Synthesis and photophysical properties of C_3-symmetric tris(3-pyridyl)truxene scaffolds of Ru(II) and Re(I)

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Electronic Supporting Information

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Materials and Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$, CD_3CN and $\{(CD_3)_2SO\}$ at room temperatutre (r.t.) on Bruker AV400 (400 MHz) spectrometer for ^1H NMR and at 100 MHz for ^{13}C NMR respectively, as mentioned in the experimental. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (1.94 ppm for CD_3CN, 7.26 ppm for $CDCl_3$, 2.50 ppm for $\{(CD_3)_2SO\}$) and the carbon resonance (118.69 ppm for CD_3CN, 77.00 ppm for $CDCl_3$, 39.43 ppm for $\{(CD_3)_2SO\}$) of the solvent. Accurate mass measurements were performed on a 6210 TOF mass spectrometer from Agilent technologies, coupled to a 1100 series LC system in positive electrospray mode. Appropriate $[M]^{n+}$, $[M\text{-}PF_6]^{n+}$ or $[M+H]^{n+}$ species were used for empirical formula determination, and exact masses were calculated using Analyst® QS Software from Applied Biosystems.

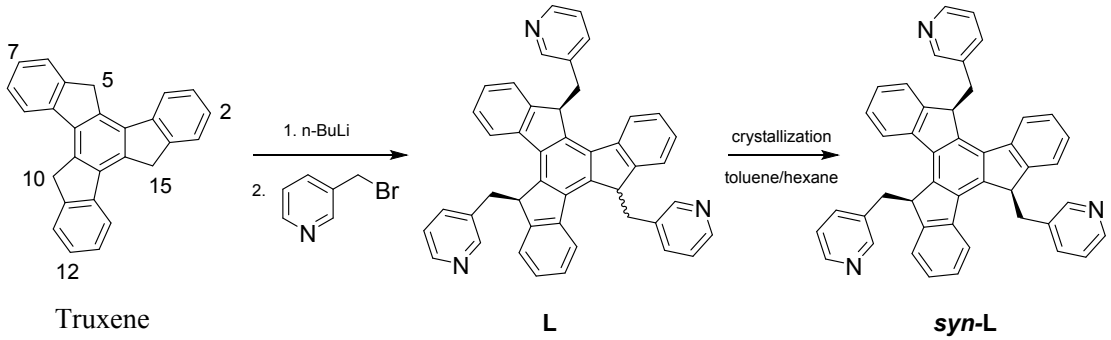
Absorption spectra were measured in deaerated *N,N′*-DMF at r.t. on a Cary 500i UV-Vis-NIR Spectrophotometer. Uncorrected phosphoorescence emission spectra (450 W Xe lamp) were obtained with a Cary Eclipse spectrofluorimeter. Luminescence lifetimes were determined by time-correlated single-photon-counting (TCSPC) with an Edinburgh EPL-405 spectrometer (light pulse: nanosecond pulse diode laser, pulse width 5 ns at 405 nm).

Electrochemical measurements were carried out in argon-purged purified *N,N′*-DMF at room temperature with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 432 mV *vs.* SCE in *N,N′*-DMF. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rate of 100 mV/s. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV.

Hydrated ruthenium trichloride, 3-(bromomethyl)pyridine hydrobromide, 2-bromopyridine, 2,6-dibromopyridine, n-butyllithium (2.5 M in hexanes) and ammonium hexafluorophosphate were

purchased from Pressure Chemicals and Aldrich Chemicals. The pro-ligand truxene[1] and precursor complex $[Re(CO)_3(H_2O)_3][Br]$[2] were synthesized following literature procedures.

Synthetic Procedures for *syn*-L:



Truxene **L** ***syn*-L**

Scheme S1: Synthesis of ligand **L** and isolation of ***syn*-L**.

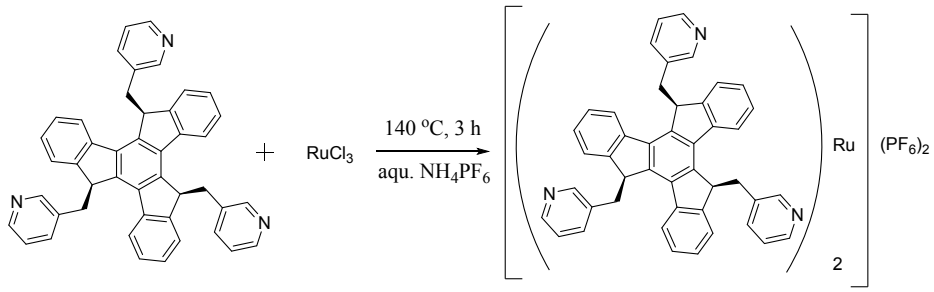
Preparation of 3-(bromomethyl)pyridine: To a flask containing 3-(bromomethyl)pyridine hydrobromide (1.0 g, 3.95 mmol, 1 eq) in anhydrous toluene (50 mL) under nitrogen atmosphere, potassium carbonate (1.64 g, 11.86 mmol, 3 eq) was added. The reaction mixture was stirred vigorously for 1 h at room temperature and 1 h at 80 °C. The solution was then allowed to cool down to room temperature.

To a solution of truxene (0.5 g , 1.46 mmol, 1 eq) in dry THF (30 mL) was added dropwise n-butyllithium (2.22 mL, 2.5 M in hexanes, 5.55 mmol) at -78 °C under an inert atmosphere of nitrogen. After stirring the mixture for 30 min at this temperature, 3-(bromomethyl)pyridine (prepared as above) was added through a cannula and the resulting mixture was stirred for 4 h at -78 °C and at room temperature overnight. The reaction mixture was quenched by adding methanol (5 mL) at -78 °C and the solvent removed under vacuum. Ligand ***syn*-L** was obtained as a yellow solid by crystallization of crude reaction mixture from toluene/hexane in 50% yield (0.45 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.29 (dd, *J* = 4.74, 1.37 Hz, 3H), 7.90 (d, *J* = 1.64 Hz, 3H), 7.48 (d, *J* = 4.02 Hz, 6H), 7.35 (m, 3H), 6.98 (dd, *J* = 7.68, 4.85 Hz, 3H), 6.87 (d, *J* = 7.40 Hz, 3H), 6.73 (d, *J* = 7.40 Hz, 3H), 3.50 (dd, *J* = 8.33, 3.65 Hz, 3H), 3.24 (dd, *J* = 13.86, 3.58 Hz, 3H), 2.43 (dd, *J* = 13.87, 8.56 Hz, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 150.4, 147.5, 146.9, 139.8, 139.7, 136.4, 135.5, 133.5, 127.2, 126.3, 125.3, 122.8, 122.5, 46.6, 35.1. HRMS (ESI),

m/z: 616.2746 $[M+H]^+$ ($C_{45}H_{34}N_3$ requires 616.2752). Anal. Calc for $C_{45}H_{33}N_3$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.79; H, 5.45; N, 6.79.

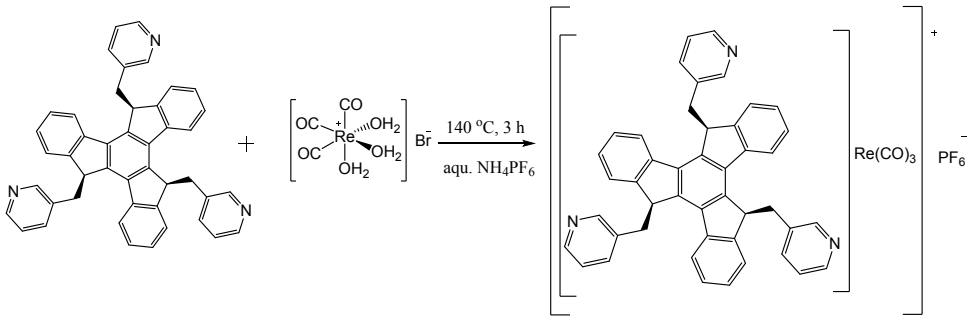
Synthesis of $[Ru(syn\text{-}L)_2](PF_6)_2$, (1):



Scheme S2: Synthesis of complex **1**.

Ligand ***syn*-L** (130 mg, 0.21 mmol) and $RuCl_3$ (26 mg, 0.1 mmol) were taken in ethylene glycol (10 mL). The mixture was refluxed for 3 h, during which the colour changed from yellowish green to yellow. After cooling to ambient temperature, 10 mL water was added. A little yellow precipitate formed. This was filtered. To the yellow filtrate a solution of NH_4PF_6 (500 mg in 3 mL of water) was added with stirring. A yellow gelatinous precipitate formed. This mixture was extracted with dichloromethane-acetonitrile. Evaporation of the solvent furnished complex **1**. Yield = 70 mg (43%). ^{1}H NMR {$(CD_3)_2SO$, 400 MHz}; 7.96 (d, J = 7.47 Hz, 6H), 7.82 (d, J = 7.47 Hz, 6H), 7.47-7.38 (m, 12H), 7.14 (d, J = 7.47 Hz, 6H), 6.78 (t , J = 7.47 Hz, 6H), 6.40 (s, 6H), 6.24 (d, J = 6.01 Hz, 6H), 4.92 (s, 6H), 3.60 (m, 6H), 3.18 (d, J = 11.34 Hz, 6H). ^{13}C NMR {$(CD_3)_2SO$, 100 MHz}; 151.99, 150.15, 149.80, 141.31, 124.72, 113.92 44.27, 19.23. HRMS (ESI), m/z: 1477.4038 $[M\text{-}PF_6]^+$ ($C_{90}H_{66}N_6F_6PRu$ requires 1477.4034). Anal. Calc for $C_{90}H_{66}N_6RuP_2F_{12}\cdot 3H_2O$: C, 64.47; H, 4.33; N, 5.01. Found: C, 64.70; H, 4.44; N, 4.75.

