Supporting Information Dalton Trans.

Synthesis and characterisation of chelated cationic $Re^{I}(CO)_3$*bis*(NHC)(WCA) complexes.

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1. Detailed Crystallographic Information

Single Crystal X-Ray Structure Determination of Compound 1a (CCDC 933791), Compound 1b (CCDC 933792), Compound 3b (CCDC 933793), Compound 3c (CCDC 933794).

General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ–CCD), a rotating anode (Bruker AXS, FR591) with MoK_α radiation (λ = 0.71073 Å) and a MONTEL-type focusing optic (compounds **1a**, **1b**) or a fine-focussed sealed tube respectively (compounds **3b**, **3c**) and a graphite monochromator by using the SMART software package.[1] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[2] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX[7] based on SIR-92[3] (compound **1a**) or the APEX 2 software[1] in conjunction with SHELXL-97[5] and SHELXLE.[8] Unless otherwise noticed, methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97[5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[4] Images of the crystal structures were generated by PLATON.[6]

Special:

1a: Full refinement was possible without running into problems.

1b: Full refinement was possible without running into problems.

3b: The PF6- anion is heavily disordered and could not be modeled adequately by split-position refinement (which is applied) or application of restraints (which had been tried intensively but due to non-improvement were not applied for the final refinement).Therefore A- alerts still remain.

3c: The unit cell contains 8 diethylether molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[6].

5a: Full refinement was possible without running into problems.

5d: Full refinement was possible without running into problems.

Compound 1a

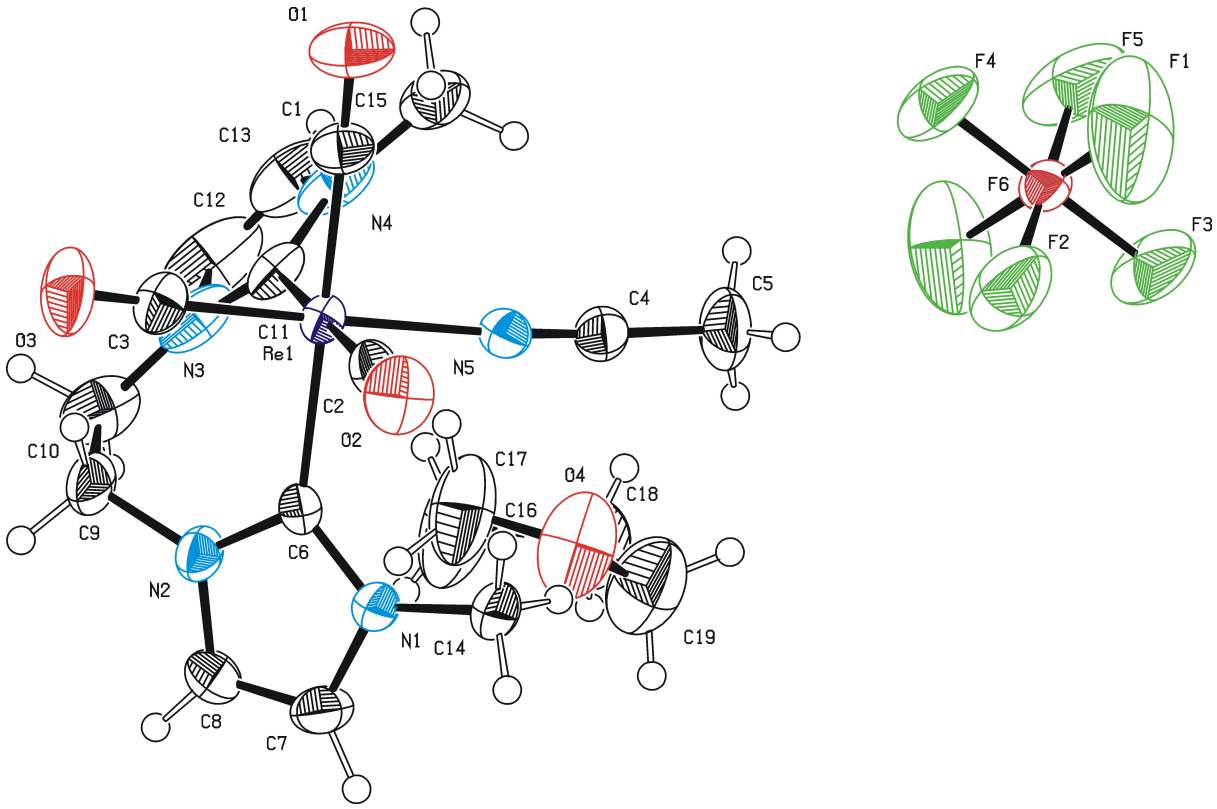

Figure S1 – Ortep drawing with 50% ellipsoids for complex **1a**.[6]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{19}\ H_{25}\ F_6\ N_5\ O_4\ P\ Re$ $[(C_{15}\ H_{17}\ N_5\ O_3\ Re)^+]$, $[(P\ F_6)^-]$, $C_4\ H_8\ O$
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.18 × 0.36 × 0.43 mm
Molecular Weight:	718.62 a.m.u.
F_{000}:	1400
Systematic Absences:	0kl: k+l≠2n; h0l: h≠2n; 00l: l≠2n
Space Group:	Orthorhombic $P\,na2_1$ (I.T.-No.: 33)
Cell Constants:	Least-squares refinement of 9833 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.92° < θ < 25.34°; Mo($K\overline{\alpha}$); λ = 71.073 pm a = 1767.69(7) pm b = 1330.06(5) pm c = 1099.01(4) pm V = 2583.92(17)· 10^6 pm^3; Z = 4; D_{calc} = 1.847 g cm^{-3}; Mos. = 0.69
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo($K\overline{\alpha}$)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	1.92° < θ < 25.34°; h: -21/21, k: -16/16, l: -13/12
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 9 runs; 2274 films / scaled: 9 runs; 2274 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 1.00°; dx = 40.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Correction:	Multi-scan; during scaling; μ = 4.842 mm^{-1} [2] Correction Factors: T_{min} = 0.3761 T_{max} = 0.7452
Reflection Data:	100127 reflections were integrated and scaled 4586 reflections systematic absent and rejected

	95541	reflections to be merged
	4700	independent reflections
	0.051	R_{int}: (basis F_o^2)
	4700	independent reflections (all) were used in refinements
	4521	independent reflections with $I_o > 2\sigma(I_o)$
	99.3 %	completeness of the data set
	329	parameter full-matrix refinement
	14.3	reflections per parameter

Solution: Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters: In the asymmetric unit:

36 Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms: In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98, 99 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme: $w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$

with a: 0.0167; b: 5.5662; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3

Shift/Err: Less than 0.001 in the last cycle of refinement:

Resid. Electron Density: +0.99 $e_{0;}^-$/Å^3; -0.91 $e_{0;}^-$/Å^3

R1: $\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[$F_o > 4\sigma(F_o)$;	N=4521]:	= 0.0210
[all reflctns;	N=4700]:	= 0.0229

wR2: $[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

[$F_o > 4\sigma(F_o)$;	N=4521]:	= 0.0515
[all reflctns;	N=4700]:	= 0.0530

Goodness of fit: $[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$ = 1.142

Flack's Parameter : x = 0.240(8)

Remarks: Refinement expression $\Sigma w(F_o^2-F_c^2)^2$

The correct enantiomere is proved by Flack's Parameter.

Compound 1b

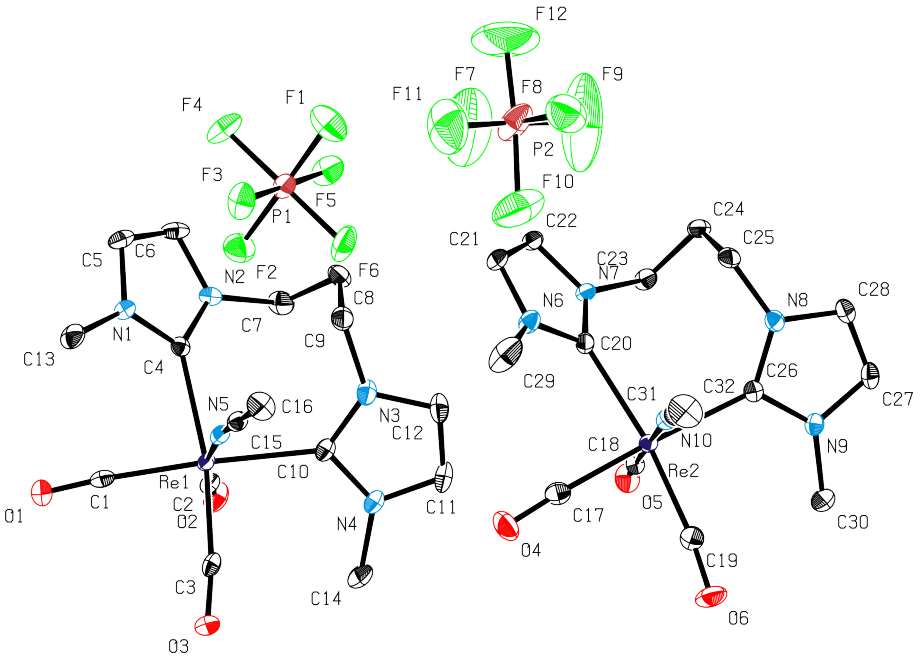

Figure S2. Ortep drawing with 50% ellipsoids for complex **1b**.[6]

Table S2. Crystal data and details of the structure determination of complex **1b**.

Crystal Data			
Formula		C16 H19 N5 O3 Re, F6 P	
Formula Weight			660.54
Crystal System			Triclinic
Space group		P-1	(No. 2)
a, b, c [Angstrom]	11.6963(4)	12.6367(4)	15.3154(5)
alpha, beta, gamma [deg]	98.234(2)	98.282(2)	90.816(2)
V [Ang**3]			2215.55(13)
Z			4
D(calc) [g/cm**3]			1.980
Mu(MoKa) [/mm]			5.635
F(000)			1272
Crystal Size [mm]		0.04 x 0.09 x 0.13	
Data Collection			
Temperature (K)			100
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			1.4, 25.4
Dataset		-14: 14 ; -15: 15 ; -18: 18	
Tot., Uniq. Data, R(int)		91463, 8099, 0.031	
Observed data [I > 2.0 sigma(I)]			7397
Refinement			
Nref, Npar			8099, 583
R, wR2, S		0.0206, 0.0481, 1.04	
w = 1/[\s^2^(Fo^2^)+(0.0175P)^2^+8.0068P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error			0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]			-0.94, 1.72

Compound 3b

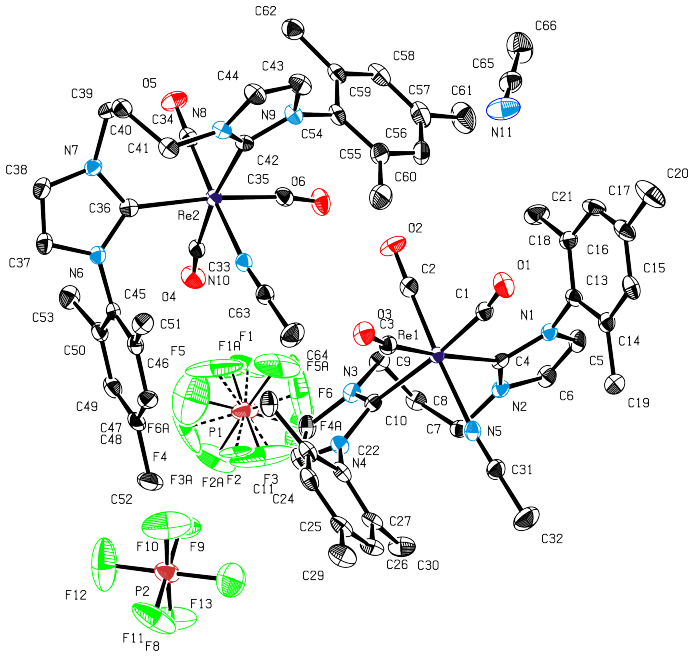

Figure S3. Ortep drawing with 50% ellipsoids for complex **3b**.[6]

Table S3. Crystal data and details of the structure determination of complex **3b**.

