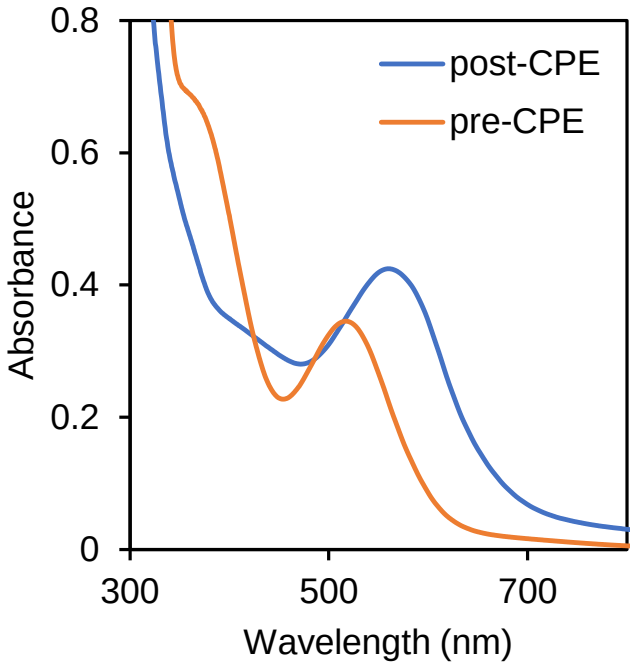


Figure S37: *UV-vis spectra of* ***Re5*** *before and after 1 h electrolysis in CO_2 saturated 0.5% water/acetonitrile mixture.*

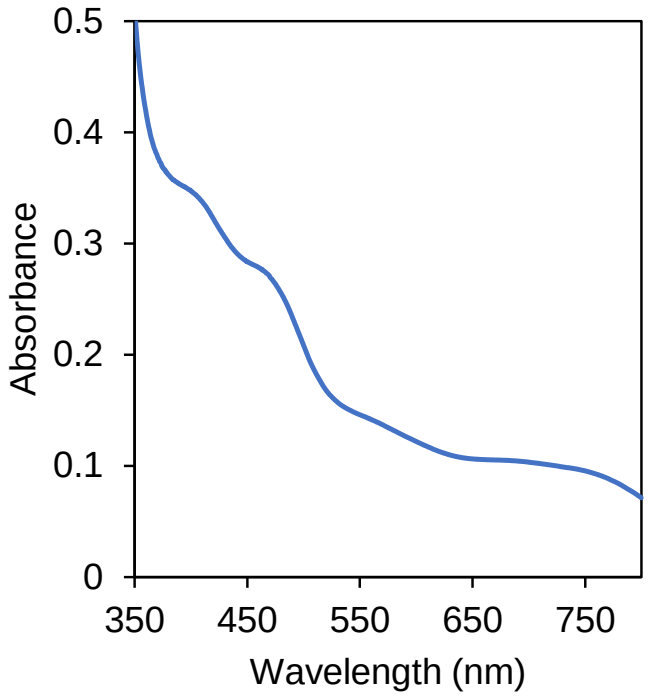


Figure S38: *UV-vis spectrum of* ***Re1*** *after 1 h electrolysis in CO_2 saturated 0.5% water/acetonitrile mixture. The pre-CPE concentration of* ***Re1*** *in the electrolyte (0.1 M Bu_4NBF_4) was 0.25 mM.*