Synthesis of $[Re(syn\text{-}L)(CO)_3]PF_6$ (2):



Scheme S3: Synthesis of complex **2**.

Ligand ***syn*-L** (130 mg, 0.21 mmol) and $[Re(CO)_3(H_2O)_3][Br]$ (85.97 mg, 0.21 mmol) were taken in ethylene glycol (10 mL). The mixture was refluxed for 3 h, during which the colour changed from yellowish green to yellow. After cooling to ambient temperature, 10 mL water and a solution of NH_4PF_6 (500 mg in 3 mL of water) were added with stirring. The reaction mixture was extracted with dichloromethane. Evaporation of the solvent furnished complex **2**. Yield = 128 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.53 (d, J = 5.49 Hz, 3H), 7.84 (d, J = 6.60 Hz, 3H), 7.61-7.46 (m, 12H) 7.04 (t, J = 6.59 Hz, 3H), 6.15 (s, 3H), 4.37 (s, 3H), 3.54 (d, J = 12.15 Hz, 3H), 3.38 (d, J = 12.15 Hz, 3H), ^{13}C NMR {CD_3CN, 100 MHz} 154.65, 148.79, 145.61, 142.47, 139.62, 138.20, 137.74, 136.11, 128.29, 127.67, 126.24, 125.89, 122.98, 46.26, 34.54. HRMS (ESI), m/z: 886.2077 $[M\text{-}PF_6]^+$ ($C_{48}H_{33}N_3O_3Re$ requires 886.2079). Anal. Calc for $C_{48}H_{33}N_3O_3RePF_6$: C, 55.92; H, 3.23; N, 4.08. Found: C, 55.87; H, 3.31; N, 4.05.

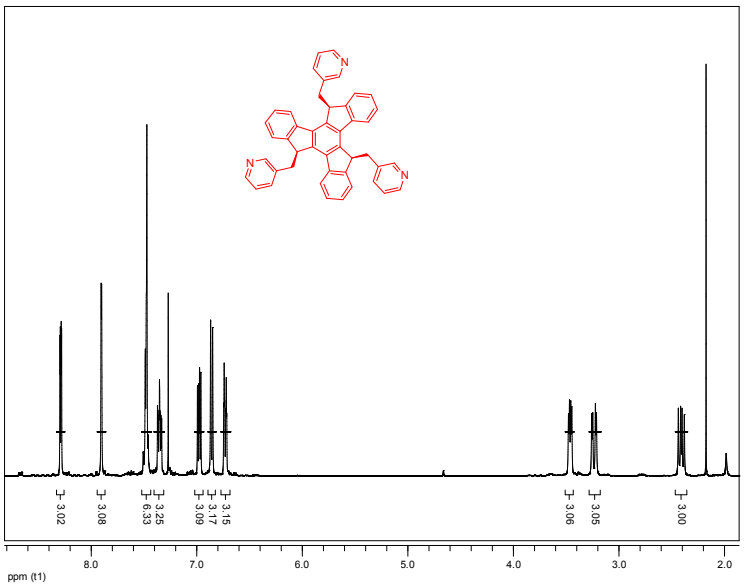


Figure S1: ^{1}H NMR spectrum of ***syn*-L** in $CDCl_3$ at ambient temperature at 400 MHz.

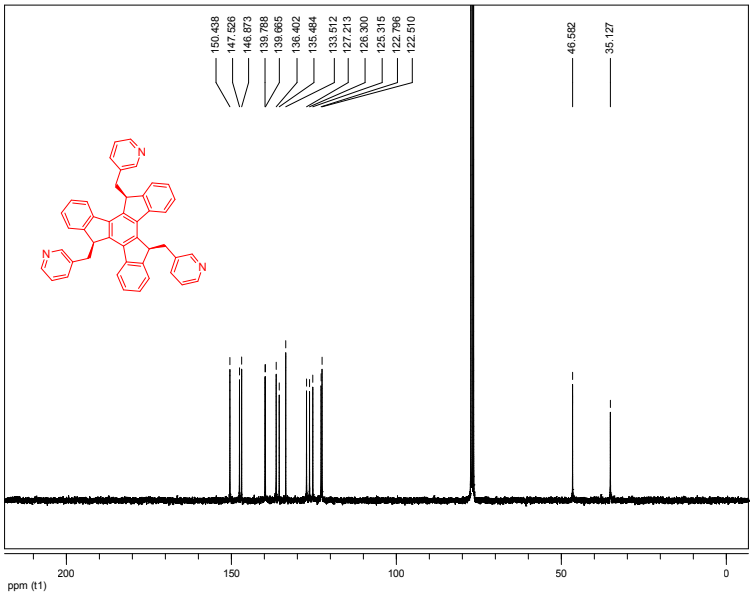


Figure S2: ^{13}C NMR spectrum of ***syn*-L** in $CDCl_3$ at ambient temperature at 400 MHz.

Determination of association constant of *syn*-L by ^{1}H NMR:

The dilution experiments were performed to determine association constants for dimerisation of this compound in $CDCl_3$. Solution of ***syn*-L** in $CDCl_3$ with the concentrations of 0.45, 0.86, 1.73, 2.07, 2.76, 3.45, 4.31, 5.69, 8.63 mM were prepared. The data were analyzed using nonlinear

regression by HypNMR2006 program.[8] The self-association constant of ***syn*-L** was calculated to be $K_{assoc} = 135\ M^{-1}$.

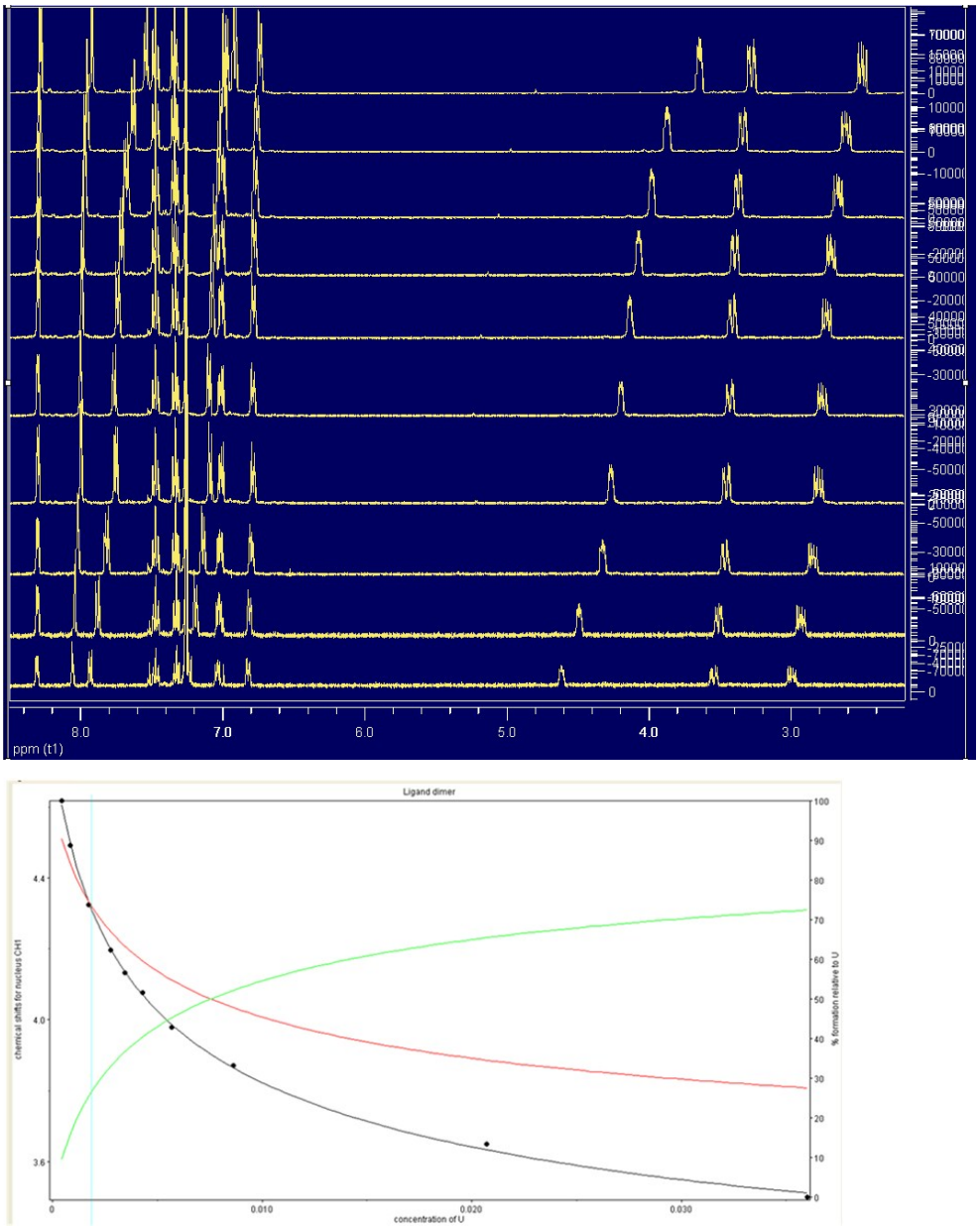


Figure S3: ^{1}H NMR spectra of different molar concentrations of ***syn*-L** (top) and determination of association constant by HypNMR2006 (bottom).