Crystal Data			
Formula	2(C32 H35 N5 O3 Re), 2(F6 P), C2 H3 N		
Formula Weight			1778.71
Crystal System			Monoclinic
Space group		P21/n	(No. 14)
a, b, c [Angstrom]	9.8542(1)	24.3821(3)	29.5971(4)
alpha, beta, gamma [deg]	90	96.311(1)	90
V [Ang**3]			7068.08(15)
Z			4
D(calc) [g/cm**3]			1.671
Mu(MoKa) [/mm]			3.557
F(000)			3528
Crystal Size [mm]		0.08 x 0.22 x 0.55	
Data Collection			
Temperature (K)			123
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			1.4, 25.5
Dataset		-11: 11 ; -29: 29 ; -35: 35	
Tot., Uniq. Data, R(int)		189575, 13124,	0.057
Observed data [I > 2.0 sigma(I)]			11348
Refinement			
Nref, Npar			13124, 962
R, wR2, S		0.0219, 0.0461,	1.03
w = 1/[\s^2^(Fo^2^)+(0.0175P)^2^+8.6376P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error			0.05, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]			-0.48, 0.94

Compound 3c

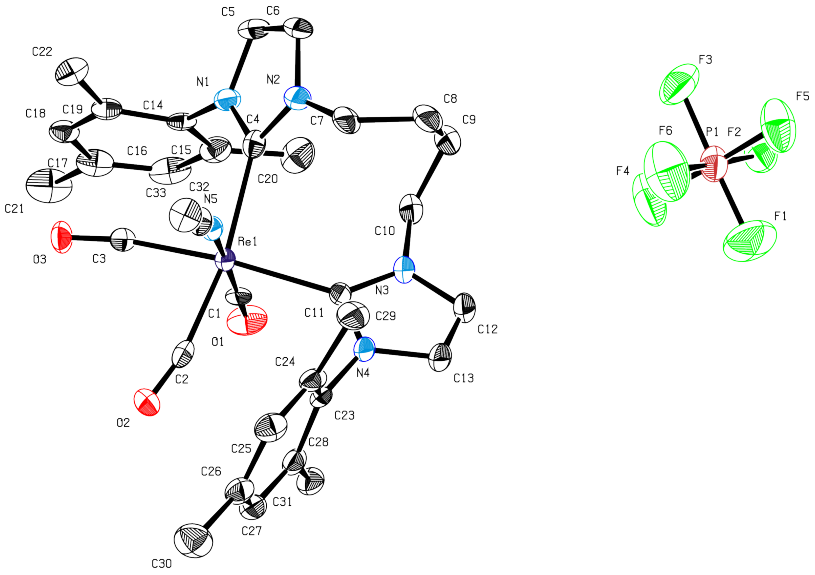

Figure S4. Ortep drawing with 50% ellipsoids for complex **3c**.[6]

Table S4. Crystal data and details of the structure determination of complex **3c**.

Crystal Data			
Formula		C33 H37 N5 O3 Re, F6 P	
Formula Weight			882.86
Crystal System			Monoclinic
Space group		C2/c	(No. 15)
a, b, c [Angstrom]	33.2454(9)	8.9066(2)	27.3469(8)
alpha, beta, gamma [deg]	90	101.758(1)	90
V [Ang**3]			7927.6(4)
Z			8
D(calc) [g/cm**3]			1.479
Mu(MoKa) [/mm]			3.170
F(000)			3504
Crystal Size [mm]		0.40 x 0.40 x 0.55	

Data Collection			
Temperature (K)			123
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			1.5, 25.5
Dataset		-39: 37 ; -10: 10 ; -32: 32	
Tot., Uniq. Data, R(int)		48269, 7320,	0.034
Observed data [I > 2.0 sigma(I)]			6969

Refinement			
Nref, Npar			7320, 449
R, wR2, S		0.0437, 0.0841, 1.29	
w = 1/[\s^2^(Fo^2^)+(0.0029P)^2^+93.1056P] where P=(Fo^2^+2Fc^2^)/			
Max. and Av. Shift/Error			0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]			-1.87, 1.88

Compound 5a

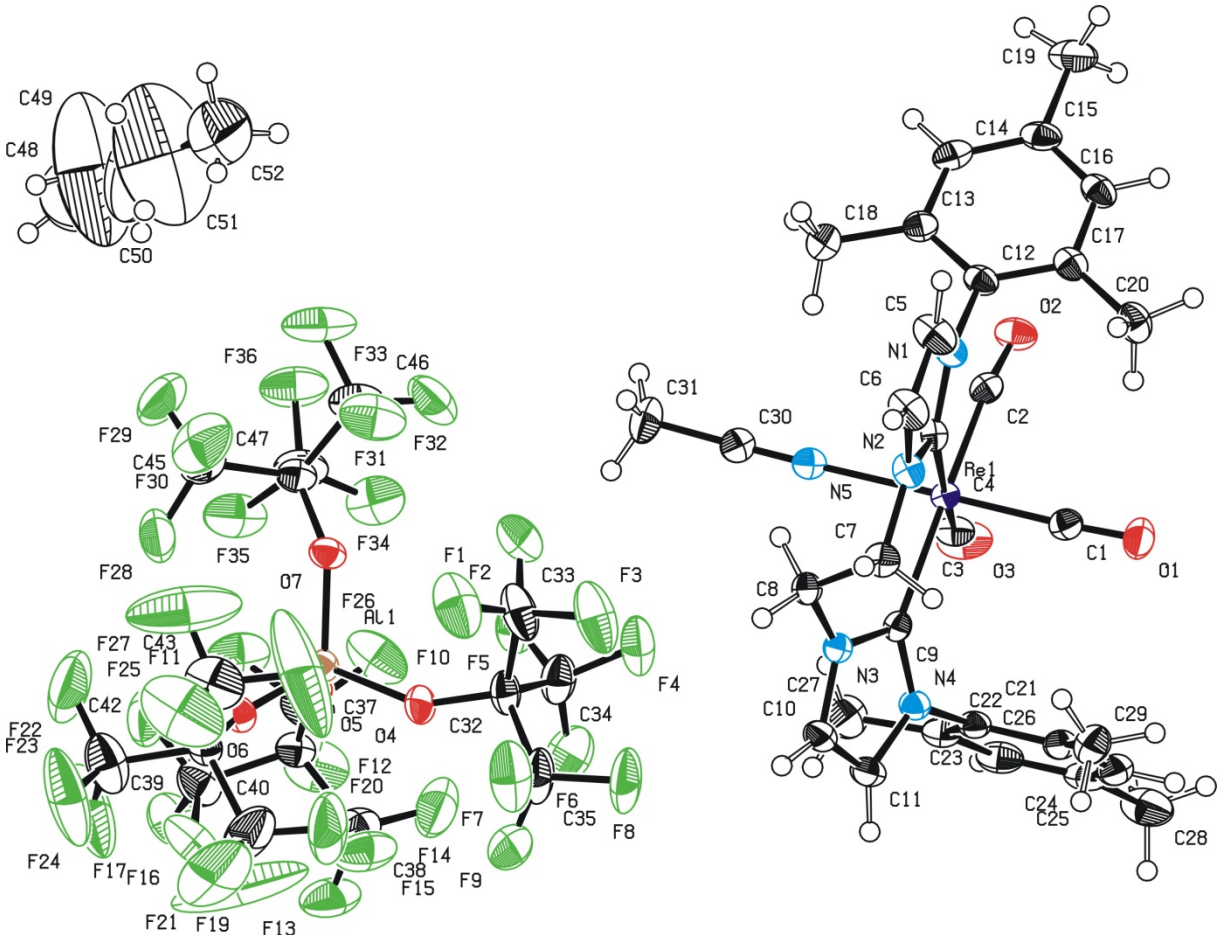

Figure S5 – Ortep drawing with 50% ellipsoids for complex **5a**.[6]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{52}\ H_{45}\ Al\ F_{36}\ N_5\ O_7\ Re$ $[(C_{31}\ H_{33}\ N_5\ O_3\ Re)^+]$, $[(C_{16}\ Al\ F_{36}\ O_4)^-]$, $(C_5\ H_{12})$
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.20 × 0.38 × 0.41 mm
Molecular Weight:	1749.12 a.m.u.
F_{000}:	3440
Systematic Absences:	h0l: l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\ 2_1/c$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9873 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.35° < θ < 25.37°; Mo(K$\overline{\alpha}$); λ = 71.073 pm a = 1548.58(4) pm b = 2816.84(8) pm β = 103.6769(10)° c = 1524.05(4) pm V = 6459.6(3)· 10^6 pm^3; Z = 4; D_{calc} = 1.799 g cm^{-3}; Mos. = 0.66
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(K$\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	1.35° < θ < 25.37°; h: -18/18, k: -33/33, l: -18/18
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 9 runs; 3579 films / scaled: 9 runs; 3579 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 60.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]

Absorption Correction:	Multi-scan; during scaling; μ = 2.052 mm^{-1} [2]	
	Correction Factors:	T_{min} = 0.5442 T_{max} = 0.7452
Reflection Data:	107191	reflections were integrated and scaled
	1380	reflections systematic absent and rejected
	105811	reflections to be merged
	11853	independent reflections
	0.026	R_{int}: (basis F_o^2)
	11853	independent reflections (all) were used in refinements
	11086	independent reflections with $I_o > 2\sigma(I_o)$
	99.9 %	completeness of the data set
	928	parameter full-matrix refinement
	12.8	reflections per parameter
Solution:	Direct Methods [3]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	102	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98, 99 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$	
	with a: 0.0275; b: 22.3170; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	+1.38 e_0^-/Å^3; -1.05 e_0^-/Å^3	
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$; N=11086]:		= 0.0310
[all reflctns; N=11853]:		= 0.0337
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=11086]:		= 0.0721
[all reflctns; N=11853]:		= 0.0743
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.032
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$	

Compound 5d

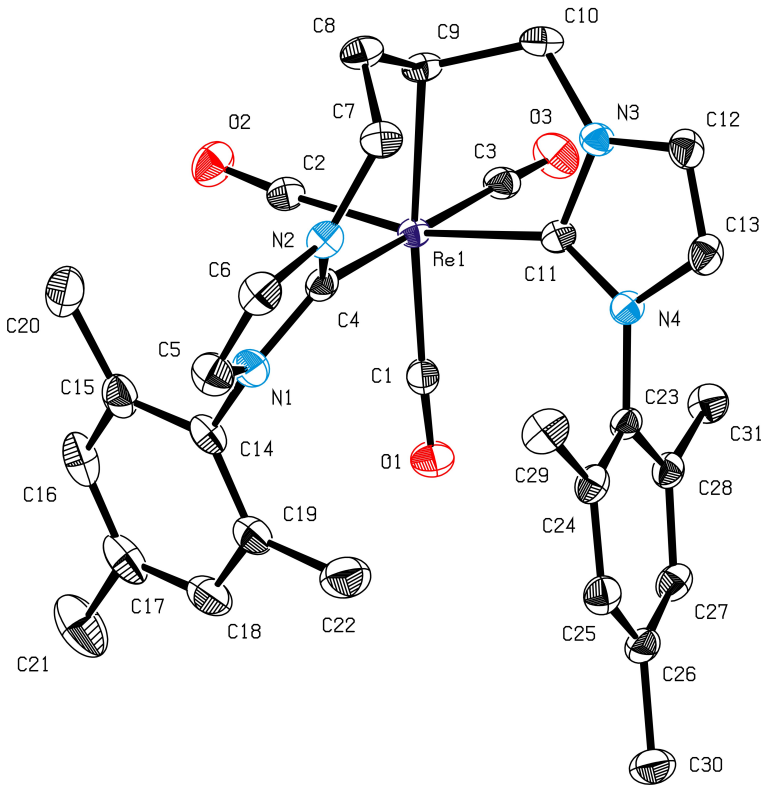

Figure S6 – Ortep drawing with 50% ellipsoids for complex **5d**.[6]