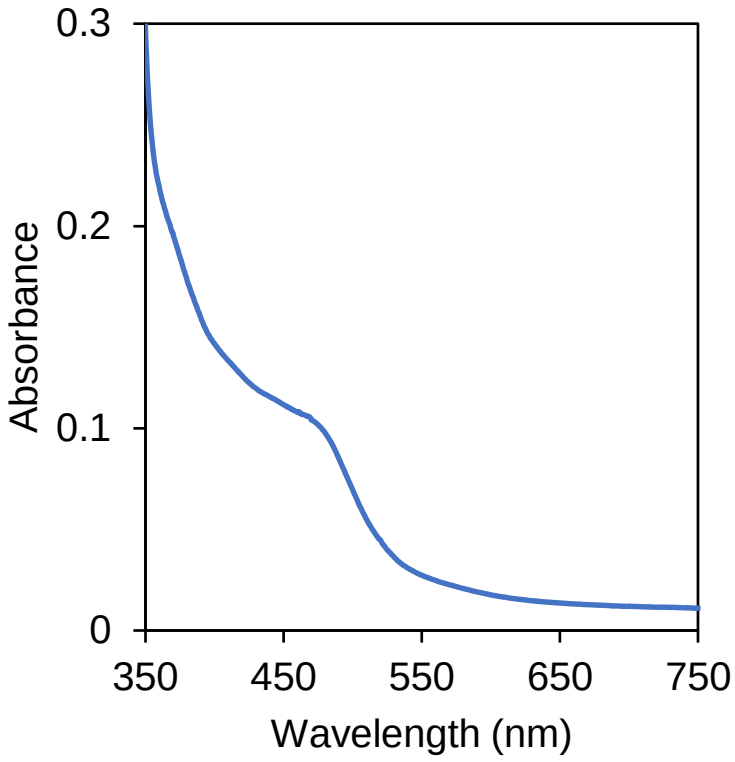


Figure S39: *UV-vis spectrum of* ***Re2*** *after 1 h electrolysis in CO_2 saturated 0.5% water/acetonitrile mixture. The pre-CPE concentration of* ***Re2*** *in the electrolyte (0.1 M Bu_4NBF_4) was 0.25 mM.*

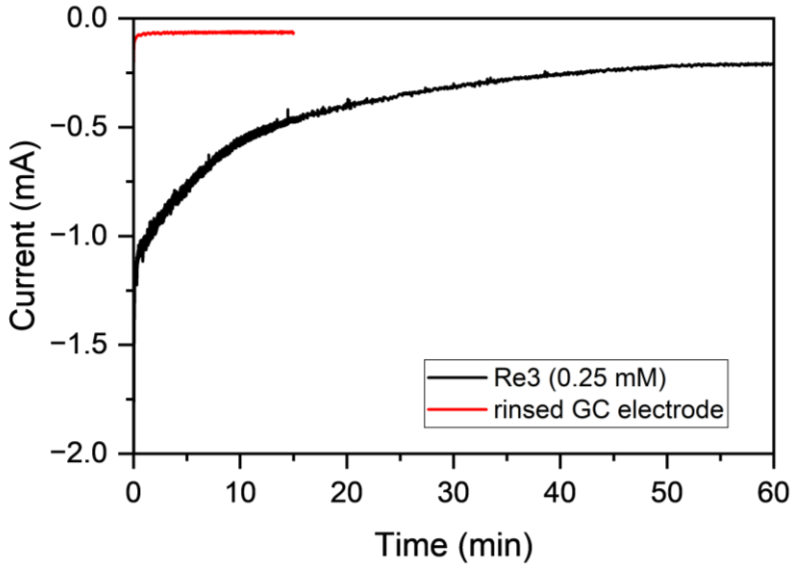


Figure S40: *Current vs. time plot for a 'Rinse test' to exclude catalytically active deposit formation on electrode. Black trace shows the current vs. time plot for electrolysis of* ***Re3****. After electrolysis, the glassy carbon working electrode was removed, rinsed with acetonitrile and reused for a 15-min controlled potential electrolysis without any catalyst (red trace). A very low current demonstrates that the catalysis is homogeneous in nature.*

References:

1 S. A. Moya, R. Pastene, H. Le Bozec, P. J. Baricelli, A. J. Pardey and J. Gimeno, Inorganica Chim. Acta, 2001, ***312****, 7–14.*

2 R. Kia and F. Safari, Inorganica Chim. Acta, 2016, ***453****, 357–368.*

3 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, and K, I. Goldberg, Organomet., 2010, ***29****, 2176–2179.*

Cartesian Coordinates

1. ***L1***

   E = -742.316928619992 au

   0 imaginary frequencies

N	*2.189845000000*	*0.125053000000*	*-0.363231000000*
N	*-0.289042000000*	*1.444332000000*	*-0.391820000000*
N	*-2.662767000000*	*0.303166000000*	*-1.311087000000*
C	*3.320650000000*	*-0.508778000000*	*-0.673542000000*
H	*3.339100000000*	*-1.577767000000*	*-0.485821000000*
C	*4.436100000000*	*0.127146000000*	*-1.206461000000*
H	*5.327723000000*	*-0.438846000000*	*-1.442853000000*
C	*4.365858000000*	*1.496480000000*	*-1.424177000000*
H	*5.205761000000*	*2.034981000000*	*-1.845481000000*
C	*3.195660000000*	*2.168464000000*	*-1.099796000000*
H	*3.111206000000*	*3.232424000000*	*-1.274674000000*
C	*2.121253000000*	*1.448379000000*	*-0.569336000000*
C	*0.842396000000*	*2.133532000000*	*-0.215100000000*
C	*-1.460564000000*	*2.011473000000*	*-0.086846000000*
C	*-2.691737000000*	*1.196507000000*	*-0.311804000000*
C	*-3.749520000000*	*-0.434006000000*	*-1.538451000000*
C	*-1.542377000000*	*3.314542000000*	*0.413506000000*
C	*0.843401000000*	*3.439254000000*	*0.283993000000*
C	*-0.370200000000*	*4.031068000000*	*0.599699000000*
H	*-0.402237000000*	*5.042010000000*	*0.986548000000*
H	*1.771168000000*	*3.972966000000*	*0.437149000000*
H	*-2.500204000000*	*3.763970000000*	*0.635444000000*
C	*-4.916678000000*	*-0.332386000000*	*-0.790056000000*
C	*-3.822914000000*	*1.363219000000*	*0.493175000000*
C	*-4.947449000000*	*0.587388000000*	*0.249413000000*
H	*-3.687531000000*	*-1.140231000000*	*-2.360537000000*
H	*-5.769651000000*	*-0.957973000000*	*-1.018603000000*
H	*-3.818822000000*	*2.074727000000*	*1.307399000000*
H	*-5.830346000000*	*0.697184000000*	*0.866908000000*