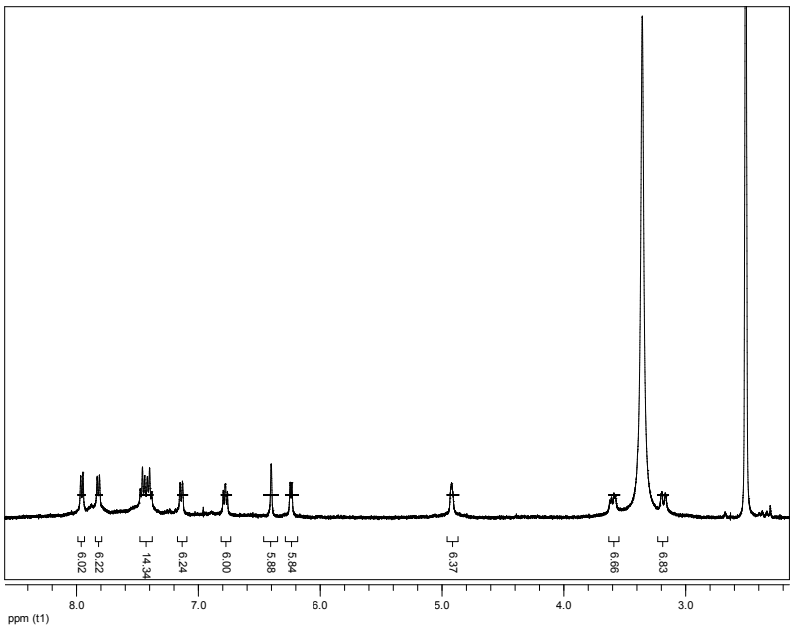


Figure S4: ^{1}H NMR spectrum of complex **1** in DMSO-d_6 at ambient temperature at 400 MHz.

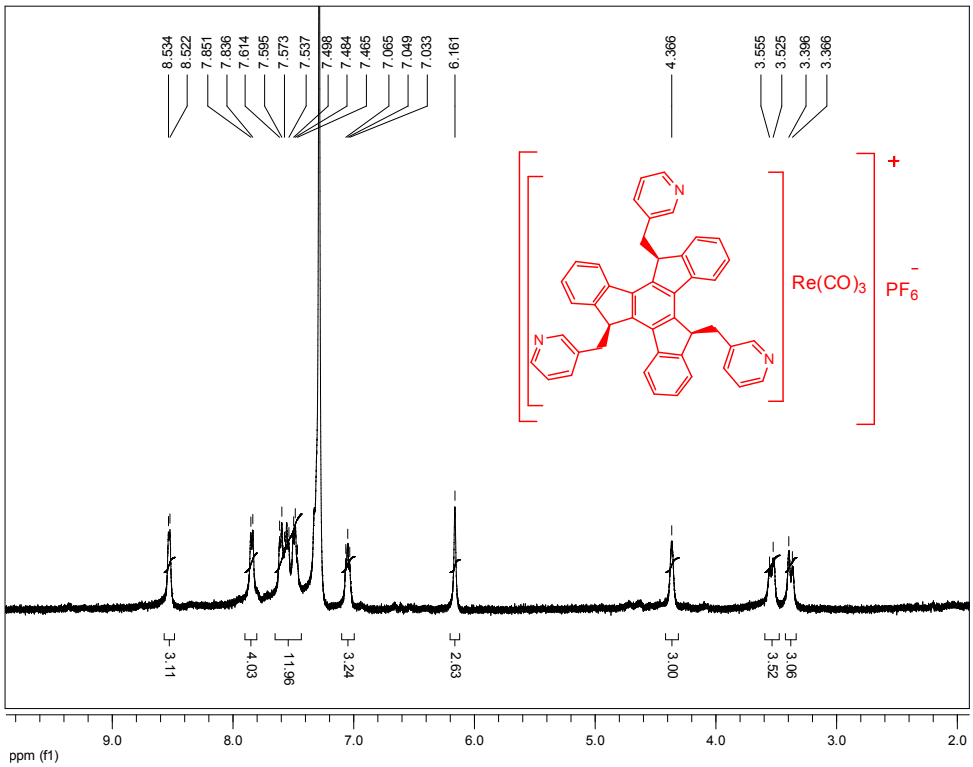


Figure S5: ^{1}H NMR spectrum of complex **2** in $CDCl_3$ at ambient temperature at 400 MHz.

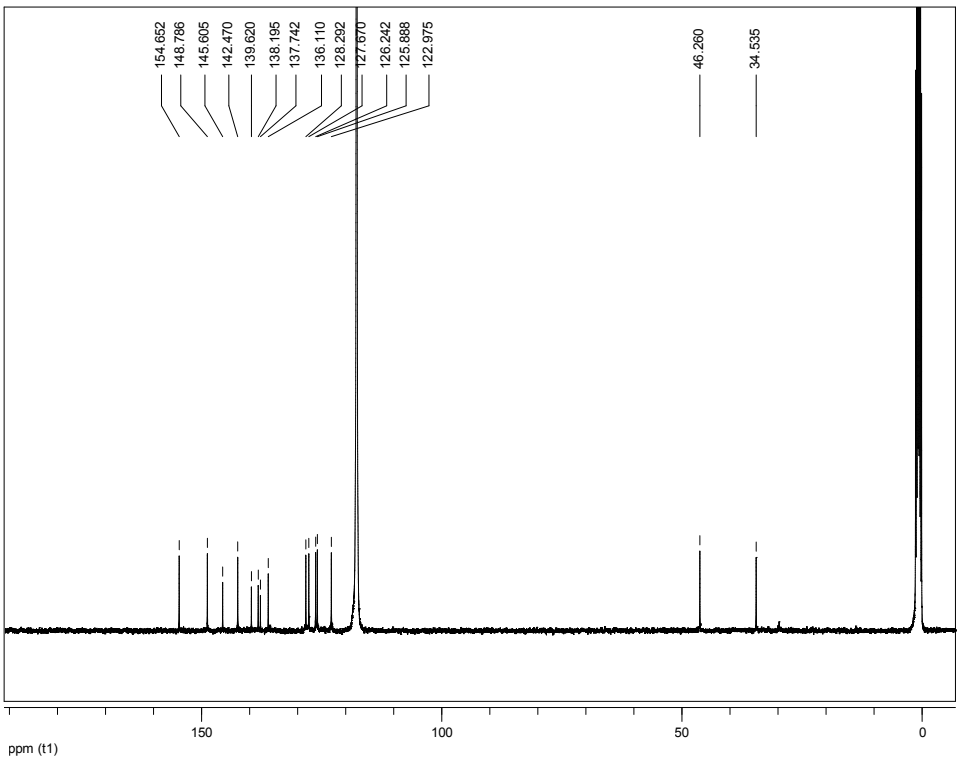


Figure S6: ^{13}C NMR spectrum of complex **2** in CD_3CN at ambient temperature at 400 MHz.

Crystallographic Section

Diffraction data were collected on a Bruker SMART 6000 with Montel 200 monochromator, equipped with a rotating anode source for Cu-K_α radiation. The diffraction quality of the crystals were checked, revealing in some cases poor diffraction with a large amount of diffuse scattering, signaling extensive crystal disorder. Cell refinement and data reduction were done using APEX2.[3] Absorption corrections were applied using SADABS.[4] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. Since the crystals lost solvent almost immediately, they were placed in Paratone-N oil and put at low temperature as quickly as possible.

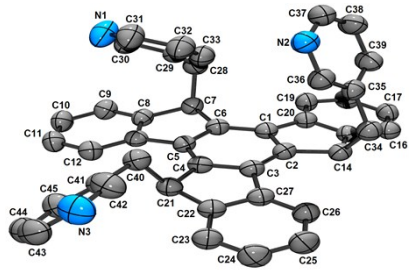
The diffraction quality of the crystals was checked, revealing a poor diffraction with a large amount of diffuse scattering, signalling extensive crystal disorder for complex **2**. During the refinement of structure of **2**, electron density peaks were located. Despite the constraint models

we endeavoured to establish, we could not achieve a reasonable solution and finally had to use *Squeeze (Platon)*[6] (*Platon* ruled out any missed twinning or superior symmetry), which resulted in a significant improvement of the agreement factor R1 (from 11% to 5%). The high electron density peaks were believed to be twenty highly disordered chloroform molecules per unit cell (by counting the number of electrons suppressed). The highest density peak (2.11 e/Å^3) was found to be in close proximity to Re-atom (0.91 Å). The structure was solved by direct methods and refined by full-matrix least squares based on *F*2 with all reflections. Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS[7] absorption correction was applied.