Operator:	*** Herdtweck ***
Molecular Formula:	C_{31} H_{33} N_4 O_3 Re
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.18 × 0.30 × 0.48 mm
Molecular Weight:	695.82 a.m.u.
F_{000}:	2768
Systematic Absences:	hkl: h+k≠2n; h0l: l≠2n
Space Group:	Monoclinic *C* 2/*c* (I.T.-No.: 15)
Cell Constants:	Least-squares refinement of 9321 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.21° < θ < 25.47°; Mo(K $\overline{\alpha}$); λ = 71.073 pm *a* = 3687.60(8) pm *b* = 851.27(2) pm β = 114.3982(8)° *c* = 2002.87(5) pm *V* = 5725.8(2)· 10^6 pm^3; *Z* = 8; D_{calc} = 1.614 g cm^{-3}; Mos. = 0.64
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(K $\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	1.21° < θ < 25.47°; h: -44/44, k: -10/10, l: -24/24
Measurement Time:	2 × 5.0 s per film
Measurement Mode:	measured: 12 runs; 6302 films / scaled: 12 runs; 6302 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 60.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Correction:	Multi-scan; during scaling; μ = 4.283 mm^{-1} [2] Correction Factors: T_{min} = 0.4028 T_{max} = 0.7452
Reflection Data:	74150 reflections were integrated and scaled 3442 reflections systematic absent and rejected 70708 reflections to be merged 5301 independent reflections 0.035 R_{int}: (basis F_o^2) 5301 independent reflections (all) were used in refinements

5170	independent reflections with $I_o > 2\sigma(I_o)$
99.8 %	completeness of the data set
358	parameter full-matrix refinement
14.8	reflections per parameter

Solution: Direct Methods [3]; Difference Fourier syntheses

Refinement Parameters: In the asymmetric unit:
39 Non-hydrogen atoms with anisotropic displacement parameters

Hydrogen Atoms: In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98, 99, 100 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors: For neutral atoms and anomalous dispersion [4]

Extinction Correction: no

Weighting Scheme: $w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$
with a: 0.0131; b: 10.6504; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3

Shift/Err: Less than 0.001 in the last cycle of refinement:

Resid. Electron Density: +0.60 $e_{0;}^-$ /Å^3; -0.68 $e_{0;}^-$ /Å^3

R1: $\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[$F_o > 4\sigma(F_o)$;	N=5170]:	= 0.0138
[all reflctns;	N=5301]:	= 0.0143

wR2: $[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

[$F_o > 4\sigma(F_o)$;	N=5170]:	= 0.0342
[all reflctns;	N=5301]:	= 0.0345

Goodness of fit: $[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$ = 1.102

Remarks: Refinement expression $\Sigma w(F_o^2-F_c^2)^2$

2. Details of DFT Calculations

All calculations were performed with GAUSSIAN-09.[7]

*a) Coordinates and Energies of the Isomers of Compound **1b***

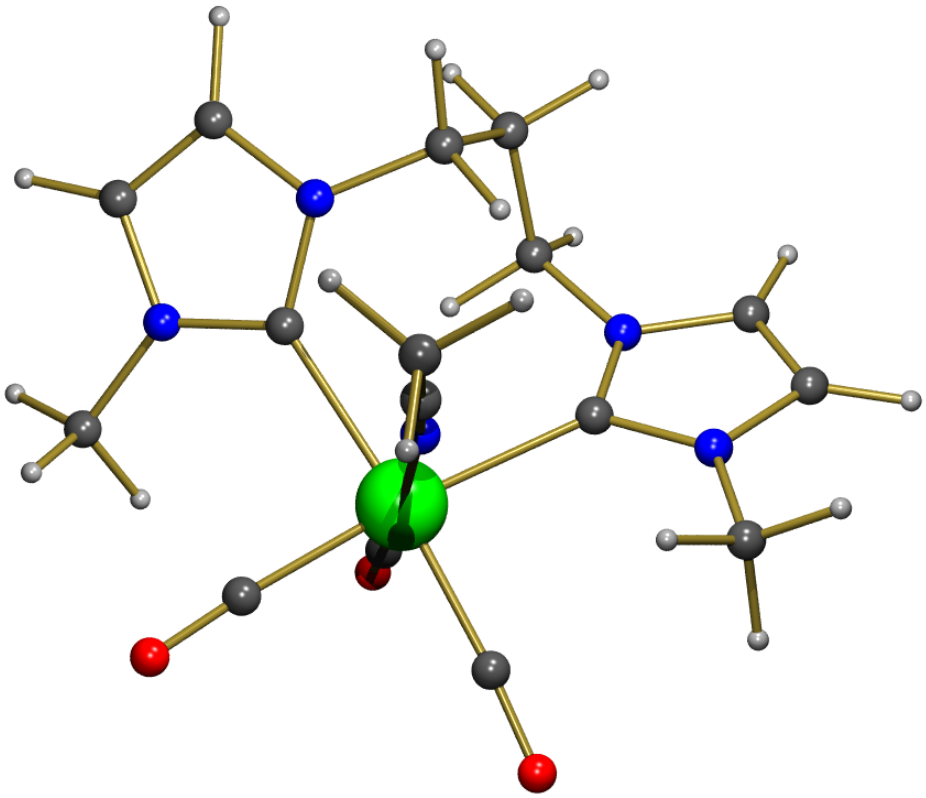

Figure S7. Ground State **1b_GS1** (Enantionmer of **1b_GS3**).

Table S5. Coordinates and Energies of **1b_GS1** (Enantionmer of **1b_GS3**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	75	0	-0.004770	-0.758941	-0.305098
2	8	0	-1.962175	-3.174330	-0.191997
3	8	0	2.060698	-2.950220	-1.091455
4	8	0	-0.493823	-0.195958	-3.299421
5	7	0	-3.001339	0.545464	-0.169959
6	7	0	-1.675324	1.802071	0.961079
7	7	0	1.642737	2.068804	-0.720349
8	7	0	2.962998	0.571431	0.072161
9	7	0	0.256577	-1.008636	1.841630
10	6	0	-1.682594	0.670452	0.187117
11	6	0	-3.777347	1.553690	0.379811
12	1	0	-4.843225	1.607717	0.221823
13	6	0	-2.944201	2.349363	1.088037
14	1	0	-3.132947	3.243701	1.661594

15	6	0	-0.488625	2.539892	1.392664
16	1	0	-0.741342	3.064749	2.318543
17	1	0	0.298735	1.821117	1.619286
18	6	0	-0.039409	3.545538	0.321269
19	1	0	0.762586	4.165539	0.740066
20	1	0	-0.869805	4.218619	0.076680
21	6	0	0.451090	2.878478	-0.973139
22	1	0	-0.314189	2.239418	-1.413029
23	1	0	0.713897	3.637947	-1.714557
24	6	0	2.906589	2.638611	-0.676336
25	1	0	3.095009	3.650762	-0.999517
26	6	0	3.737849	1.692774	-0.182655
27	1	0	4.801151	1.709187	-0.000289
28	6	0	1.650079	0.775756	-0.267463
29	6	0	-1.279373	-2.241272	-0.249709
30	6	0	0.317004	-1.223834	2.978185
31	6	0	0.384868	-1.514396	4.405420
32	1	0	-0.559453	-1.243359	4.888467
33	1	0	1.197973	-0.948355	4.870962
34	1	0	0.564484	-2.583690	4.557939
35	6	0	1.332908	-2.109934	-0.768800
36	6	0	-0.299087	-0.428646	-2.180610
37	6	0	-3.604532	-0.475985	-1.031457
38	1	0	-3.833906	-1.381516	-0.467052
39	1	0	-4.529243	-0.067286	-1.442755
40	1	0	-2.935063	-0.715547	-1.855219
41	6	0	3.564620	-0.643975	0.623637
42	1	0	3.911285	-1.306556	-0.172174
43	1	0	4.415535	-0.353014	1.243459
44	1	0	2.840068	-1.167773	1.243361

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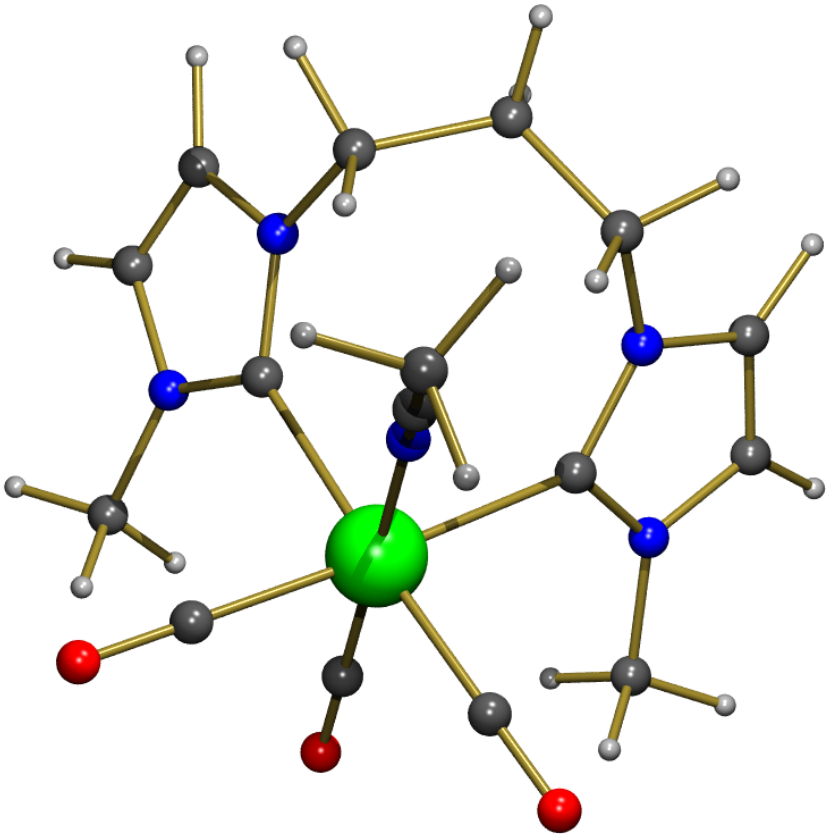

Figure S8. Ground State **1b_GS2** (Diastereomer of **1b_GS1** and **1b_GS3**).

Table S6. Coordinates and Energies of **1b_GS2** (Diastereomer of **1b_GS1** and **1b_GS3**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	75	0	-0.814164	-0.004290	0.001609
2	8	0	-2.850166	-2.292408	0.585221
3	8	0	-2.876495	2.243053	0.646825
4	7	0	0.769866	-2.425678	-1.514451
5	7	0	1.958867	-1.804744	0.163800
6	7	0	1.936951	1.822007	0.209383
7	7	0	0.741166	2.473963	-1.452223
8	6	0	-2.098263	-1.440994	0.370602
9	6	0	0.760655	-1.554136	-0.455206
10	6	0	1.943259	-3.160713	-1.564586
11	1	0	2.128161	-3.895639	-2.332221
12	6	0	2.692042	-2.772873	-0.509387
13	1	0	3.657460	-3.108185	-0.163960
14	6	0	2.422980	-1.305305	1.460849
15	1	0	3.051366	-2.099141	1.873623
16	1	0	1.558072	-1.215005	2.116291
17	6	0	3.228330	0.000967	1.439834
18	1	0	3.914229	0.016574	0.584795
19	1	0	3.856360	-0.006274	2.339634

20	6	0	2.404699	1.294808	1.494005
21	1	0	3.020431	2.086087	1.930110
22	1	0	1.539211	1.174288	2.143558
23	6	0	0.741320	1.575161	-0.415966
24	6	0	1.906960	3.222127	-1.483120
25	1	0	2.084089	3.978651	-2.231374
26	6	0	2.660037	2.814664	-0.438387
27	1	0	3.621983	3.150868	-0.084233
28	6	0	-2.114959	1.406580	0.408785
29	6	0	-0.331292	2.732618	-2.416018
30	1	0	-1.299919	2.691546	-1.920657
31	1	0	-0.190060	3.738843	-2.814314
32	1	0	-0.307640	2.017069	-3.239109
33	6	0	-0.299989	-2.669809	-2.484822
34	1	0	-0.285330	-1.930857	-3.287114
35	1	0	-0.146960	-3.662557	-2.911536
36	1	0	-1.268599	-2.654261	-1.987923
37	7	0	-0.493998	-0.032322	2.200596
38	6	0	-0.670838	-0.050256	3.346538
39	6	0	-0.914539	-0.072491	4.783618
40	1	0	-0.057133	-0.503357	5.310568
41	1	0	-1.083922	0.945383	5.149603
42	1	0	-1.801973	-0.677234	4.998103
43	6	0	-1.419871	0.015916	-1.810271
44	8	0	-1.870923	0.027453	-2.882431