2. ***L2***

   E = -973.313988510752 au

   0 imaginary frequencies

N	*2.136872000000*	*0.434943000000*	*-0.514697000000*
N	*-0.378926000000*	*1.607386000000*	*-0.162857000000*
N	*-2.828116000000*	*0.530311000000*	*-1.013177000000*
C	*3.260568000000*	*-0.103674000000*	*-0.987389000000*
H	*3.335452000000*	*-1.185132000000*	*-0.931150000000*
C	*4.301787000000*	*0.642748000000*	*-1.526760000000*
H	*5.191717000000*	*0.151848000000*	*-1.898464000000*
C	*4.159537000000*	*2.022905000000*	*-1.574284000000*
H	*4.938840000000*	*2.646683000000*	*-1.994360000000*

C	*2.995855000000*	*2.595516000000*	*-1.080371000000*
H	*2.856391000000*	*3.667153000000*	*-1.121917000000*
C	*1.999877000000*	*1.767958000000*	*-0.553507000000*
C	*0.729956000000*	*2.338519000000*	*-0.012434000000*
C	*-1.533060000000*	*2.086377000000*	*0.310967000000*
C	*-2.750084000000*	*1.242073000000*	*0.120177000000*
C	*-3.905676000000*	*-0.227922000000*	*-1.215232000000*
C	*-1.621296000000*	*3.321298000000*	*0.953610000000*
C	*0.722572000000*	*3.581894000000*	*0.620016000000*
C	*-0.474269000000*	*4.099213000000*	*1.118035000000*
H	*1.640255000000*	*4.143221000000*	*0.722228000000*
H	*-2.575032000000*	*3.671857000000*	*1.321655000000*
C	*-4.954019000000*	*-0.328665000000*	*-0.307862000000*
C	*-3.757135000000*	*1.199802000000*	*1.088507000000*
C	*-4.871181000000*	*0.401388000000*	*0.870126000000*
H	*-3.935427000000*	*-0.781701000000*	*-2.148308000000*
H	*-5.804515000000*	*-0.962395000000*	*-0.522690000000*
H	*-3.662825000000*	*1.766620000000*	*2.004792000000*
H	*-5.658206000000*	*0.347848000000*	*1.612201000000*
C	*-0.524423000000*	*5.420253000000*	*1.790486000000*
C	*-1.635094000000*	*6.259970000000*	*1.637119000000*
C	*0.537061000000*	*5.858142000000*	*2.592714000000*
C	*-1.680338000000*	*7.500188000000*	*2.262680000000*
C	*0.487207000000*	*7.095591000000*	*3.223729000000*
C	*-0.620480000000*	*7.922300000000*	*3.059875000000*
H	*-2.460566000000*	*5.951354000000*	*1.008041000000*
H	*1.399056000000*	*5.219759000000*	*2.740543000000*
H	*-2.543799000000*	*8.139278000000*	*2.123044000000*
H	*1.313942000000*	*7.412194000000*	*3.848128000000*
H	*-0.657231000000*	*8.887969000000*	*3.549167000000*

3. *L3*

E = -1012.617136712920 au

0 imaginary frequencies

N	*2.144839000000*	*0.444352000000*	*-0.478228000000*
N	*-0.382655000000*	*1.606841000000*	*-0.162536000000*
N	*-2.825170000000*	*0.511465000000*	*-1.008025000000*
C	*3.273706000000*	*-0.095136000000*	*-0.937743000000*
H	*3.357622000000*	*-1.174449000000*	*-0.857531000000*
C	*4.309330000000*	*0.647899000000*	*-1.492312000000*
H	*5.203887000000*	*0.156474000000*	*-1.852075000000*
C	*4.155472000000*	*2.025525000000*	*-1.570268000000*
H	*4.930233000000*	*2.646342000000*	*-2.003041000000*
C	*2.986448000000*	*2.599102000000*	*-1.090293000000*
H	*2.837447000000*	*3.668330000000*	*-1.155258000000*
C	*1.996791000000*	*1.774909000000*	*-0.546423000000*
C	*0.721733000000*	*2.346287000000*	*-0.017767000000*