Table S1. Crystal data for ligand ***syn*-L·C_7H_8** and complex **2·20($CHCl_3$)**

		2·20($CHCl_3$)	***syn*-L·C_7H_8**
CCDC		916397	916394
Formula		$[C_{48}H_{33}N_3O_3Re][PF_6]\cdot 20(CHCl_3)$	$C_{45}H_{33}N_3\cdot C_7H_8$
M_w (g/mol); F(000)		1030.965; 3060	707.88; 2992
Crystal color and form		colourless block	Colourless block
Crystal size (mm)		0.04 x0.04x 0.06	0.09x0.09x0.15
T (K); wavelength		150; 1.54178	150; 1.54178
Crystal System		Trigonal	Monoclinic
Space Group		*R*-3	*C*2/c
Unit Cell:	a (Å)	13.4468(3)	27.2441(17)
	b (Å)	13.4468(3)	12.2005(8)
	c (Å)	53.0891(12)	23.5008(16)
	α (°)	90	90
	β (°)	90	103.574(2)
	γ (°)	120	90
V (Å^3); Z; $d_{calcd.}$ (g/cm^3)		8313.3(3); 6; 1.236	7593.3(9); 8; 1.238
θ range (°); completeness		2.50-70.64; 0.992	3.34-67.19; 0.993
collected reflections; R_σ		38162; 0.0277	44174; 0.0623
unique reflections; R_{int}		3571; 0.0565	7376; 0.0821
restraints; parameters		0; 187	0; 498
μ (mm^{-1}); Abs. Corr.		5.040; multi-scan	0.550; multi-scan
R1(F); wR(F^2) [I > 2σ(I)]		0.0531; 0.1444	0.0835; 0.2104
R1(F); wR(F^2) (all data)		0.0585; 0.1479	0.1272; 0.2356
GoF(F^2)		1.087	0.968
Residual electron density (max; min) e$^-$/Å^3		2.112; -1.600	0.541; -0.303

a)


N1
C31
C32
C33
C30
C29
C28
C37
C38
N2
C39
C36
C35
C17
C19
C20
C1
C16
C34
C14
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C40
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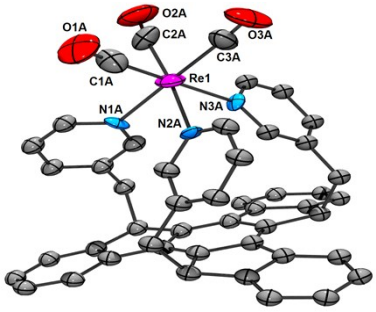
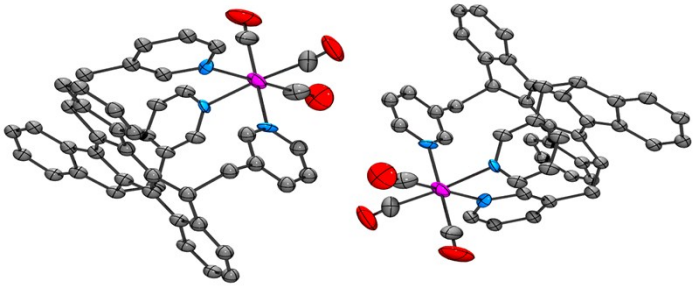
C26
C44
N3
C43
C23
C24
C25

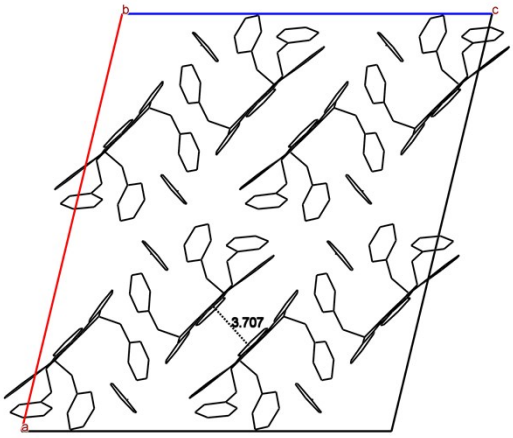
b)


O1A
O2A
C2A
O3A
C3A
C1A
Re1
N1A
N3A
N2A

c)



d)


b
c
a
3.707

e)

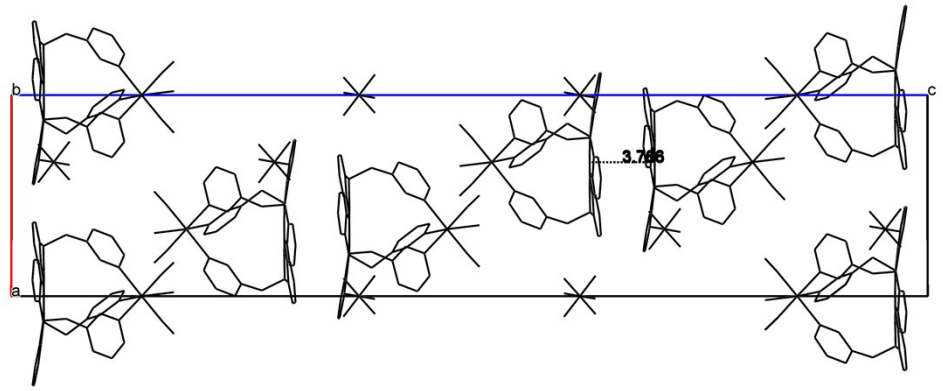


Figure S7: (a) Crystal structures of ***syn*-L** and (b) Re(I) complex, **2**, in side-view. Hydrogen atoms (for ***syn*-L** and **2**) and toluene solvated molecule (for ***syn*-L**) were not shown for clarity; the ellipsoids correspond to 50% probability. (c) Two enantiomers of the complex **2**, (d) packing diagram of ligand ***syn*-L** along b-axis with π-π interaction of 3.707 Å and intercalated toluene molecules, (e) packing diagram of complex **2** along b-axis with π-π interaction of 3.766 Å. Colour code: grey-carbon, blue-nitrogen, red-oxygen.

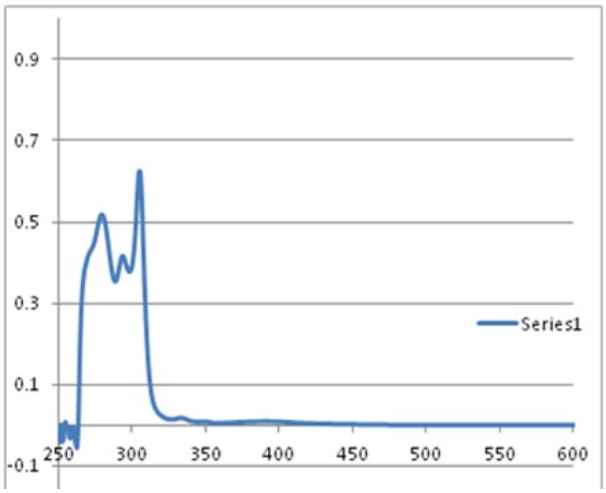


Figure S8: UV-vis absorption spectra of the ***syn*-L** in *N,N′*-DMF.

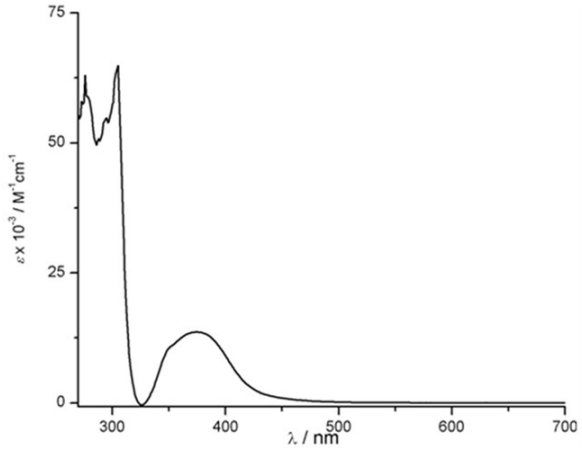


Figure S9: UV-vis absorption spectrum of complex **1** in *N,N′*-DMF.

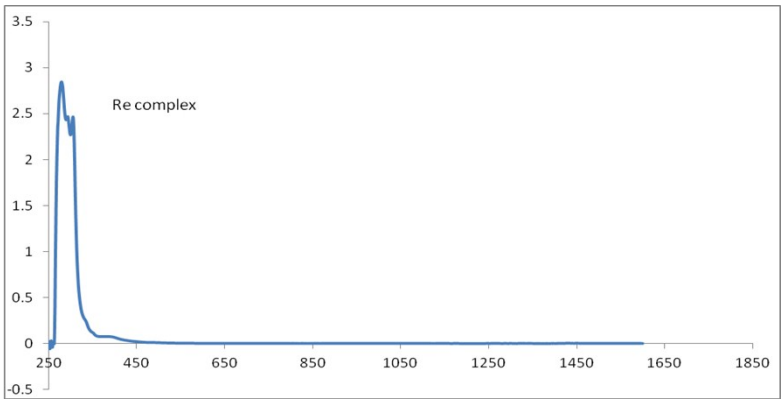


Figure S10: UV-vis absorption spectrum of complex **2** in *N,N′*-DMF.

DFT Calculations:

Computational details:

All calculations were performed with the Gaussian09, Revision D.01[9] suite of programs employing the DFT method, the Becke three-parameter hybrid functional,[10] and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).[11] Singlet ground state geometry optimizations for [**1**]$^{2+}$ and [**2**]$^{+}$ were carried out at the (R)B3LYP level in the gas phase, using their respective crystallographic structures as starting points. Doublet ground state geometry optimizations for [**1**]$^{3+}$ and [**2**]$^{2+}$ were carried out at the UB3LYP level in the gas phase. All elements except the metal centers were assigned the 6-31G(d,p) basis set.[12] The double-ζ quality LANL2DZ ECP basis set[13] with an effective core potential and one additional f-type polarization was employed for the Ru(II)- and Re(I)-ions. Vertical electronic excitations based on (R)B3LYP-optimized geometries were computed for [**1**]$^{2+}$ and [**2**]$^{+}$ using the TD-DFT formalism[14a,b] in acetonitrile using conductor-like polarizable continuum model (CPCM).[15a-c] Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. The electronic distribution and localization of the singlet excited states were visualized using the electron density difference maps (ED-DMs).[16] *Gausssum 2.2*[17] and *Chemissian*[18] were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 cm^{-1}) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures and Kohn-Sham orbitals were visualized with ChemCraft.[19] The predicted emission maximum of complex **2** was calculated using the equation Error = $|[\lambda_{em}$ (298 K)-$E_{AE}]/\lambda_{em}$ (298 K)| in eV (E_{AE} = adiabatic electronic emission).