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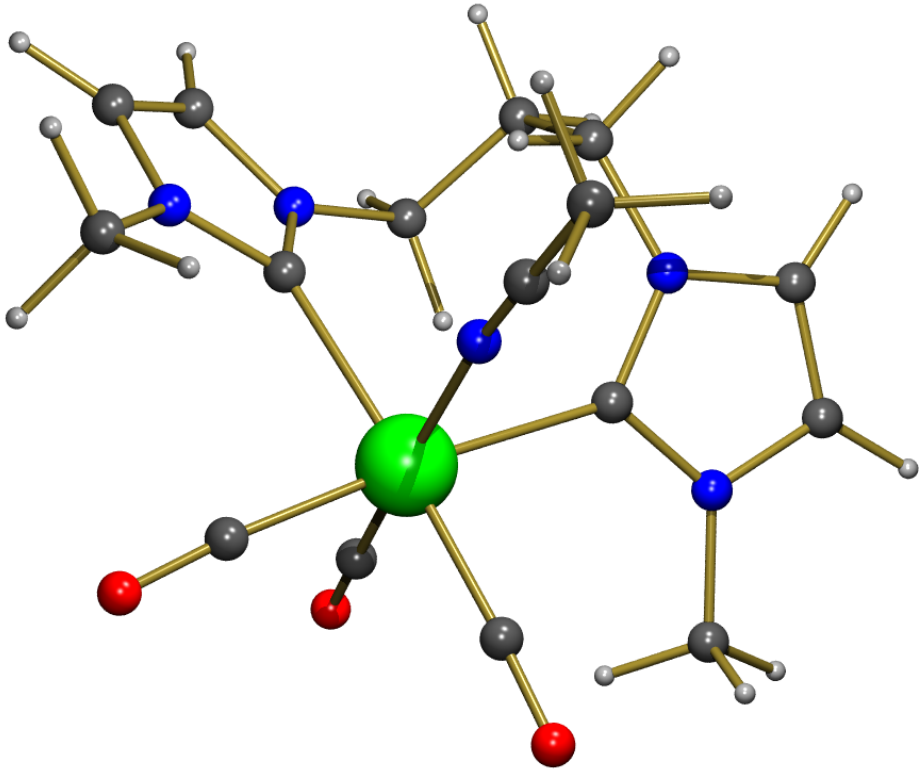

Figure S9. Ground State **1b_GS3** (Enantionmer of **1b_GS1**).

Table S7. Coordinates and Energies of **1b_GS3** (Enantionmer of **1b_GS1**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	75	0	0.004535	-0.758736	-0.305406
2	8	0	0.493319	-0.195540	-3.299742
3	8	0	-2.060014	-2.951858	-1.088994
4	8	0	1.961929	-3.174094	-0.191885
5	7	0	-0.257106	-1.008791	1.841276
6	7	0	-2.963016	0.572393	0.071261
7	7	0	-1.641931	2.069740	-0.719900
8	7	0	1.675853	1.801150	0.961899
9	7	0	3.001450	0.544886	-0.170015
10	6	0	0.298711	-0.428321	-2.180930
11	6	0	-1.332971	-2.110132	-0.768403
12	6	0	-0.317978	-1.224570	2.977698
13	6	0	-0.386349	-1.515817	4.404764
14	1	0	-0.568282	-2.584807	4.556677
15	1	0	-1.198167	-0.948275	4.870730
16	1	0	0.558615	-1.247124	4.887869
17	6	0	-1.649895	0.776447	-0.267713
18	6	0	-3.737387	1.694134	-0.183258
19	1	0	-4.800756	1.710812	-0.001308
20	6	0	-2.905605	2.639954	-0.676091
21	1	0	-3.093541	3.652352	-0.998781

22	6	0	-0.449938	2.879128	-0.971964
23	1	0	-0.712308	3.639071	-1.713053
24	1	0	0.315221	2.240027	-1.412011
25	6	0	0.040484	3.545380	0.322891
26	1	0	-0.761454	4.165323	0.741888
27	1	0	0.871058	4.218424	0.078797
28	6	0	0.489338	2.539066	1.393814
29	1	0	0.742127	3.063375	2.319984
30	1	0	-0.298230	1.820378	1.619990
31	6	0	1.682769	0.670001	0.187251
32	6	0	3.777763	1.552582	0.380303
33	1	0	4.843643	1.606423	0.222260
34	6	0	2.944880	2.348039	1.089084
35	1	0	3.133902	3.241996	1.663145
36	6	0	1.279055	-2.241110	-0.249976
37	6	0	3.604285	-0.476152	-1.032254
38	1	0	4.528881	-0.067303	-1.443661
39	1	0	3.833791	-1.381996	-0.468407
40	1	0	2.934499	-0.715238	-1.855896
41	6	0	-3.565235	-0.643134	0.621802
42	1	0	-4.416853	-0.352308	1.240717
43	1	0	-3.911016	-1.305557	-0.174521
44	1	0	-2.841385	-1.167056	1.242251

HF=-1199.5796893/NImag=0
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b) Coordinates and Energies of the connecting transition states of all the isomers of ***1b***

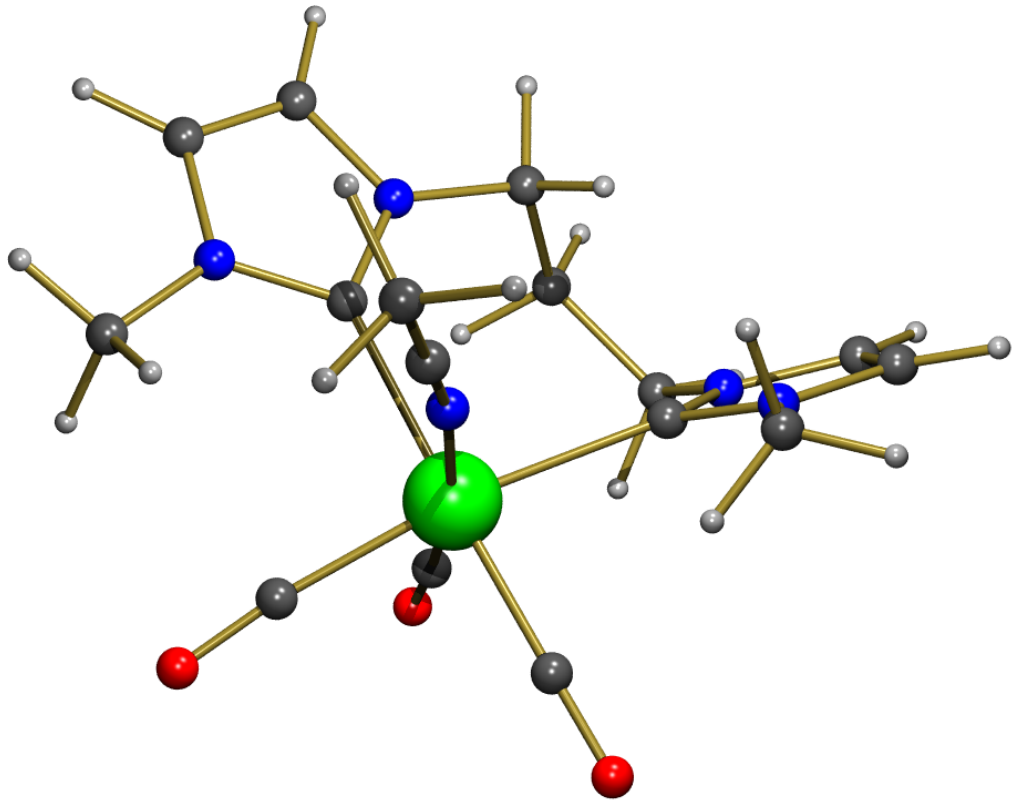

Figure S10. Transition state **1b_TS12.**

Table S8. Coordinates and Energies of Transition state **1b_TS12.**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.920577	0.513999	0.844643
2	7	0	2.744358	0.772538	0.155731
3	6	0	1.798488	-0.194161	0.383572
4	7	0	2.444367	-1.068507	1.221205
5	6	0	3.732163	-0.645489	1.513327
6	6	0	2.611248	1.951397	-0.704348
7	6	0	1.595188	3.025819	-0.217803
8	6	0	0.878007	2.738304	1.116660
9	7	0	-0.555439	2.447756	0.982448
10	6	0	-1.144511	1.338139	0.433414
11	7	0	-2.484007	1.578884	0.613576
12	6	0	-2.710010	2.795709	1.234439
13	6	0	-1.496296	3.343802	1.465939
14	6	0	-3.605783	0.732231	0.207207
15	6	0	1.930187	-2.324005	1.764170
16	75	0	-0.220728	-0.461166	-0.581182
17	6	0	0.603976	-2.050844	-1.377003

18	8	0	1.098464	-2.986877	-1.841562
19	7	0	-0.974502	-1.533962	1.167269
20	6	0	-1.514549	-2.104515	2.018527
21	6	0	-2.190864	-2.834952	3.084264
22	6	0	0.207736	0.583403	-2.137860
23	8	0	0.392884	1.219574	-3.091039
24	6	0	-1.866761	-0.962054	-1.511132
25	8	0	-2.778404	-1.342774	-2.115276
26	1	0	-1.465539	-3.414319	3.664951
27	1	0	-2.927152	-3.522864	2.655762
28	1	0	-2.703511	-2.137496	3.754528
29	1	0	-3.703075	3.156871	1.451002
30	1	0	-1.218796	4.276521	1.931127
31	1	0	0.936192	3.617793	1.760351
32	1	0	1.344872	1.919610	1.663794
33	1	0	2.133691	3.973202	-0.119586
34	1	0	0.843230	3.184144	-0.994847
35	1	0	3.609932	2.389150	-0.755769
36	1	0	2.369753	1.619636	-1.711625
37	1	0	4.391820	-1.210063	2.153473
38	1	0	4.780123	1.162589	0.780889
39	1	0	1.303680	-2.823357	1.028712
40	1	0	2.778846	-2.970162	1.996170
41	1	0	1.357423	-2.145770	2.677954
42	1	0	-3.422795	-0.302878	0.490076
43	1	0	-4.499984	1.084852	0.724305
44	1	0	-3.773898	0.792946	-0.869264