C	-1.539968000000	2.086799000000	0.303331000000
C	-2.752693000000	1.234654000000	0.118518000000
C	-3.898826000000	-0.253802000000	-1.204553000000
C	-1.635586000000	3.327594000000	0.932876000000
C	0.706197000000	3.597711000000	0.597853000000
C	-0.493585000000	4.115709000000	1.089963000000
H	1.621740000000	4.164025000000	0.691768000000
H	-2.592218000000	3.674574000000	1.296674000000
C	-4.948361000000	-0.350857000000	-0.298147000000
C	-3.761561000000	1.197121000000	1.085189000000
C	-4.871379000000	0.391198000000	0.872741000000
H	-3.924215000000	-0.816713000000	-2.132325000000
H	-5.795246000000	-0.991050000000	-0.508163000000
H	-3.671744000000	1.773887000000	1.995705000000
H	-5.659554000000	0.341144000000	1.613878000000
C	-0.551294000000	5.442291000000	1.747549000000
C	-1.677474000000	6.262750000000	1.623399000000
C	0.521635000000	5.917029000000	2.514583000000
C	-1.726340000000	7.508831000000	2.238040000000
C	0.464024000000	7.158124000000	3.131365000000
C	-0.659894000000	7.981308000000	3.004444000000
H	-2.518960000000	5.938294000000	1.023838000000
H	1.402585000000	5.301513000000	2.648320000000
H	-2.608930000000	8.126163000000	2.114505000000
H	1.305969000000	7.493359000000	3.727168000000
C	-0.707574000000	9.328743000000	3.672129000000
H	-1.660128000000	9.828265000000	3.491414000000
H	-0.571768000000	9.238417000000	4.753284000000
H	0.090805000000	9.979190000000	3.303976000000

4. L4

E = -3546.759084658975 au

0 imaginary frequencies

N	2.138119000000	0.436426000000	-0.508972000000
N	-0.376481000000	1.612040000000	-0.166316000000
N	-2.824321000000	0.525132000000	-1.008137000000
C	3.261594000000	-0.106037000000	-0.977613000000
H	3.335576000000	-1.187185000000	-0.914665000000
C	4.303750000000	0.636274000000	-1.520940000000
H	5.193474000000	0.142339000000	-1.889116000000
C	4.162794000000	2.016210000000	-1.576855000000
H	4.942922000000	2.636700000000	-2.000245000000
C	2.999348000000	2.592923000000	-1.086967000000
H	2.860980000000	3.664456000000	-1.134948000000
C	2.002479000000	1.769287000000	-0.555923000000
C	0.732531000000	2.343399000000	-0.018703000000
C	-1.531091000000	2.091974000000	0.304991000000
C	-2.747652000000	1.246054000000	0.119402000000
C	-3.901765000000	-0.234601000000	-1.205046000000
C	-1.619840000000	3.329413000000	0.942540000000

C	*0.725237000000*	*3.589163000000*	*0.609377000000*
C	*-0.472376000000*	*4.106483000000*	*1.104749000000*
H	*1.642847000000*	*4.150867000000*	*0.710758000000*
H	*-2.573405000000*	*3.681260000000*	*1.309710000000*
C	*-4.951120000000*	*-0.327674000000*	*-0.297975000000*
C	*-3.755537000000*	*1.211770000000*	*1.087148000000*
C	*-4.869489000000*	*0.411837000000*	*0.874138000000*
H	*-3.930593000000*	*-0.796172000000*	*-2.133458000000*
H	*-5.801493000000*	*-0.962992000000*	*-0.508508000000*
H	*-3.662099000000*	*1.785783000000*	*1.999009000000*
H	*-5.657259000000*	*0.364511000000*	*1.615842000000*
C	*-0.524689000000*	*5.426140000000*	*1.778214000000*
C	*-1.635796000000*	*6.264125000000*	*1.628563000000*
C	*0.532013000000*	*5.864555000000*	*2.584421000000*
C	*-1.695973000000*	*7.499850000000*	*2.260052000000*
C	*0.482973000000*	*7.094629000000*	*3.228244000000*
C	*-0.634115000000*	*7.900815000000*	*3.058831000000*
H	*-2.461416000000*	*5.963252000000*	*0.996572000000*
H	*1.399025000000*	*5.233903000000*	*2.733400000000*
H	*-2.560335000000*	*8.135266000000*	*2.122406000000*
H	*1.305331000000*	*7.409590000000*	*3.856178000000*
Br	*-0.710778000000*	*9.599376000000*	*3.944836000000*