Table S2. MO Composition of **[1]$^{2+}$** in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

MO	Energy (eV)	Composition		
		Ru	Pyridine	Truxene
LUMO+5	-1.56	7	80	13
LUMO+4	-1.60	4	88	8
LUMO+3	-1.60	3	85	12
LUMO+2	-1.75	4	92	4
LUMO+1	-1.77	8	88	4
LUMO	**-1.77**	**31**	**67**	**2**
HOMO	**-5.97**	**67**	**31**	**2**
HOMO-1	-5.97	24	9	68
HOMO-2	-6.00	9	3	88
HOMO-3	-6.00	0	1	99
HOMO-4	-6.12	1	1	98
HOMO-5	-6.12	61	16	23
HOMO-6	-6.13	61	17	22

Table S3. MO Composition of **[2]$^{+}$** in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Re]6-31G**[C,H,N]).

MO	Energy (eV)	Composition			
		Re	Pyridine	CO	Truxene
LUMO+5	-1.73	1	95	0	4
LUMO+4	-1.39	1	13	2	84
LUMO+3	-1.39	1	13	2	84
LUMO+2	-1.74	2	94	3	1
LUMO+1	-1.82	5	80	7	7
LUMO	**-1.82**	**6**	**80**	**7**	**7**
HOMO	**-5.98**	**0**	**3**	**0**	**97**
HOMO-1	-5.98	0	3	0	97
HOMO-2	-6.77	61	9	28	2
HOMO-3	-6.78	61	9	28	2
HOMO-4	-6.78	6	3	3	89
HOMO-5	-6.91	55	7	25	13

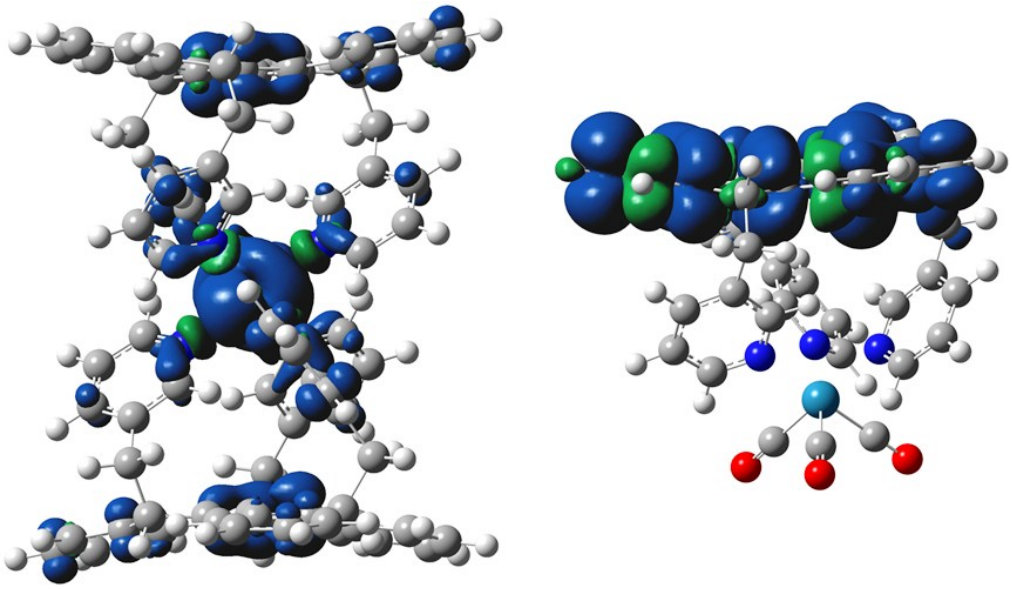


Figure S11: DFT calculated spin density plots of oxidised versions of complex **1**, i.e., $[\mathbf{1}]^{3+}$ (left) and complex **2**, i.e., $[\mathbf{2}]^{2+}$ (right).

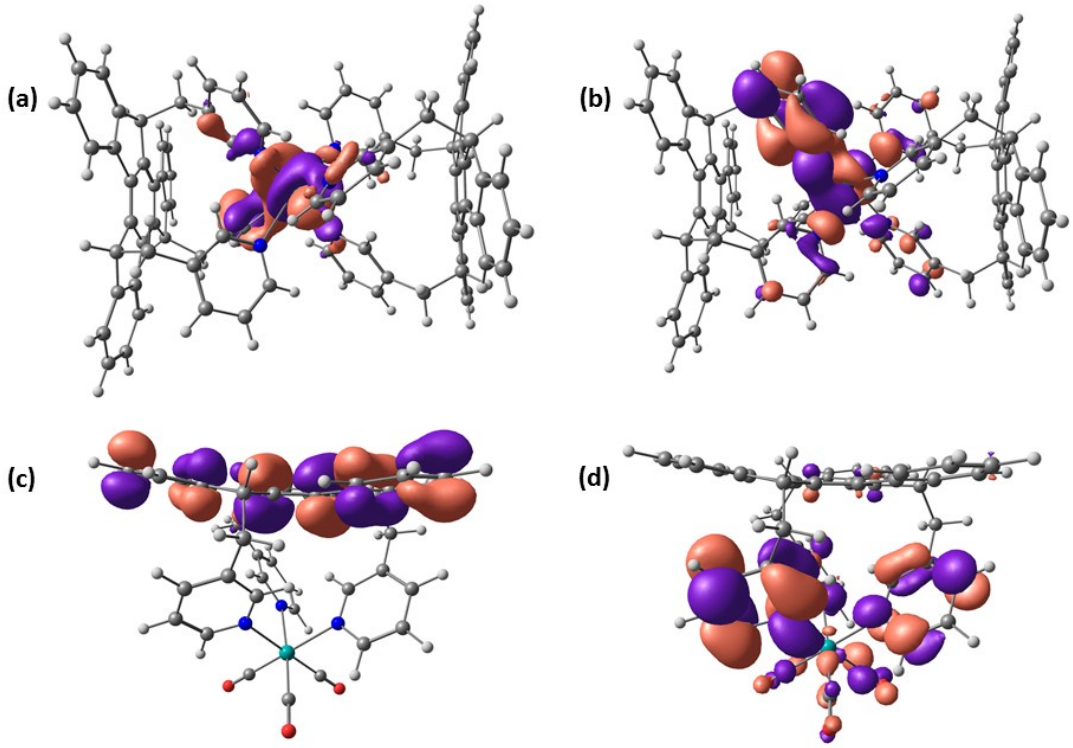


Figure S12: Calculated Kohn-Sham MOs of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{+}$ obtained from DFT [(B3LYP/ LANL2DZ ECP for Ru(II) and Re(I)) and (6-31g** for C,H,N,(O)] with CPCM(CH_3CN) and

0.5 eV threshold of degeneracy (orbitals are isocontoured at 0.03); (a) HOMO of $[\mathbf{1}]^{2+}$, (b) LUMO of $[\mathbf{1}]^{2+}$, (c) HOMO of $[\mathbf{2}]^{+}$, (d) LUMO of $[\mathbf{2}]^{+}$.

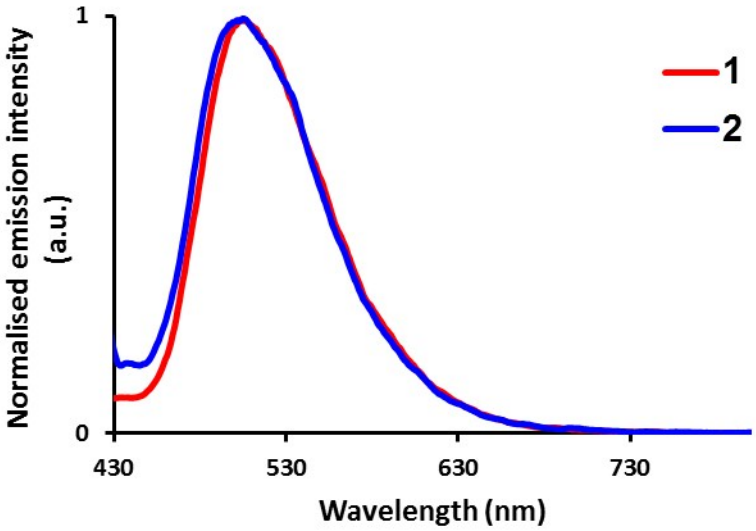


Figure S13: Normalised emission profiles of complexes **1** and **2** at r.t. in dry, degassed MeCN (λ_{ex} = 377 nm for **1** and 385 nm for **2**).