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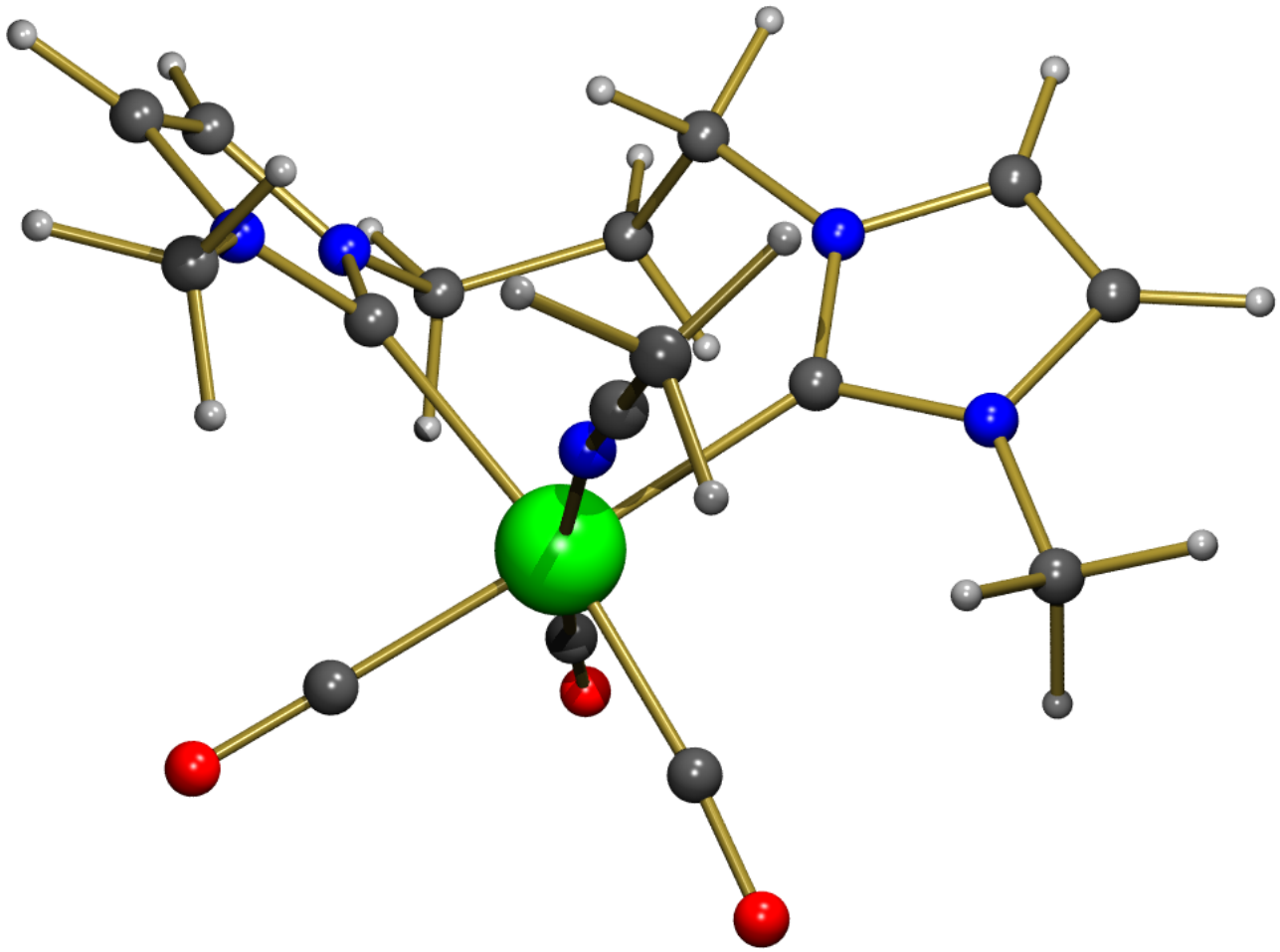

Figure S11. Transition state **1b_TS23**.

Table S9. Coordinates and Energies of Transition state **1b_TS23**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.498160	3.343182	1.465189
2	7	0	0.556810	2.447453	0.982070
3	6	0	1.145278	1.337533	0.432995
4	7	0	2.484921	1.577794	0.612706
5	6	0	2.711590	2.794584	1.233383
6	6	0	-0.876474	2.738793	1.116240
7	6	0	-1.593424	3.026518	-0.218311
8	6	0	-2.610159	1.952650	-0.704667
9	7	0	-2.743964	0.774027	0.155611
10	6	0	-1.798683	-0.193224	0.383543
11	7	0	-2.445079	-1.067075	1.221298
12	6	0	-3.732588	-0.643203	1.513430
13	6	0	-3.920311	0.516322	0.844618
14	6	0	-1.931808	-2.322932	1.764368
15	6	0	3.606223	0.730780	0.205814

16	75	0	0.220426	-0.461584	-0.581101
17	6	0	1.866178	-0.964191	-1.510581
18	8	0	2.777604	-1.346128	-2.114294
19	7	0	0.973476	-1.534138	1.167819
20	6	0	1.513465	-2.104032	2.019554
21	6	0	2.189925	-2.832997	3.086239
22	6	0	-0.207042	0.583083	-2.137981
23	8	0	-0.391553	1.219399	-3.091187
24	6	0	-0.605401	-2.050741	-1.376788
25	8	0	-1.100622	-2.986350	-1.841415
26	1	0	2.579293	-2.134526	3.833871
27	1	0	3.022081	-3.412253	2.672844
28	1	0	1.492424	-3.521487	3.574442
29	1	0	-4.392535	-1.207270	2.153729
30	1	0	-4.779453	1.165446	0.780864
31	1	0	-3.608581	2.391001	-0.756126
32	1	0	-2.368885	1.620558	-1.711895
33	1	0	-2.131314	3.974273	-0.120323
34	1	0	-0.841333	3.184169	-0.995363
35	1	0	3.704864	3.155401	1.449557
36	1	0	1.221164	4.276094	1.930291
37	1	0	3.773137	0.790641	-0.870886
38	1	0	4.500991	1.083786	0.721648
39	1	0	3.423509	-0.304083	0.489742
40	1	0	-1.359939	-2.145241	2.678801
41	1	0	-2.780899	-2.968956	1.995167
42	1	0	-1.304668	-2.822125	1.029338
43	1	0	-1.343808	1.920427	1.663464
44	1	0	-0.934199	3.618402	1.759810

HF=-1199.5632242/NImag=1 (-53.2399 cm^{-1})
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3. NMR Spectra of Complex 3b

***fac*-acetonitrile-tricarbonyl(1,1'-dimesityl-3,3'-propylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (3b).**

^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm): 1.95 (s, 3H, *ortho*-CH_3), 1.98 (s, 3H, *ortho*-CH_3), 2.08 (s, 3H, *ortho*-CH_3), 2.10 (s, 3H, *ortho*-CH_3), 2.12 (m, 2H, NCH$_2$CH_2CH$_2$N), 2.34 (s, 3H, NCCH_3), 2.34 (s, 3H, *para*-CH_3), 2.34 (s, 3H, *para*-CH_3), 4.09 (dddd, 2H, ^{2}J = 14.7, ^{2}J = 12.6, ^{3}J = 8.4, ^{3}J = 2.7 Hz, NCH*H*CH$_2$C*H*HN), 4.17 (dt, 1H, ^{2}J = 14.1, ^{3}J = 3.4 Hz, NC*H*HCH$_2$CHHN), 4.36 (dt, 1H, ^{2}J = 14.3, ^{3}J = 3.2 Hz, NCHHCH$_2$C*H*HN), 7.00 (m, 1H, *meta*-C*H*), 6.98 (m, 1H, *meta*-C*H*), 7.01 (d, 1H, ^{3}J = 1.9 Hz, NCHC*H*N-Mes), 7.02 (m, 1H, *meta*-C*H*), 7.01 (m, 1H, *meta*-C*H*), 7.03 (d, 2H, ^{3}J = 1.9 Hz, NCHC*H*N-Mes), 7.27 (d, 1H, ^{3}J = 1.9 Hz, NC*H*CHN-Mes), 7.34 (d, 1H, ^{3}J = 1.9 Hz, NC*H*CHN-Mes).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 3.98 (NC*C*H$_3$), 18.44 (*ortho*-*C*H$_3$), 18.50 (*ortho*-*C*H$_3$), 18.60 (*ortho*-*C*H$_3$), 18.89 (*ortho*-*C*H$_3$), 21.41 (*para*-*C*H$_3$), 21.42 (*para*-*C*H$_3$), 34.27 (NCH$_2$*C*H$_2$CH$_2$N), 46.56 (NCH$_2$CH$_2$*C*H$_2$N), 47.31 (N*C*H$_2$CH$_2$CH$_2$N), 123.27 (N*C*CH$_3$), 123.46 (N*C*HCHN-Mes), 123.85 (N*C*HCHN-Mes), 125.67 (NCH*C*HN-Mes), 125.89 (NCH*C*HN-Mes), 129.34 (*C*-*ortho*-CH$_3$), 129.82 (*C*-*ortho*-CH$_3$), 129.98 (*C*-*ortho*-CH$_3$), 130.37 (*C*-*ortho*-CH$_3$), 135.83 (*meta*-*C*), 136.25 (*meta*-*C*), 136.94 (*meta*-*C*), 137.50 (*ipso*-*C*N), 137.55 (*ipso*-*C*N), 137.59 (*meta*-*C*), 140.46 (*C*-*para*-CH$_3$), 140.81 (*C*-*para*-CH$_3$), 175.30 (N*C*N), 176.50 (N*C*N), 188.89 (*C*O$_{trans\text{-}NHC}$), 189.03 (*C*O$_{trans\text{-}NHC}$), 193.04 (*C*O$_{cis\text{-}NHC}$).

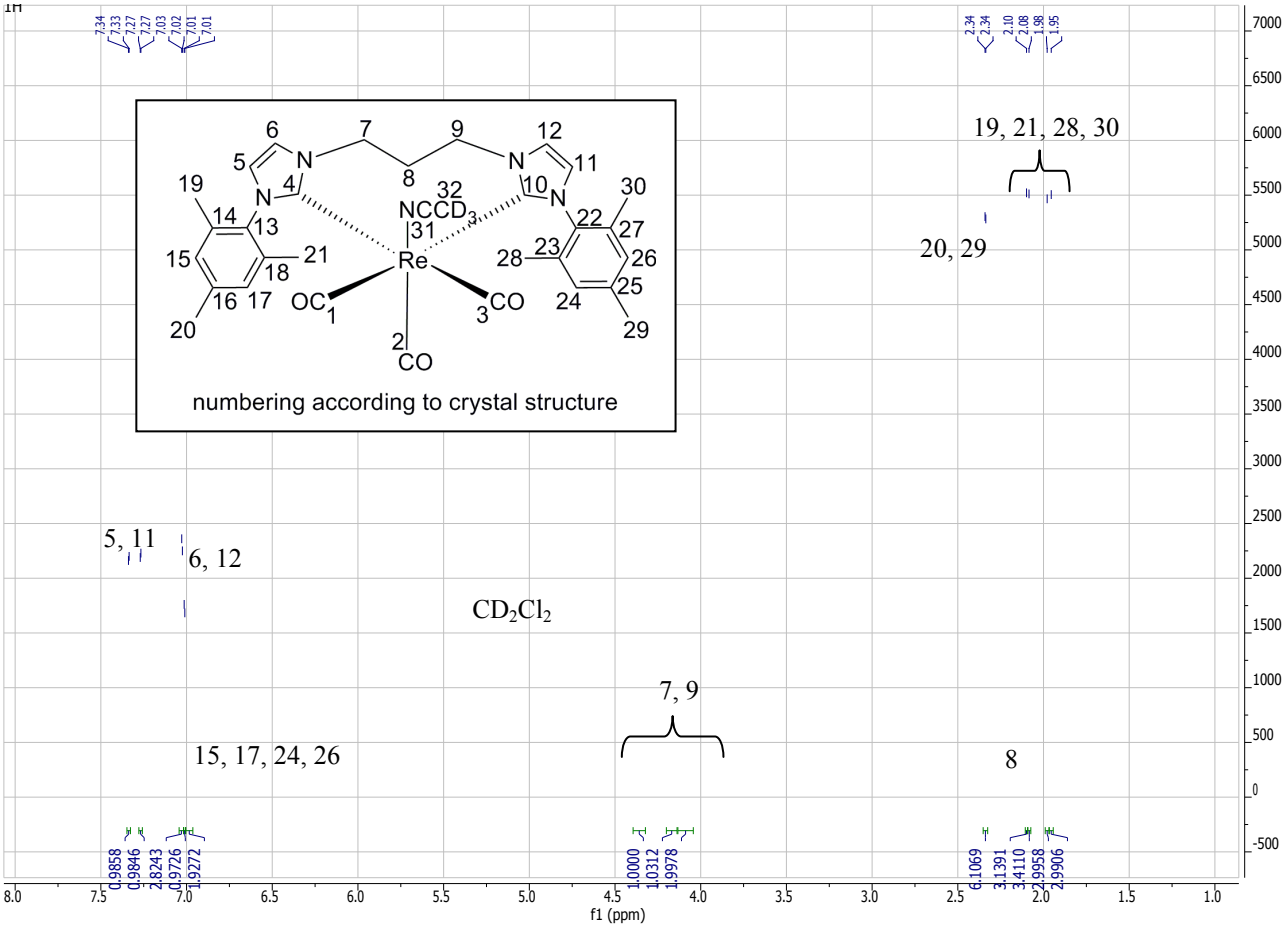

Figure S12. ^{1}H NMR spectrum of compound **3b** in CD_2Cl_2 (bearing a CD_3CN ligand).