5. *L5*

E = -2391.766938733877 au

0 imaginary frequencies

N	*2.138271000000*	*0.444137000000*	*-0.709081000000*
N	*-0.393384000000*	*1.599335000000*	*-0.374721000000*
N	*-2.836872000000*	*0.567435000000*	*-1.303494000000*
C	*3.274154000000*	*-0.074086000000*	*-1.175992000000*
H	*3.355714000000*	*-1.156173000000*	*-1.148532000000*
C	*4.319989000000*	*0.693429000000*	*-1.675146000000*
H	*5.220034000000*	*0.218852000000*	*-2.043649000000*
C	*4.168988000000*	*2.073520000000*	*-1.687967000000*
H	*4.951714000000*	*2.713099000000*	*-2.076881000000*
C	*2.992643000000*	*2.624723000000*	*-1.200227000000*
H	*2.844733000000*	*3.695889000000*	*-1.214543000000*
C	*1.993096000000*	*1.776813000000*	*-0.713589000000*
C	*0.711219000000*	*2.327502000000*	*-0.179376000000*
C	*-1.554177000000*	*2.065375000000*	*0.099723000000*
C	*-2.770113000000*	*1.231649000000*	*-0.140939000000*
C	*-3.913098000000*	*-0.180441000000*	*-1.547882000000*
C	*-1.653989000000*	*3.276337000000*	*0.781714000000*
C	*0.694189000000*	*3.546779000000*	*0.496189000000*
C	*-0.510784000000*	*4.052696000000*	*0.990346000000*
H	*1.616848000000*	*4.086253000000*	*0.652041000000*
H	*-2.619228000000*	*3.618899000000*	*1.125400000000*
C	*-4.971327000000*	*-0.316568000000*	*-0.656995000000*
C	*-3.788288000000*	*1.151653000000*	*0.813577000000*

C	-4.900833000000	0.364898000000	0.550685000000
H	-3.933525000000	-0.695287000000	-2.503265000000
H	-5.819972000000	-0.939977000000	-0.906610000000
H	-3.701879000000	1.681297000000	1.752700000000
H	-5.696445000000	0.282331000000	1.280857000000
Fe	-1.041702000000	7.201111000000	0.916372000000
C	0.517729000000	6.249921000000	1.905807000000
C	-0.342106000000	7.928813000000	-0.906066000000
C	-0.566773000000	5.330355000000	1.713230000000
C	0.049553000000	7.339416000000	2.686346000000
C	-0.838717000000	9.000815000000	-0.109983000000
C	-1.411183000000	7.014440000000	-1.125939000000
C	-1.710256000000	5.888016000000	2.377623000000
C	-1.325832000000	7.115876000000	2.978012000000
C	-2.213552000000	8.747402000000	0.162164000000
C	-2.567621000000	7.518268000000	-0.465293000000
H	1.518347000000	6.143117000000	1.518848000000
H	0.669868000000	7.820063000000	-1.264020000000
H	0.630601000000	8.198526000000	2.983540000000
H	-0.268183000000	9.846068000000	0.242660000000
H	-1.349788000000	6.088099000000	-1.675971000000
H	-2.695722000000	5.452766000000	2.418743000000
H	-1.971676000000	7.773832000000	3.538340000000
H	-2.866151000000	9.367211000000	0.757230000000
H	-3.536301000000	7.044243000000	-0.431991000000

6. Re1

E = -3734.835146463211 au

0 imaginary frequencies

Re	0.274653000000	-0.879752000000	-0.076046000000
Br	0.813799000000	-0.272336000000	2.495956000000
O	-2.385549000000	-2.185616000000	0.786550000000
O	1.433536000000	-3.700067000000	0.310963000000
O	-0.301282000000	-1.591578000000	-3.007923000000
N	2.169979000000	0.138151000000	-0.555618000000
N	-0.227075000000	1.335982000000	-0.239063000000
N	-2.852761000000	0.480544000000	-1.410382000000
C	-1.414477000000	-1.659726000000	0.454208000000
C	0.999103000000	-2.638924000000	0.163904000000
C	-0.092650000000	-1.297773000000	-1.907592000000
C	3.312022000000	-0.508401000000	-0.836072000000
H	3.268001000000	-1.587321000000	-0.844327000000
C	4.496225000000	0.151365000000	-1.107673000000
H	5.387343000000	-0.419411000000	-1.329561000000
C	4.502666000000	1.539443000000	-1.091883000000
H	5.407835000000	2.093183000000	-1.304608000000
C	3.326588000000	2.211694000000	-0.806221000000
H	3.312435000000	3.290510000000	-0.805815000000
C	2.165281000000	1.488023000000	-0.537177000000
C	0.868668000000	2.136993000000	-0.261911000000