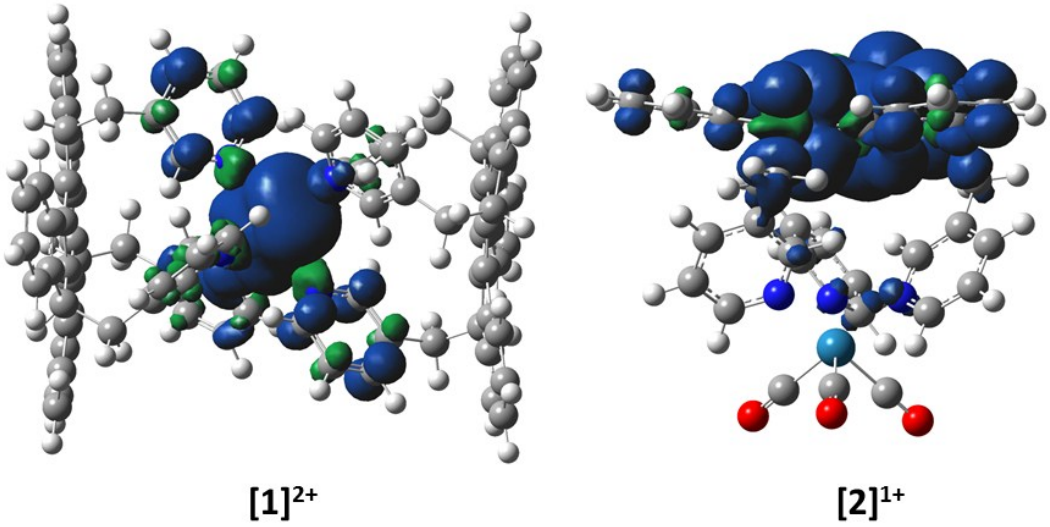


Figure S14: Unrestricted DFT calculated spin density plots of complex $[\mathbf{1}]^{2+}$ (left) and complex $[\mathbf{2}]^{+}$ (right).

Table S4: Optimized atomic coordinates of complex [**1**]$^{2+}$.

Ru	0.00000000	0.00000000	0.00000000
N	0.83035000	1.60430000	1.25828400
C	1.28776200	-0.56702900	5.73256500
C	1.14129300	0.82123500	5.71044700
C	2.20093900	1.90704300	5.69306800
H	2.92986800	1.76930600	6.50154100
C	1.37797100	3.16156200	5.91712000
C	1.81988900	4.46321600	6.12850600
H	2.88220500	4.69048500	6.16261200
C	0.87577900	5.48150100	6.31021500
H	1.20744600	6.50111000	6.48201800
C	2.47566800	-1.42932800	5.88945800
C	3.82972200	-1.12626200	6.07582400
H	4.18534300	-0.10217600	6.08048400
C	4.73833100	-2.16846300	6.28366000
H	5.78920700	-1.93870200	6.43273800
C	3.01697900	1.95072800	4.35437800
H	3.82355100	2.68041400	4.47617900
H	3.49082800	0.97716400	4.20187700
C	2.20543500	2.32028500	3.13295300
C	1.57375800	1.34099900	2.36084500
H	1.67829100	0.29885400	2.62629600
C	0.68602300	2.90421200	0.91197700
H	0.09231800	3.11296200	0.03661300
C	1.28280100	3.94328300	1.61433400
H	1.14153400	4.96317200	1.27472100
C	2.05887300	3.65303800	2.73100200
H	2.54565900	4.44843100	3.28498800
N	0.97418900	-1.52125400	1.25828400
C	-1.13494200	-0.83172000	5.73256500
C	0.14056400	-1.39900600	5.71044700
C	0.55107900	-2.85959000	5.69306800
H	0.06733000	-3.42199300	6.50154100
C	2.04900700	-2.77413800	5.91712000
C	2.95531400	-3.80767900	6.12850600
H	2.62097600	-4.84130600	6.16261200
C	4.30922900	-3.49919700	6.31021500
H	5.02640300	-4.29623400	6.48201800
C	-2.47566800	-1.42932800	5.88945800
C	-2.89023300	-2.75350600	6.07582400
H	-2.18115900	-3.57352600	6.08048400
C	-4.24711000	-3.01928300	6.28366000
H	-4.57356900	-4.04424900	6.43273800

C	0.18089100	-3.58814500	4.35437800
H	0.40953100	-4.65149900	4.47617900
H	-0.89916500	-3.51172800	4.20187700
C	0.90670900	-3.07010500	3.13295300
C	0.37446000	-2.03341400	2.36084500
H	-0.58033100	-1.60287000	2.62629600
C	2.17211000	-2.04621900	0.91197700
H	2.64974500	-1.63643000	0.03661300
C	2.77358300	-3.08257900	1.61433400
H	3.72746600	-3.47018300	1.27472100
C	2.13418700	-3.60955500	2.73100200
H	2.57962500	-4.42882100	3.28498800
N	-1.80453900	-0.08304600	1.25828400
C	-0.15282000	1.39874900	5.73256500
C	-1.28185700	0.57777100	5.71044700
C	-2.75201700	0.95254700	5.69306800
H	-2.99719800	1.65268700	6.50154100
C	-3.42697800	-0.38742300	5.91712000
C	-4.77520300	-0.65553800	6.12850600
H	-5.50318200	0.15082100	6.16261200
C	-5.18500800	-1.98230300	6.31021500
H	-6.23384900	-2.20487600	6.48201800
C	0.00000000	2.85865500	5.88945800
C	-0.93949000	3.87976800	6.07582400
H	-2.00418500	3.67570200	6.08048400
C	-0.49122100	5.18774600	6.28366000
H	-1.21563800	5.98295100	6.43273800
C	-3.19787000	1.63741600	4.35437800
H	-4.23308200	1.97108600	4.47617900
H	-2.59166300	2.53456400	4.20187700
C	-3.11214300	0.74982000	3.13295300
C	-1.94821800	0.69241500	2.36084500
H	-1.09796100	1.30401600	2.62629600
C	-2.85813300	-0.85799300	0.91197700
H	-2.74206300	-1.47653100	0.03661300
C	-4.05638300	-0.86070400	1.61433400
H	-4.86900000	-1.49298900	1.27472100
C	-4.19306000	-0.04348300	2.73100200
H	-5.12528400	-0.01961000	3.28498800
N	-0.83035000	-1.60430000	-1.25828400
C	-1.28776200	0.56702900	-5.73256500
C	-1.14129300	-0.82123500	-5.71044700
C	-2.20093900	-1.90704300	-5.69306800
H	-2.92986800	-1.76930600	-6.50154100
C	-1.37797100	-3.16156200	-5.91712000

C	-1.81988900	-4.46321600	-6.12850600
H	-2.88220500	-4.69048500	-6.16261200
C	-0.87577900	-5.48150100	-6.31021500
H	-1.20744600	-6.50111000	-6.48201800
C	-2.47566800	1.42932800	-5.88945800
C	-3.82972200	1.12626200	-6.07582400
H	-4.18534300	0.10217600	-6.08048400
C	-4.73833100	2.16846300	-6.28366000
H	-5.78920700	1.93870200	-6.43273800
C	-3.01697900	-1.95072800	-4.35437800
H	-3.82355100	-2.68041400	-4.47617900
H	-3.49082800	-0.97716400	-4.20187700
C	-2.20543500	-2.32028500	-3.13295300
C	-1.57375800	-1.34099900	-2.36084500
H	-1.67829100	-0.29885400	-2.62629600
C	-0.68602300	-2.90421200	-0.91197700
H	-0.09231800	-3.11296200	-0.03661300
C	-1.28280100	-3.94328300	-1.61433400
H	-1.14153400	-4.96317200	-1.27472100
C	-2.05887300	-3.65303800	-2.73100200
H	-2.54565900	-4.44843100	-3.28498800
N	-0.97418900	1.52125400	-1.25828400
C	1.13494200	0.83172000	-5.73256500
C	-0.14056400	1.39900600	-5.71044700
C	-0.55107900	2.85959000	-5.69306800
H	-0.06733000	3.42199300	-6.50154100
C	-2.04900700	2.77413800	-5.91712000
C	-2.95531400	3.80767900	-6.12850600
H	-2.62097600	4.84130600	-6.16261200
C	-4.30922900	3.49919700	-6.31021500
H	-5.02640300	4.29623400	-6.48201800
C	2.47566800	1.42932800	-5.88945800
C	2.89023300	2.75350600	-6.07582400
H	2.18115900	3.57352600	-6.08048400
C	4.24711000	3.01928300	-6.28366000
H	4.57356900	4.04424900	-6.43273800
C	-0.18089100	3.58814500	-4.35437800
H	-0.40953100	4.65149900	-4.47617900
H	0.89916500	3.51172800	-4.20187700
C	-0.90670900	3.07010500	-3.13295300
C	-0.37446000	2.03341400	-2.36084500
H	0.58033100	1.60287000	-2.62629600
C	-2.17211000	2.04621900	-0.91197700
H	-2.64974500	1.63643000	-0.03661300
C	-2.77358300	3.08257900	-1.61433400

H	-3.72746600	3.47018300	-1.27472100
C	-2.13418700	3.60955500	-2.73100200
H	-2.57962500	4.42882100	-3.28498800
N	1.80453900	0.08304600	-1.25828400
C	0.15282000	-1.39874900	-5.73256500
C	1.28185700	-0.57777100	-5.71044700
C	2.75201700	-0.95254700	-5.69306800
H	2.99719800	-1.65268700	-6.50154100
C	3.42697800	0.38742300	-5.91712000
C	4.77520300	0.65553800	-6.12850600
H	5.50318200	-0.15082100	-6.16261200
C	5.18500800	1.98230300	-6.31021500
H	6.23384900	2.20487600	-6.48201800
C	0.00000000	-2.85865500	-5.88945800
C	0.93949000	-3.87976800	-6.07582400
H	2.00418500	-3.67570200	-6.08048400
C	0.49122100	-5.18774600	-6.28366000
H	1.21563800	-5.98295100	-6.43273800
C	3.19787000	-1.63741600	-4.35437800
H	4.23308200	-1.97108600	-4.47617900
H	2.59166300	-2.53456400	-4.20187700
C	3.11214300	-0.74982000	-3.13295300
C	1.94821800	-0.69241500	-2.36084500
H	1.09796100	-1.30401600	-2.62629600
C	2.85813300	0.85799300	-0.91197700
H	2.74206300	1.47653100	-0.03661300
C	4.05638300	0.86070400	-1.61433400
H	4.86900000	1.49298900	-1.27472100
C	4.19306000	0.04348300	-2.73100200
H	5.12528400	0.01961000	-3.28498800

Table S5: Optimized atomic coordinates of complex [**2**]$^{+}$.