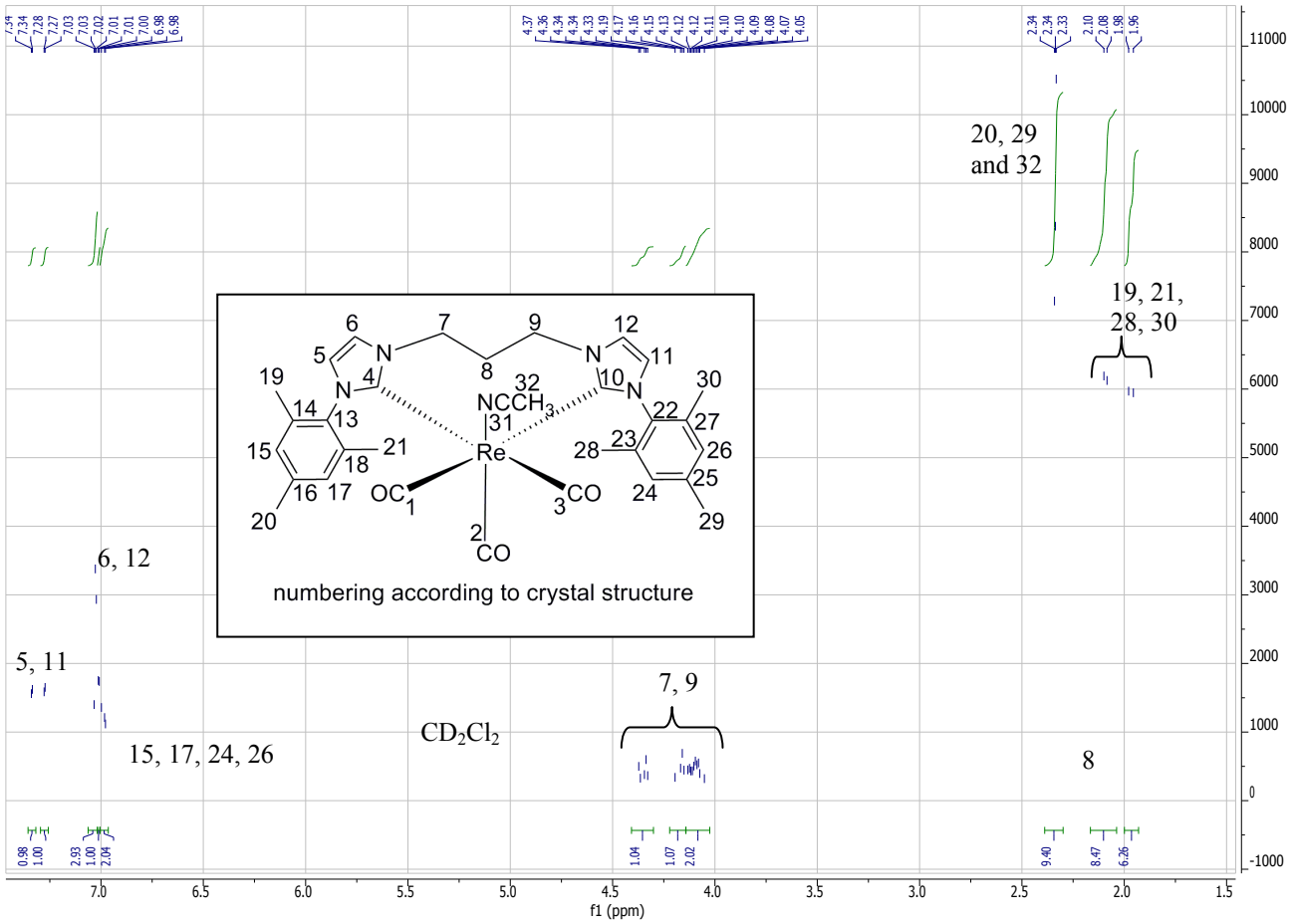

Figure S13. ^{1}H NMR spectrum of compound **3b** in CD_2Cl_2 (bearing a CH_3CN ligand).

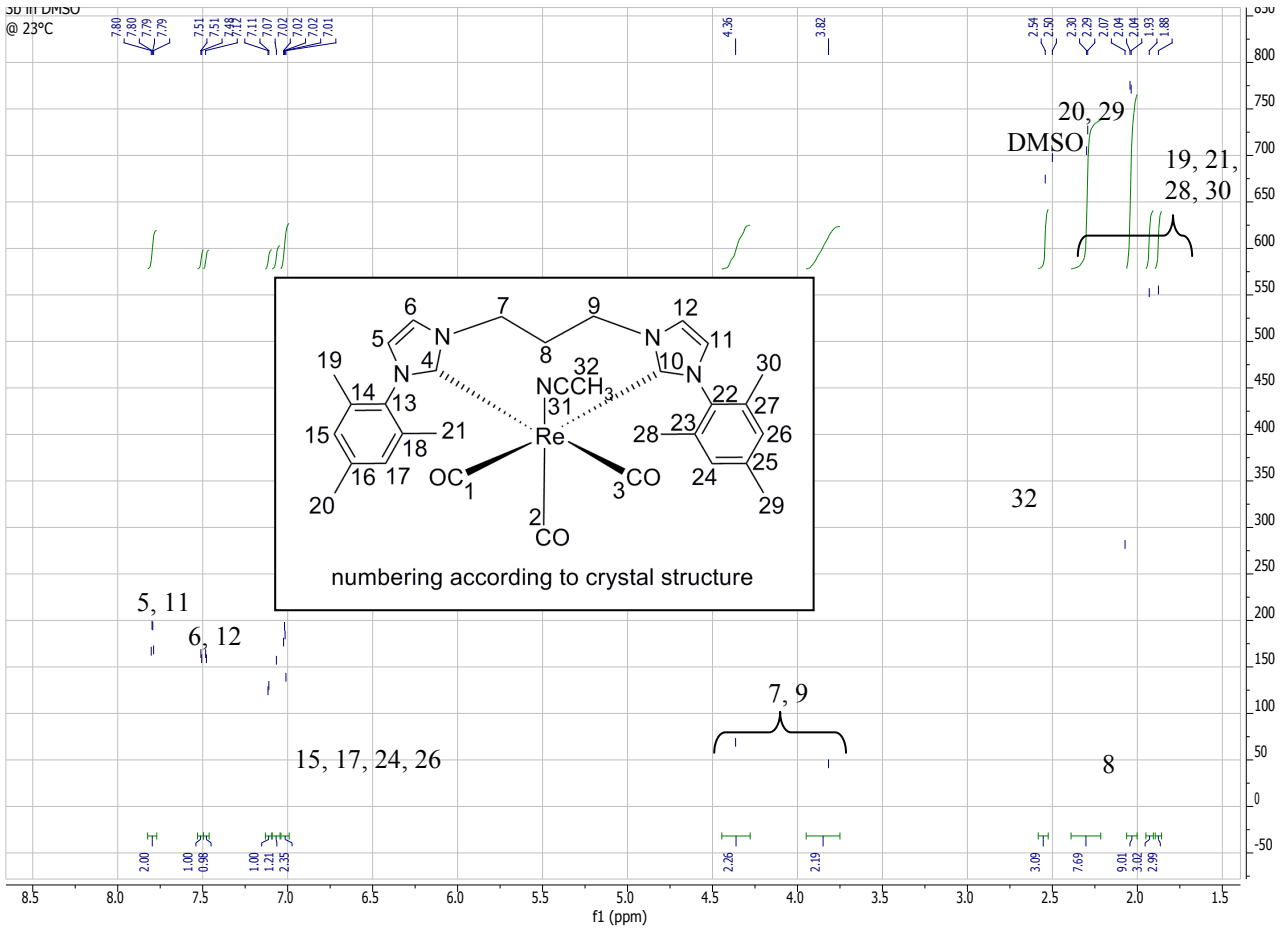

Figure S14. ^{1}H NMR spectrum of compound **3b** in DMSO at 23°C (bearing a CH_3CN ligand).

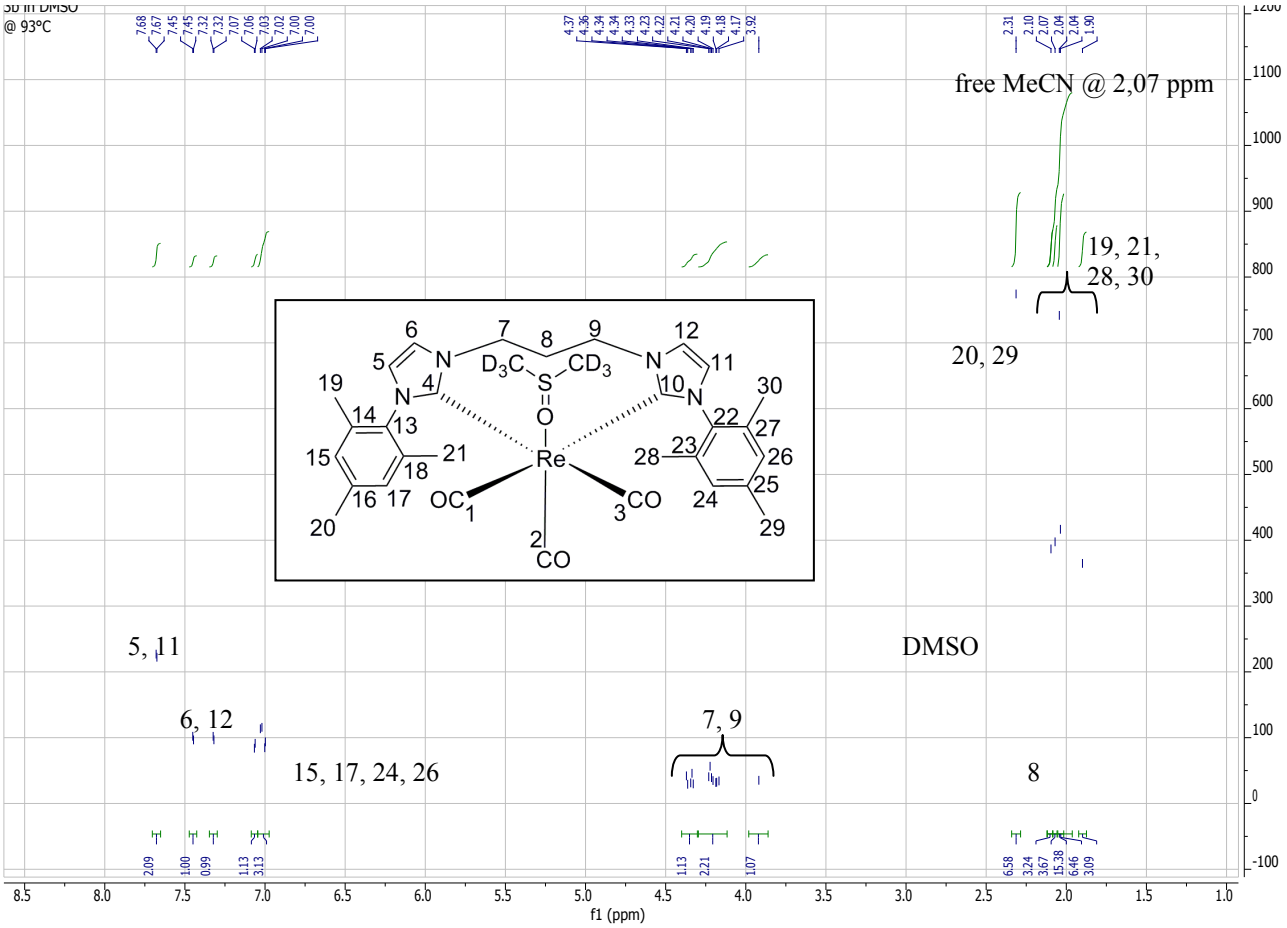

Figure S15. ^{1}H NMR spectrum of compound **3b** in DMSO at 93°C.