C	-1.440029000000	1.908982000000	-0.084022000000
C	-2.689647000000	1.109285000000	-0.240100000000
C	-4.000425000000	-0.163250000000	-1.623805000000
C	-1.578130000000	3.273384000000	0.157935000000
C	0.779755000000	3.509153000000	-0.046300000000
C	-0.455699000000	4.081683000000	0.191401000000
H	-0.543319000000	5.143942000000	0.378321000000
H	1.667293000000	4.122400000000	-0.049713000000
H	-2.566876000000	3.689168000000	0.290600000000
C	-5.031460000000	-0.214542000000	-0.692186000000
C	-3.669435000000	1.118112000000	0.751760000000
C	-4.857800000000	0.438266000000	0.520206000000
H	-4.103637000000	-0.657193000000	-2.584441000000
H	-5.943402000000	-0.751710000000	-0.918037000000
H	-3.498658000000	1.638787000000	1.684725000000
H	-5.633181000000	0.419839000000	1.275936000000

7. Re2

E = -3965.832843722565 au

0 imaginary frequencies

Re	0.254279000000	-0.716825000000	-0.341322000000
Br	1.082775000000	-0.642060000000	2.227088000000
O	-2.273687000000	-2.274559000000	0.499850000000
O	1.490448000000	-3.512536000000	-0.660113000000
O	-0.656264000000	-0.852047000000	-3.270981000000
N	2.071939000000	0.443214000000	-0.808184000000
N	-0.277529000000	1.462845000000	0.017525000000
N	-3.001867000000	0.843371000000	-1.058099000000
C	-1.354200000000	-1.651124000000	0.189436000000
C	1.024413000000	-2.461223000000	-0.544039000000
C	-0.319213000000	-0.772481000000	-2.165989000000
C	3.171081000000	-0.090021000000	-1.363311000000
H	3.130892000000	-1.142761000000	-1.601193000000
C	4.306448000000	0.651447000000	-1.632355000000
H	5.164069000000	0.171923000000	-2.083526000000
C	4.306661000000	2.003424000000	-1.317759000000
H	5.172719000000	2.620396000000	-1.518845000000
C	3.173887000000	2.559750000000	-0.748413000000
H	3.154212000000	3.614113000000	-0.519372000000
C	2.061614000000	1.756917000000	-0.496748000000
C	0.802420000000	2.283619000000	0.068237000000
C	-1.466736000000	1.962159000000	0.416295000000
C	-2.723587000000	1.185439000000	0.205662000000
C	-4.161994000000	0.234077000000	-1.303838000000
C	-1.583624000000	3.229517000000	0.973088000000
C	0.733042000000	3.561552000000	0.605272000000
C	-0.469643000000	4.057336000000	1.103714000000
H	1.618521000000	4.176263000000	0.637967000000
H	-2.558512000000	3.559719000000	1.301397000000
C	-5.092720000000	-0.062743000000	-0.314244000000

C	-3.595600000000	0.931049000000	1.263193000000
C	-4.798655000000	0.291357000000	0.995189000000
H	-4.359995000000	-0.024185000000	-2.339021000000
H	-6.020820000000	-0.557094000000	-0.570159000000
H	-3.332690000000	1.222887000000	2.271343000000
H	-5.492728000000	0.073993000000	1.797407000000
C	-0.560146000000	5.399578000000	1.718915000000
C	-1.717995000000	6.176443000000	1.582533000000
C	0.511545000000	5.918201000000	2.457576000000
C	-1.798449000000	7.435755000000	2.163718000000
C	0.424854000000	7.173591000000	3.046104000000
C	-0.728915000000	7.938187000000	2.899294000000
H	-2.552905000000	5.806388000000	1.001091000000
H	1.409226000000	5.328269000000	2.593481000000
H	-2.697307000000	8.026935000000	2.038282000000
H	1.258898000000	7.552719000000	3.623954000000
H	-0.794225000000	8.918429000000	3.355395000000

8. Re3

E = -4005.136265536305 au

0 imaginary frequencies

Re	0.254032000000	-0.712366000000	-0.333985000000
Br	1.074575000000	-0.624302000000	2.237161000000
O	-2.279174000000	-2.263251000000	0.503684000000
O	1.492559000000	-3.509727000000	-0.628718000000
O	-0.643231000000	-0.865467000000	-3.266952000000
N	2.074056000000	0.444578000000	-0.800781000000
N	-0.277967000000	1.469648000000	0.010010000000
N	-3.001230000000	0.843478000000	-1.062074000000
C	-1.357591000000	-1.642147000000	0.194595000000
C	1.024459000000	-2.458285000000	-0.521923000000
C	-0.310845000000	-0.779150000000	-2.160977000000
C	3.175569000000	-0.093099000000	-1.346901000000
H	3.136658000000	-1.147951000000	-1.575375000000
C	4.311686000000	0.646296000000	-1.618131000000
H	5.171420000000	0.162976000000	-2.061097000000
C	4.309841000000	2.001182000000	-1.316206000000
H	5.176201000000	2.616829000000	-1.519919000000
C	3.174700000000	2.562031000000	-0.756090000000
H	3.153600000000	3.618429000000	-0.536964000000
C	2.061969000000	1.760969000000	-0.500707000000
C	0.801293000000	2.291606000000	0.057851000000
C	-1.467058000000	1.971321000000	0.407159000000
C	-2.724272000000	1.194428000000	0.199618000000
C	-4.161563000000	0.233551000000	-1.305108000000
C	-1.583282000000	3.239486000000	0.960922000000
C	0.731679000000	3.572080000000	0.588009000000
C	-0.470283000000	4.070612000000	1.088357000000
H	1.617361000000	4.186505000000	0.614893000000