Re	-3.08604600	-0.00069200	-0.00155900
O	-4.88547200	1.32418200	-2.11899500
N	-1.75450900	-0.69905000	-1.71118100
C	-4.20195400	0.84252200	-1.31136100
C	-2.12272900	-1.77742100	-2.44180600
H	-2.99703500	-2.31951300	-2.10843500
C	-1.43253100	-2.18113800	-3.57559900
H	-1.77882400	-3.04526600	-4.13079600
C	-0.30946700	-1.46403200	-3.97781300
H	0.24099900	-1.76048800	-4.86430700
C	0.10628400	-0.35685000	-3.22950500
C	-0.66063100	-0.01259900	-2.11395700
H	-0.39221300	0.84920700	-1.51813600
C	1.33942800	0.43490400	-3.59993500
H	1.18753200	1.48892100	-3.35238800
H	1.48407000	0.38120700	-4.68332400
C	2.65999700	-0.05862300	-2.91292400
H	3.48104600	0.50840900	-3.36972900
C	2.65801700	0.09943900	-1.40279500
C	2.67899000	1.26099600	-0.62744100
C	2.84126000	2.68290600	-0.99039400
C	3.02747800	3.31500200	-2.22580300
H	3.02960200	2.75536800	-3.15414500
C	3.23825100	4.69673600	-2.25902600
H	3.38644400	5.19118200	-3.21448100
C	2.88127200	-1.55033000	-3.07863400
C	3.09772700	-2.26977200	-4.24914500
H	3.13671500	-1.76630200	-5.21158100
C	3.27921700	-3.65615900	-4.17227800
H	3.45465100	-4.22890800	-5.07797500
N	-1.75657000	-1.13428400	1.45869500
C	-2.12778700	-1.23111300	2.75680300
H	-3.00372200	-0.67339800	3.05858800
C	-1.43855800	-2.01170700	3.67358000
H	-1.78721100	-2.06272800	4.69864000
C	-0.31364900	-2.71628600	3.25491500
H	0.23633000	-3.33615900	3.95493500
C	0.10439100	-2.61952900	1.92287000
C	-0.66122200	-1.82471200	1.06665800
H	-0.39052300	-1.73778300	0.02312400
C	1.33845300	-3.33550100	1.42394400
H	1.18777000	-3.64881400	0.38737400
H	1.48251200	-4.24649800	2.01289300

C	2.65846000	-2.49321400	1.50956400
H	3.48020000	-3.17198300	1.24818400
C	2.65749900	-1.26438200	0.61771800
C	2.68022600	-1.17360100	-0.77581400
C	2.84431200	-2.19884700	-1.82541400
C	3.03211100	-3.58452000	-1.75428400
H	3.03402700	-4.10819700	-0.80517400
C	3.24506800	-4.30441100	-2.93370200
H	3.39444500	-5.37889200	-2.88357100
C	2.87709800	-1.89088000	2.88464200
C	3.09081800	-2.54488800	4.09340000
H	3.12967100	-3.63010800	4.13860700
C	3.26945100	-1.78518000	5.25609400
H	3.44264800	-2.28322700	6.20533000
N	-1.75603300	1.83063000	0.24945000
C	-2.12660300	3.00288800	-0.31695400
H	-3.00158300	2.98484200	-0.95215000
C	-1.43817000	4.18746100	-0.09856800
H	-1.78657700	5.10036400	-0.56774200
C	-0.31459100	4.17796700	0.72287500
H	0.23455400	5.09453100	0.91034400
C	0.10312600	2.97626000	1.30590400
C	-0.66196300	1.83714200	1.04504500
H	-0.39165300	0.89031000	1.49245900
C	1.33609900	2.90209100	2.17706100
H	1.18397600	2.16139800	2.96673500
H	1.48017900	3.86779400	2.67117700
C	2.65702600	2.55411600	1.40679800
H	3.47785900	2.66695800	2.12644800
C	2.65641700	1.16736600	0.78852700
C	2.67833400	-0.08488100	1.40674400
C	2.83997100	-0.48130600	2.81968500
C	3.02501400	0.27305300	3.98460100
H	3.02662300	1.35680600	3.96340200
C	3.23524800	-0.38839700	5.19823900
H	3.38240000	0.19224400	6.10407100
C	2.87742800	3.44375000	0.19799900
C	3.09153000	4.81751800	0.16079500
H	3.12946300	5.39878900	1.07840900
C	3.27163000	5.44491800	-1.07808400
H	3.44522200	6.51595600	-1.12094700
O	-4.88695700	-2.49568900	-0.09246500
C	-4.20283900	-1.55587700	-0.07789600
O	-4.88633000	1.17008600	2.20413700
C	-4.20265600	0.71181200	1.38315600

Table S6: Optimized atomic coordinates of the mono-oxidised complex **1**, i.e., $[\mathbf{1}]^{3+}$.

Ru	0.00004095	-0.00023206	-0.00035394
N	-1.24559117	-1.68150717	-0.62360399
C	-5.69096449	0.42099107	-1.34434405
C	-5.66891648	-0.94253403	-1.04580202
C	-5.65962852	-2.13925713	-1.97911009
H	-6.46325656	-2.07783011	-2.72299315
C	-5.89288355	-3.29356721	-1.02245402
C	-6.11822157	-4.63404431	-1.31826704
H	-6.16084558	-4.97637333	-2.34896012
C	-6.30274864	-5.54039436	-0.26689096
H	-6.48553265	-6.58849345	-0.48357898
C	-5.85450646	1.14619713	-2.61959114
C	-6.04063148	0.69449009	-3.93151924
H	-6.03756352	-0.36229799	-4.17300226
C	-6.25904452	1.62887617	-4.94824132
H	-6.40817752	1.28395215	-5.96702642
C	-4.31768442	-2.28355416	-2.77984116
H	-4.43251643	-3.10845822	-3.48942521
H	-4.15704139	-1.37647410	-3.36820320
C	-3.11032132	-2.55120320	-1.91155509
C	-2.31853725	-1.50384813	-1.43805706
H	-2.54697825	-0.48880705	-1.72413608
C	-0.94382617	-2.94854627	-0.24633496
H	-0.09974110	-3.08412329	0.40812409
C	-1.66428024	-4.04600834	-0.69146000
H	-1.36351323	-5.03777142	-0.37498997
C	-2.75108532	-3.85204031	-1.53756706
H	-3.31808638	-4.70083736	-1.90257109
N	-1.24756012	1.38389407	-1.14365303
C	-5.69206248	0.95171211	1.03633214
C	-5.67017545	1.37499214	-0.29383897
C	-5.66187842	2.78157525	-0.86391601
H	-6.46700049	3.39399831	-0.43996898
C	-5.89336447	2.52971823	-2.34214312
C	-6.11701346	3.45579831	-3.35575120
H	-6.15969345	4.51964139	-3.13734718
C	-6.30002946	2.99807527	-4.66647730
H	-6.48148651	3.70958433	-5.46629335
C	-5.85758547	1.69303117	2.30205323
C	-6.04705644	3.05458628	2.56688125
H	-6.04437742	3.79236633	1.77263119
C	-6.26871947	3.46706631	3.88414035

H	-6.42071648	4.52141639	4.09478537
C	-4.32137732	3.54928528	-0.58724399
H	-4.43793331	4.57624936	-0.94614202
H	-4.16158931	3.60486829	0.49264409
C	-3.11247624	2.93369022	-1.25286004
C	-2.32140819	1.99869013	-0.58323499
H	-2.55137922	1.73668512	0.43795409
C	-0.94428109	1.69254309	-2.42839713
H	-0.09953104	1.19422804	-2.87270716
C	-1.66350313	2.62858017	-3.15550618
H	-1.36093411	2.85201418	-4.17176626
C	-2.75093921	3.26344924	-2.56498114
H	-3.31693724	4.00510230	-3.11715818
N	-1.24448514	0.29999899	1.76674419
C	-5.69048749	-1.37549307	0.30559008
C	-5.66922446	-0.43508200	1.33723116
C	-5.66015849	-0.64470201	2.84036327
H	-6.46288556	-1.32076306	3.15902630
C	-5.89564951	0.76071110	3.36138631
C	-6.12269349	1.17466413	4.66992841
H	-6.16544249	0.45338308	5.48186148
C	-6.30958249	2.53812424	4.92875243
H	-6.49390148	2.87438227	5.94454051
C	-5.85432156	-2.84246818	0.31470408
C	-6.04151256	-3.75306424	1.36144816
H	-6.03848255	-3.43428422	2.39757024
C	-6.26150763	-5.10034535	1.05996914
H	-6.41173761	-5.81032841	1.86772920
C	-4.31758940	-1.26434108	3.36638032
H	-4.43268941	-1.46570710	4.43566040
H	-4.15653140	-2.22772716	2.87572528
C	-3.11059829	-0.37807803	3.16340830
C	-2.31576123	-0.49613306	2.02239021
H	-2.53948726	-1.25626111	1.29006115
C	-0.94605410	1.26505805	2.67141126
H	-0.10292302	1.90032909	2.46035125
C	-1.66827215	1.43118908	3.84290935
H	-1.36963312	2.20427814	4.54097940
C	-2.75434625	0.60093303	4.09947737
H	-3.32308329	0.71242005	5.01560244
N	1.24543608	1.68102805	0.62278911
C	5.69061439	-0.42055918	1.34482916
C	5.66843239	0.94297892	1.04638314
C	5.65880242	2.13962802	1.97978821
H	6.46221149	2.07821400	2.72390527