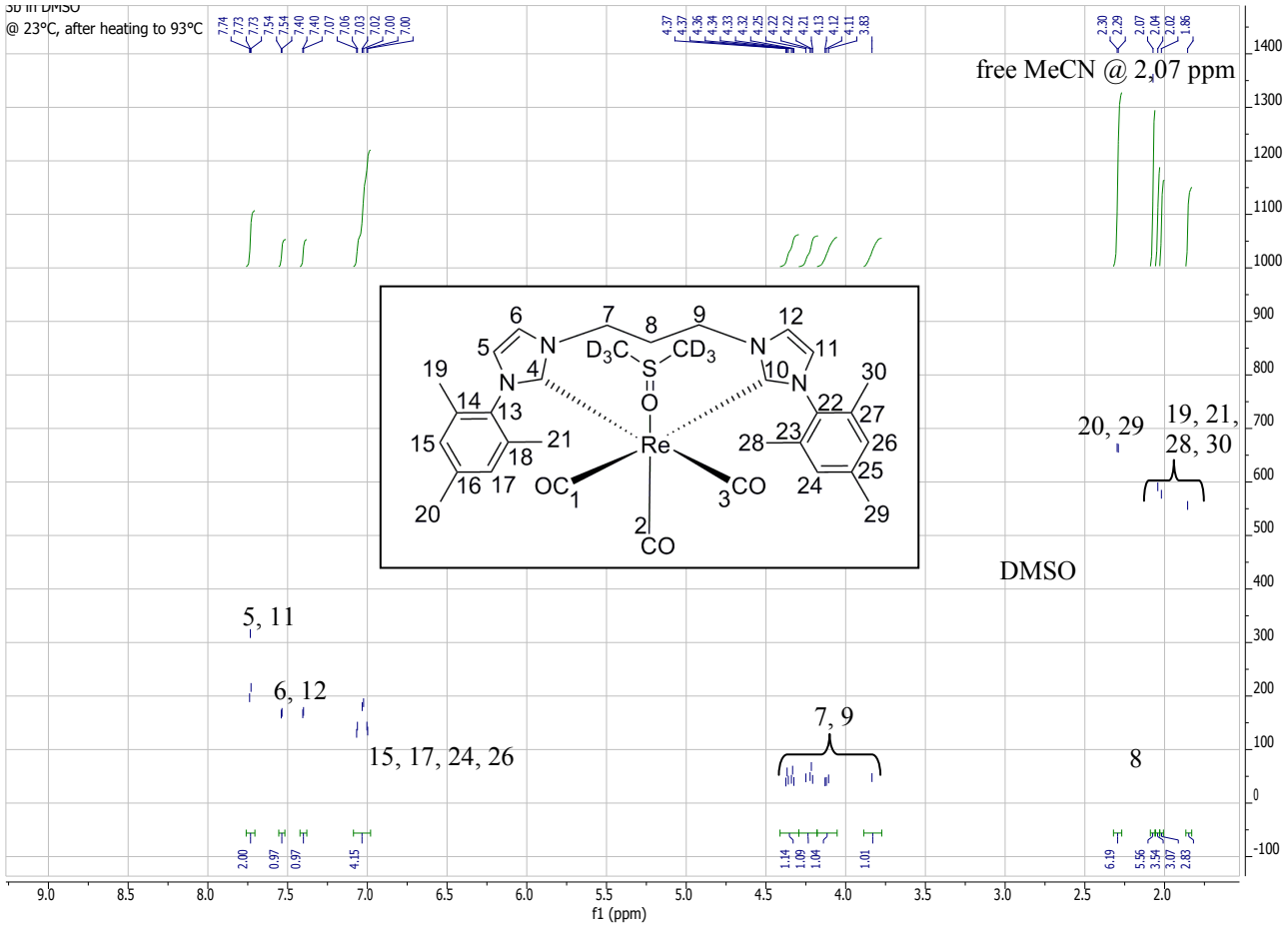

Figure S16. ^{1}H NMR spectrum of compound **3b** in DMSO at 23°C, after heating to 93 °C.

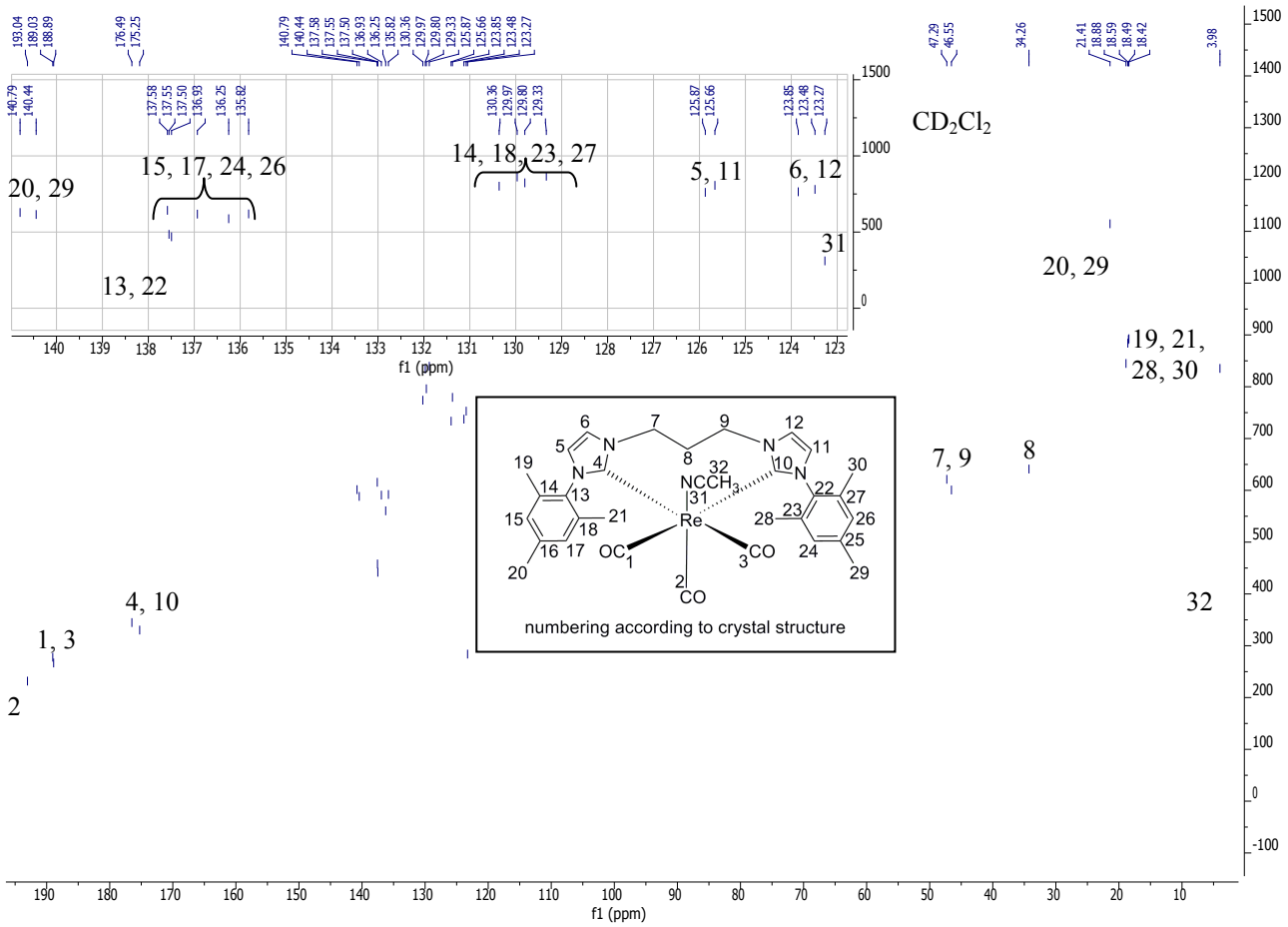

Figure S17. ^{13}C NMR spectrum of compound **3b**.

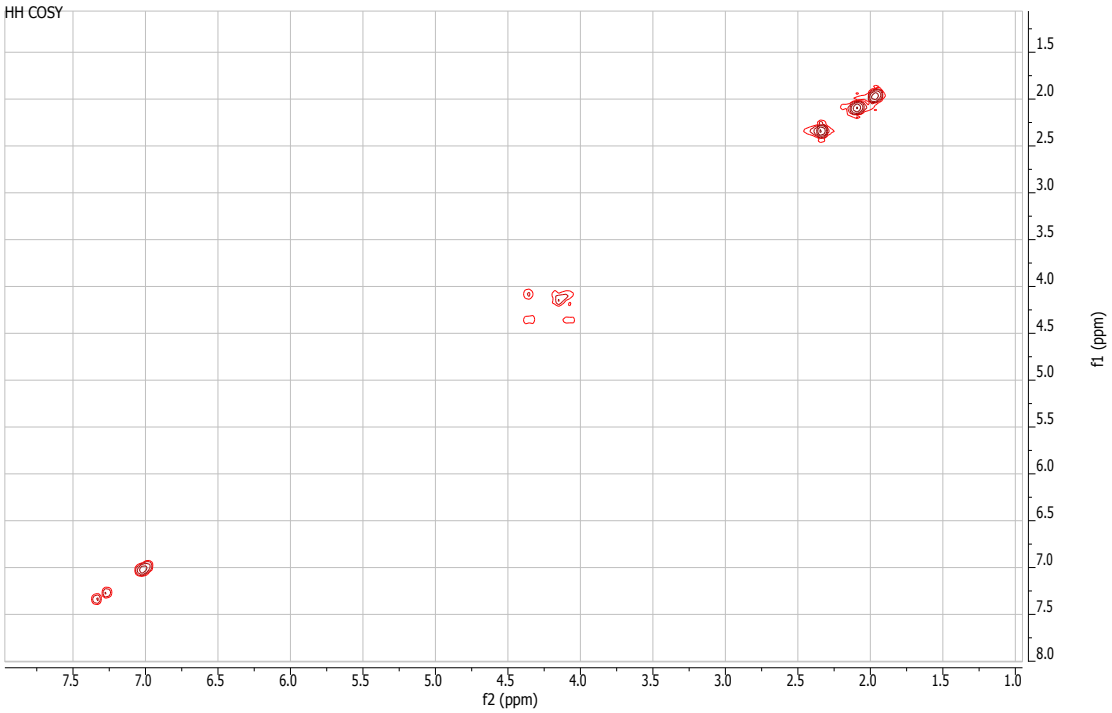

Figure S18. $^{1}H/^{1}H$ COSY NMR spectrum of compound **3b** in CD_2Cl_2.