H	*-2.557762000000*	*3.569232000000*	*1.290312000000*
C	*-5.094119000000*	*-0.055368000000*	*-0.314908000000*
C	*-3.598166000000*	*0.947853000000*	*1.257572000000*
C	*-4.801519000000*	*0.307615000000*	*0.992416000000*
H	*-4.358234000000*	*-0.031980000000*	*-2.338689000000*
H	*-6.022316000000*	*-0.550571000000*	*-0.568709000000*
H	*-3.336387000000*	*1.246060000000*	*2.264115000000*
H	*-5.496879000000*	*0.096585000000*	*1.795183000000*
C	*-0.562292000000*	*5.411111000000*	*1.702192000000*
C	*-1.737535000000*	*6.166571000000*	*1.621345000000*
C	*0.525319000000*	*5.961693000000*	*2.395494000000*
C	*-1.819172000000*	*7.423292000000*	*2.208173000000*
C	*0.433435000000*	*7.212098000000*	*2.986478000000*
C	*-0.739585000000*	*7.970308000000*	*2.903940000000*
H	*-2.592245000000*	*5.784553000000*	*1.077426000000*
H	*1.443561000000*	*5.396895000000*	*2.497386000000*
H	*-2.738940000000*	*7.990113000000*	*2.120410000000*
H	*1.286254000000*	*7.605883000000*	*3.528183000000*
C	*-0.824883000000*	*9.327717000000*	*3.545464000000*
H	*-1.815956000000*	*9.765039000000*	*3.420403000000*
H	*-0.610243000000*	*9.270723000000*	*4.615973000000*
H	*-0.093475000000*	*10.014664000000*	*3.110426000000*

9. Re4

E = -6539.277625232964 au

0 imaginary frequencies

Re	*0.255110000000*	*-0.714429000000*	*-0.336620000000*
Br	*1.079574000000*	*-0.624375000000*	*2.232384000000*
O	*-2.274909000000*	*-2.267214000000*	*0.507410000000*
O	*1.498322000000*	*-3.509291000000*	*-0.633067000000*
O	*-0.648590000000*	*-0.868397000000*	*-3.267703000000*
N	*2.072659000000*	*0.444428000000*	*-0.807479000000*
N	*-0.278919000000*	*1.467609000000*	*0.010128000000*
N	*-3.001184000000*	*0.836501000000*	*-1.060966000000*
C	*-1.354535000000*	*-1.645811000000*	*0.195685000000*
C	*1.027964000000*	*-2.459058000000*	*-0.525766000000*
C	*-0.313710000000*	*-0.781979000000*	*-2.162624000000*
C	*3.172553000000*	*-0.090237000000*	*-1.359540000000*
H	*3.134352000000*	*-1.144593000000*	*-1.590428000000*
C	*4.306382000000*	*0.651792000000*	*-1.633919000000*
H	*5.164835000000*	*0.170859000000*	*-2.081956000000*
C	*4.304038000000*	*2.005908000000*	*-1.328856000000*
H	*5.168516000000*	*2.623334000000*	*-1.535169000000*
C	*3.170452000000*	*2.563717000000*	*-0.762395000000*
H	*3.148014000000*	*3.619647000000*	*-0.540891000000*
C	*2.060424000000*	*1.760016000000*	*-0.504298000000*
C	*0.801125000000*	*2.288113000000*	*0.058983000000*
C	*-1.468473000000*	*1.967328000000*	*0.407262000000*
C	*-2.724919000000*	*1.189310000000*	*0.200237000000*