C	5.89221245	3.29402110	1.02327014
C	6.11744749	4.63448320	1.31924116
H	6.15988449	4.97671723	2.34997324
C	6.30208251	5.54093629	0.26797508
H	6.48479254	6.58902332	0.48478309
C	5.85381837	-1.14584924	2.62007725
C	6.03936543	-0.69422720	3.93211436
H	6.03610744	0.36254287	4.17367737
C	6.25743339	-1.62867328	4.94885744
H	6.40610944	-1.28381526	5.96773250
C	4.31658332	2.28377305	2.78011627
H	4.43106634	3.10876111	3.48965932
H	4.15587129	1.37671198	3.36848331
C	3.10954823	2.55114809	1.91131020
C	2.31779816	1.50365702	1.43808617
H	2.54577015	0.48875994	1.72506419
C	0.94421707	2.94786415	0.24443808
H	0.10075301	3.08317618	-0.41086397
C	1.66456714	4.04547423	0.68936911
H	1.36422914	5.03709331	0.37204408
C	2.75076922	3.85182919	1.53631817
H	3.31772528	4.70073225	1.90113220
N	1.24743903	-1.38472518	1.14286314
C	5.69242936	-0.95109522	-1.03589302
C	5.67029234	-1.37447425	0.29424108
C	5.66212735	-2.78110736	0.86418812
H	6.46761037	-3.39324942	0.44051409
C	5.89294235	-2.52934134	2.34253423
C	6.11622334	-3.45548142	3.35616531
H	6.15908733	-4.51930150	3.13769330
C	6.29863439	-2.99784639	4.66700841
H	6.47979737	-3.70940444	5.46684745
C	5.85852836	-1.69229228	-2.30161112
C	6.04850236	-3.05377239	-2.56646814
H	6.04580938	-3.79160545	-1.77226708
C	6.27071039	-3.46609942	-3.88368424
H	6.42310037	-4.52038851	-4.09434726
C	4.32199222	-3.54918139	0.58686510
H	4.43874122	-4.57619448	0.94555913
H	4.16262121	-3.60456640	-0.49309598
C	3.11258314	-2.93422133	1.25214815
C	2.32196510	-1.99863525	0.58279610
H	2.55288712	-1.73544723	-0.43787098
C	0.94302499	-1.69484420	2.42697624
H	0.09763994	-1.19734115	2.87097928

C	1.66184404	-2.63141628	3.15380130
H	1.35838401	-2.85599330	4.16954338
C	2.74997911	-3.26539135	2.56361325
H	3.31566514	-4.00749142	3.11551830
N	1.24501604	-0.30035210	-1.76707408
C	5.69020443	1.37604696	-0.30497897
C	5.66931839	0.43571589	-1.33670904
C	5.66058739	0.64541690	-2.83984216
H	6.46319544	1.32173394	-3.15825718
C	5.89665140	-0.75989621	-3.36087220
C	6.12423741	-1.17369325	-4.66937130
H	6.16701843	-0.45233819	-5.48123938
C	6.31162342	-2.53707835	-4.92822432
H	6.49637041	-2.87321538	-5.94397541
C	5.85388346	2.84303807	-0.31393897
C	6.04113748	3.75374913	-1.36057305
H	6.03823246	3.43507511	-2.39672913
C	6.26102153	5.10101123	-1.05893503
H	6.41130956	5.81108228	-1.86660709
C	4.31796930	1.26464697	-3.36625620
H	4.43329631	1.46594898	-4.43552328
H	4.15650931	2.22802404	-2.87571616
C	3.11120320	0.37802792	-3.16348619
C	2.31595814	0.49620594	-2.02277410
H	2.53917917	1.25670700	-1.29068904
C	0.94735500	-1.26601717	-2.67136915
H	0.10455193	-1.90170121	-2.46014913
C	1.66994105	-1.43223620	-3.84262823
H	1.37189902	-2.20578925	-4.54043829
C	2.75566416	-0.60151814	-4.09927026
H	3.32471720	-0.71313017	-5.01518333

Table S7: Optimized atomic coordinates of the mono-oxidised complex **2**, i.e., $[\mathbf{2}]^{2+}$.

Re	-3.11342927	-0.00557666	-0.02792100
O	-4.89040134	1.00350454	-2.33007218
N	-1.75364823	-0.93097883	-1.60466612
C	-4.21610831	0.64181547	-1.45569611
C	-2.09382735	-2.11294489	-2.16925316
H	-2.97173345	-2.60784587	-1.77725413
C	-1.37091533	-2.67901699	-3.20984225
H	-1.69715642	-3.62156404	-3.63387528
C	-0.24157620	-2.02197602	-3.68865328
H	0.33271582	-2.44671509	-4.50493134
C	0.14396792	-0.80711495	-3.10942424
C	-0.65774811	-0.30057486	-2.08486716
H	-0.42024302	0.65121320	-1.62938012
C	1.37712107	-0.06163199	-3.56840027
H	1.22571013	1.01456911	-3.45422826
H	1.53577107	-0.24752801	-4.63403935
C	2.70820814	-0.46677211	-2.83232721
H	3.52248324	0.04776787	-3.35708625
C	2.72042617	-0.10756708	-1.36655010
C	2.73783226	1.17407401	-0.76182706
C	2.90017537	2.51368811	-1.33527110
C	3.12260042	2.95001212	-2.64869820
H	3.16434937	2.25806407	-3.48109927
C	3.31540952	4.31155221	-2.87877322
H	3.49134957	4.66281722	-3.89036929
C	2.93909005	-1.96555624	-2.79353021
C	3.17033101	-2.83097132	-3.85492129
H	3.21871903	-2.46324130	-4.87559737
C	3.34927293	-4.19398744	-3.58671427
H	3.53340489	-4.88218050	-4.40560134
N	-1.79505924	-0.91808182	1.59437713
C	-2.16714225	-0.81276379	2.89136522
H	-3.04167628	-0.21282968	3.10269624
C	-1.48089125	-1.44448589	3.91899130
H	-1.83214527	-1.33801585	4.93871038
C	-0.35598722	-2.20574503	3.61663528
H	0.18764279	-2.71391710	4.40611534
C	0.06368281	-2.31434106	2.28557118
C	-0.70214121	-1.66447796	1.31534710
H	-0.43608019	-1.74688898	0.27042202
C	1.29663284	-3.10287821	1.90299415
H	1.15467580	-3.56050224	0.92024907
H	1.43529780	-3.92137928	2.61488120

C	2.62943500	-2.27404924	1.87296214
H	3.44508302	-2.99146836	1.72560814
C	2.65799308	-1.19320816	0.81238506
C	2.72759308	-1.30212817	-0.56335904
C	2.89370901	-2.44540427	-1.46593011
C	3.07766793	-3.81111439	-1.20318409
H	3.06995190	-4.20094942	-0.19232701
C	3.30037188	-4.67722947	-2.27257017
H	3.44806182	-5.73534955	-2.08268116
C	2.85878808	-1.47082520	3.13401724
C	3.07709506	-1.92591225	4.42359234
H	3.11138799	-2.98758733	4.64625136
C	3.26494714	-0.98470219	5.44540841
H	3.44056914	-1.32631023	6.46042451
N	-1.79290904	1.85255139	-0.02151900
C	-2.14820899	2.92702650	-0.76384006
H	-3.01804306	2.81891755	-1.39705911
C	-1.45010085	4.12575554	-0.72366705
H	-1.78762381	4.95962862	-1.32804610
C	-0.32987576	4.23177846	0.09487701
H	0.22516635	5.16232850	0.14396001
C	0.07215819	3.12908935	0.85775407
C	-0.70699695	1.97335732	0.77565106
H	-0.45988099	1.10680924	1.37381211
C	1.29801529	3.18076927	1.74252313
H	1.14033624	2.56096023	2.62892720
H	1.44201437	4.20540534	2.09596316
C	2.63654436	2.73676714	1.04685108
H	3.44604044	2.95555710	1.75424913
C	2.66254226	1.28051702	0.63583405
C	2.67772418	0.10802594	1.42915611
C	2.83441018	-0.07133309	2.85109722
C	3.03327626	0.86614397	3.89064330
H	3.04695733	1.93082105	3.69697528
C	3.24069724	0.39910292	5.17798240
H	3.39977931	1.10224396	5.98817345
C	2.88319343	3.44348318	-0.26917002
C	3.08056254	4.79893527	-0.50530104
H	3.08217359	5.51449631	0.31168903
C	3.29628259	5.22879728	-1.81925514
H	3.45941568	6.28308335	-2.01928615
O	-4.90110559	-2.50093172	0.20527202
C	-4.22223047	-1.56399670	0.09845401
O	-4.94722831	1.44799058	1.97230515
C	-4.25168730	0.88516749	1.23100710

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