C	-4.160644000000	0.224593000000	-1.303030000000
C	-1.585319000000	3.235679000000	0.962160000000
C	0.732609000000	3.566508000000	0.595256000000
C	-0.470315000000	4.061543000000	1.092848000000
H	1.618469000000	4.180707000000	0.628957000000
H	-2.559870000000	3.566507000000	1.290873000000
C	-5.092489000000	-0.064566000000	-0.312144000000
C	-3.598097000000	0.943196000000	1.258823000000
C	-4.800409000000	0.300549000000	0.994676000000
H	-4.357147000000	-0.042537000000	-2.336212000000
H	-6.019926000000	-0.561613000000	-0.565140000000
H	-3.336571000000	1.243250000000	2.264902000000
H	-5.495277000000	0.089397000000	1.797835000000
C	-0.559664000000	5.401144000000	1.712766000000
C	-1.712647000000	6.183354000000	1.577285000000
C	0.507652000000	5.912888000000	2.460249000000
C	-1.801847000000	7.438008000000	2.165720000000
C	0.428326000000	7.161187000000	3.062626000000
C	-0.728540000000	7.912638000000	2.907472000000
H	-2.548213000000	5.825955000000	0.989487000000
H	1.405901000000	5.325071000000	2.598856000000
H	-2.697256000000	8.031312000000	2.039774000000
H	1.258334000000	7.533091000000	3.647604000000
Br	-0.844089000000	9.636236000000	3.736055000000

10.Re5

E = -5384.286714240699 au

0 imaginary frequencies

Re	0.258215000000	-0.742999000000	-0.329794000000
Br	1.045967000000	-0.636532000000	2.251553000000
O	-2.287587000000	-2.284880000000	0.486267000000
O	1.490537000000	-3.547121000000	-0.587500000000
O	-0.590122000000	-0.916129000000	-3.276143000000
N	2.084636000000	0.411677000000	-0.776613000000
N	-0.281107000000	1.439616000000	-0.010738000000
N	-2.990066000000	0.808696000000	-1.112527000000
C	-1.360741000000	-1.668167000000	0.183711000000
C	1.028099000000	-2.491686000000	-0.494507000000
C	-0.277785000000	-0.822278000000	-2.164764000000
C	3.196121000000	-0.129610000000	-1.298714000000
H	3.161585000000	-1.186127000000	-1.520204000000
C	4.336999000000	0.608041000000	-1.553793000000
H	5.205076000000	0.121816000000	-1.976910000000
C	4.329196000000	1.965193000000	-1.261557000000
H	5.199241000000	2.579587000000	-1.453111000000
C	3.183631000000	2.529643000000	-0.727129000000
H	3.158052000000	3.587655000000	-0.516077000000
C	2.066582000000	1.729996000000	-0.485950000000
C	0.796090000000	2.264012000000	0.046746000000

C	*-1.474900000000*	*1.944099000000*	*0.372892000000*
C	*-2.729888000000*	*1.167389000000*	*0.150648000000*
C	*-4.147793000000*	*0.198571000000*	*-1.367658000000*
C	*-1.599341000000*	*3.213405000000*	*0.918578000000*
C	*0.721206000000*	*3.545061000000*	*0.571781000000*
C	*-0.487313000000*	*4.047809000000*	*1.054951000000*
H	*1.613034000000*	*4.147586000000*	*0.631285000000*
H	*-2.581784000000*	*3.550424000000*	*1.214583000000*
C	*-5.094459000000*	*-0.082947000000*	*-0.388815000000*
C	*-3.618907000000*	*0.927899000000*	*1.197803000000*
C	*-4.819429000000*	*0.287715000000*	*0.920212000000*
H	*-4.330543000000*	*-0.073365000000*	*-2.402155000000*
H	*-6.019675000000*	*-0.578683000000*	*-0.652374000000*
H	*-3.370496000000*	*1.231765000000*	*2.206053000000*
H	*-5.526077000000*	*0.082512000000*	*1.714641000000*
Fe	*-1.077046000000*	*7.176431000000*	*0.767728000000*
C	*0.488963000000*	*6.318271000000*	*1.827879000000*
C	*-0.372149000000*	*7.830518000000*	*-1.080651000000*
C	*-0.577500000000*	*5.367488000000*	*1.679684000000*
C	*-0.009127000000*	*7.439277000000*	*2.539425000000*
C	*-0.894984000000*	*8.928651000000*	*-0.338967000000*
C	*-1.423074000000*	*6.888555000000*	*-1.267995000000*
C	*-1.740338000000*	*5.941412000000*	*2.297702000000*
C	*-1.383582000000*	*7.206628000000*	*2.829621000000*
C	*-2.267584000000*	*8.663722000000*	*-0.068303000000*
C	*-2.594389000000*	*7.401340000000*	*-0.641828000000*
H	*1.497096000000*	*6.207783000000*	*1.462137000000*
H	*0.645031000000*	*7.723465000000*	*-1.424044000000*
H	*0.551884000000*	*8.325273000000*	*2.792701000000*
H	*-0.342249000000*	*9.797656000000*	*-0.017070000000*
H	*-1.340788000000*	*5.940541000000*	*-1.777028000000*
H	*-2.717662000000*	*5.490140000000*	*2.356320000000*
H	*-2.047363000000*	*7.884287000000*	*3.343505000000*
H	*-2.936535000000*	*9.298283000000*	*0.492159000000*
H	*-3.555042000000*	*6.912367000000*	*-0.595221000000*