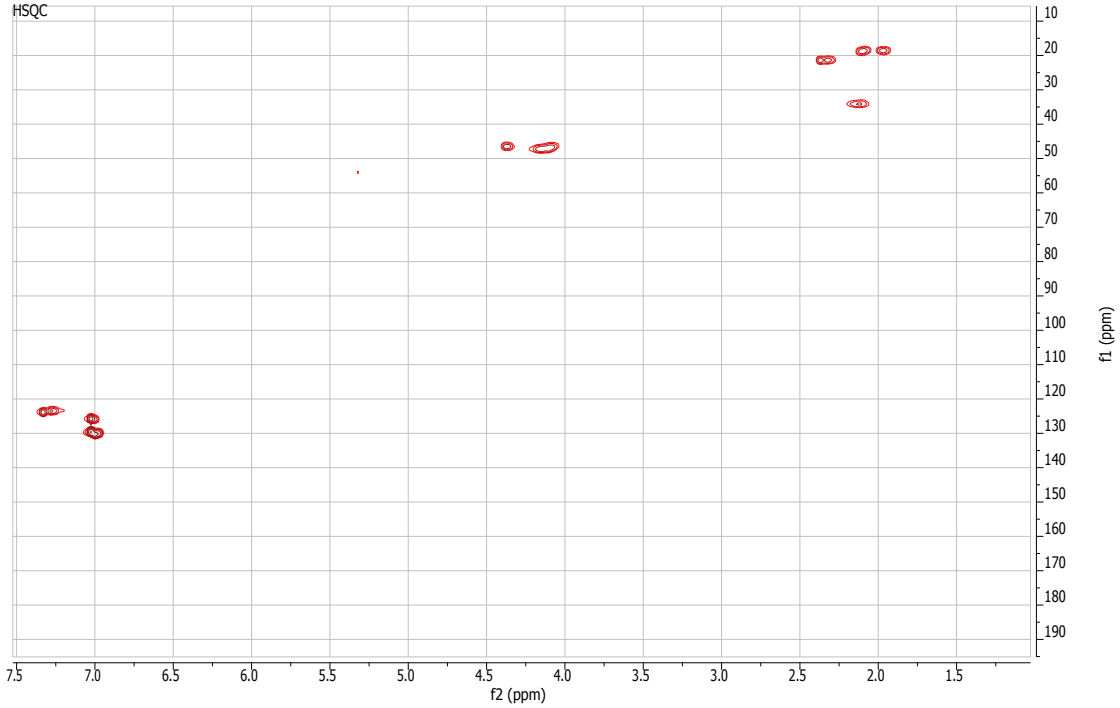

Figure S19. $^{1}H/^{13}C$ HSQC NMR spectrum of compound **3b** in CD_2Cl_2.

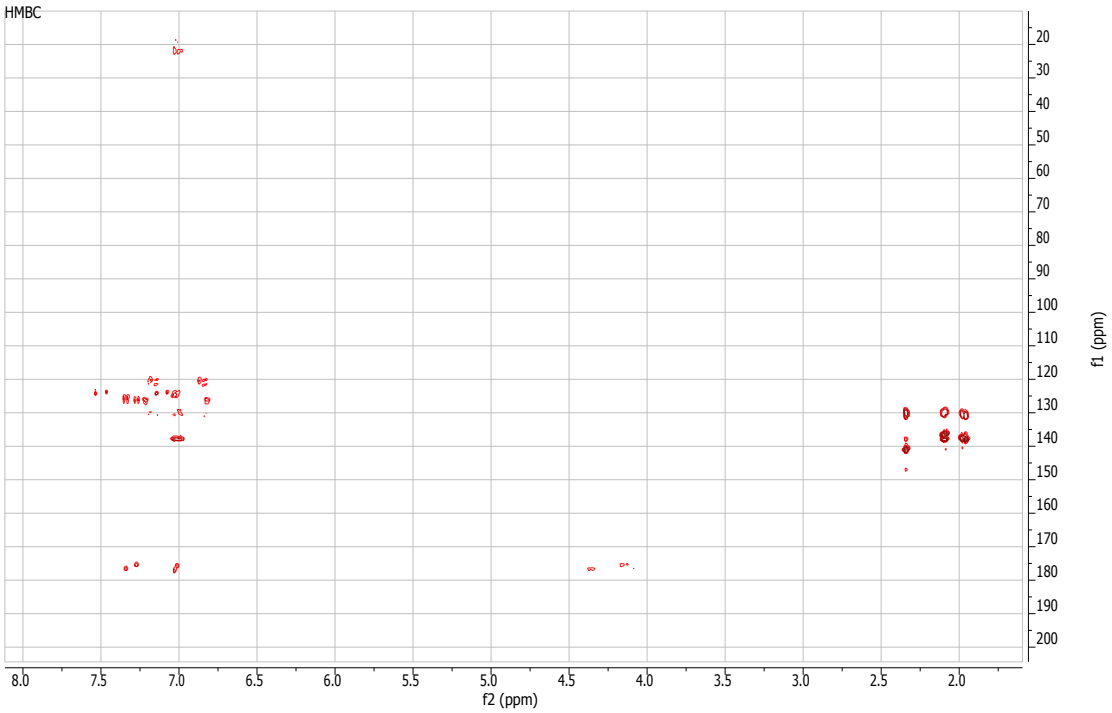

Figure S20. $^{1}H/^{13}C$ HMBC NMR spectrum of compound **3b** in CD_2Cl_2.

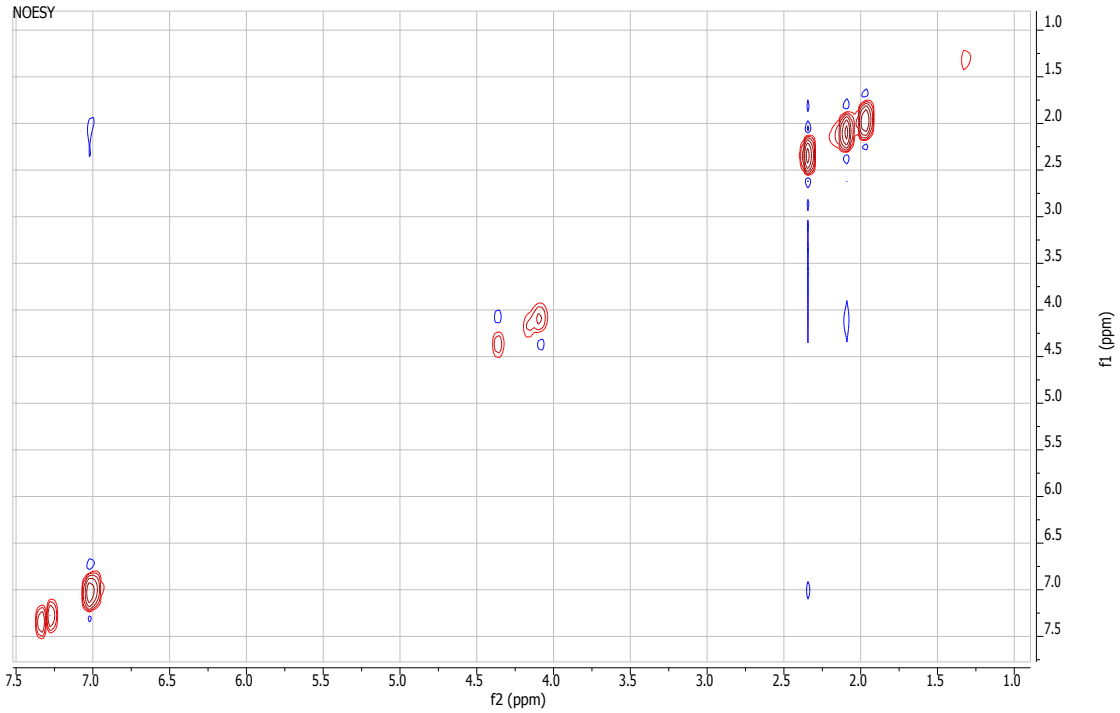

Figure S21. $^{1}H/^{1}H$ NOESY NMR spectrum of compound **3b** in CD_2Cl_2.

4. ^{1}H and ^{13}C NMR Spectra of Complexes 1a, 1b, 1c, 2a, 2b, 3a, 3c, 4, 5a, 5b and 5c

fac-acetonitrile-tricarbonyl(1,1'-dimethyl-3,3'-ethylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (1a)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 2.42 (s, 3H, NCC*H*$_3$), 3.94 (s, 3H, NC*H*$_3$), 4.53 (dd, 2H, ^{3}J = 8.3 Hz, ^{2}J = 15.5 Hz, NCH*H*CH*H*N), 4.80 (dd, 2H, ^{3}J = 8.3 Hz, ^{2}J = 15.5 Hz, NC*H*HC*H*HN), 7.06 (s, 2H, NC*H*CHNCH$_3$), 7.08 (s, 2H, NCHC*H*NCH$_3$).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.10 (NC*C*H$_3$), 40.63 (NCHCHNC*H*$_3$), 50.47 (NC*H*$_2$C*H*$_2$N), 123.79 (NC*H*CHN-CH$_3$), 124.49 (NCH*C*HN-CH$_3$), 124.68 (N*C*CH$_3$), 171.73 (N*C*N), 192.65 (*C*O$_{cis\text{-}NHC}$), 193.71 (*C*O$_{trans\text{-}NHC}$).

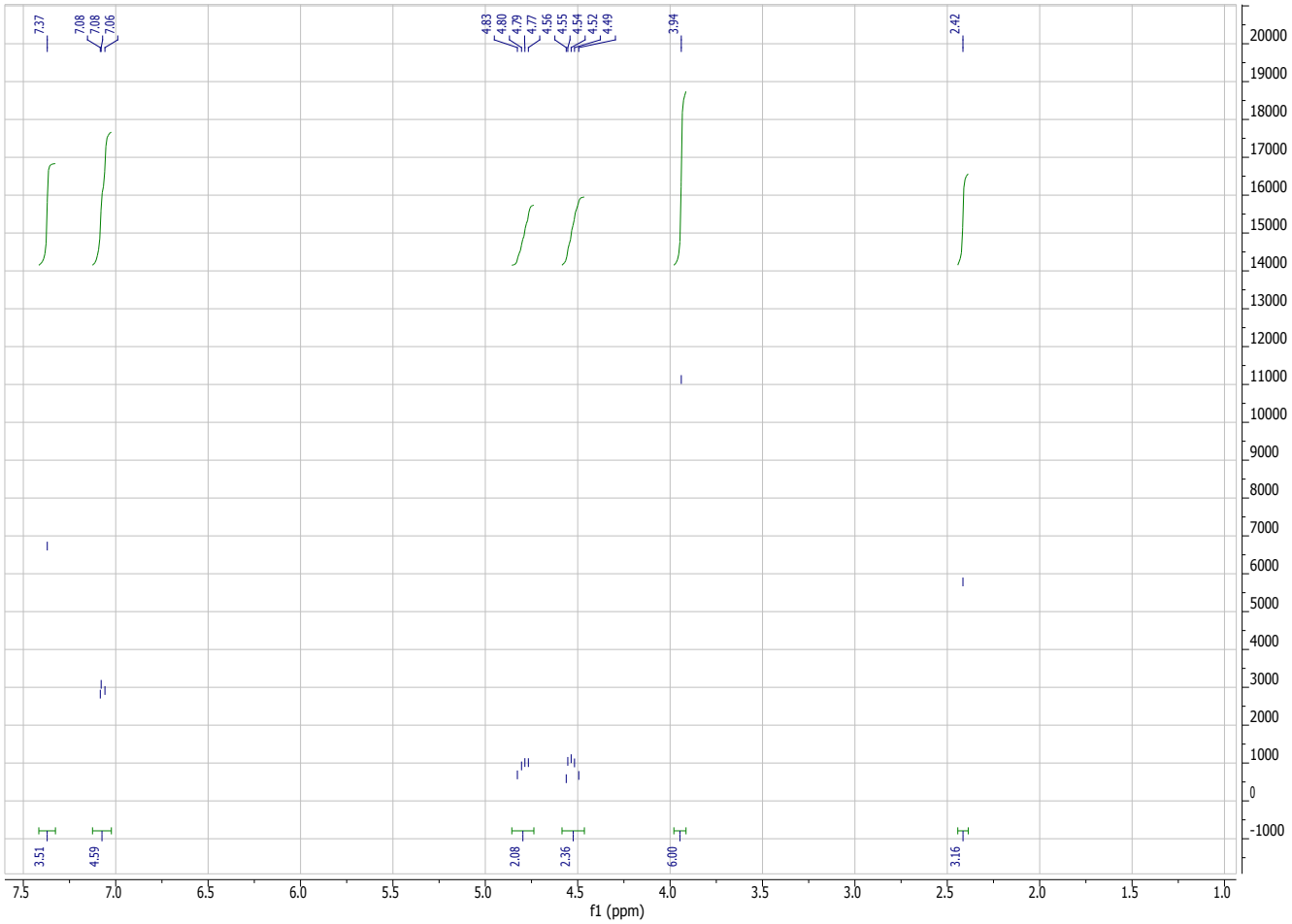

Figure S22. ^{1}H NMR spectrum of compound **1a** in CD_2Cl_2 at 23°C.

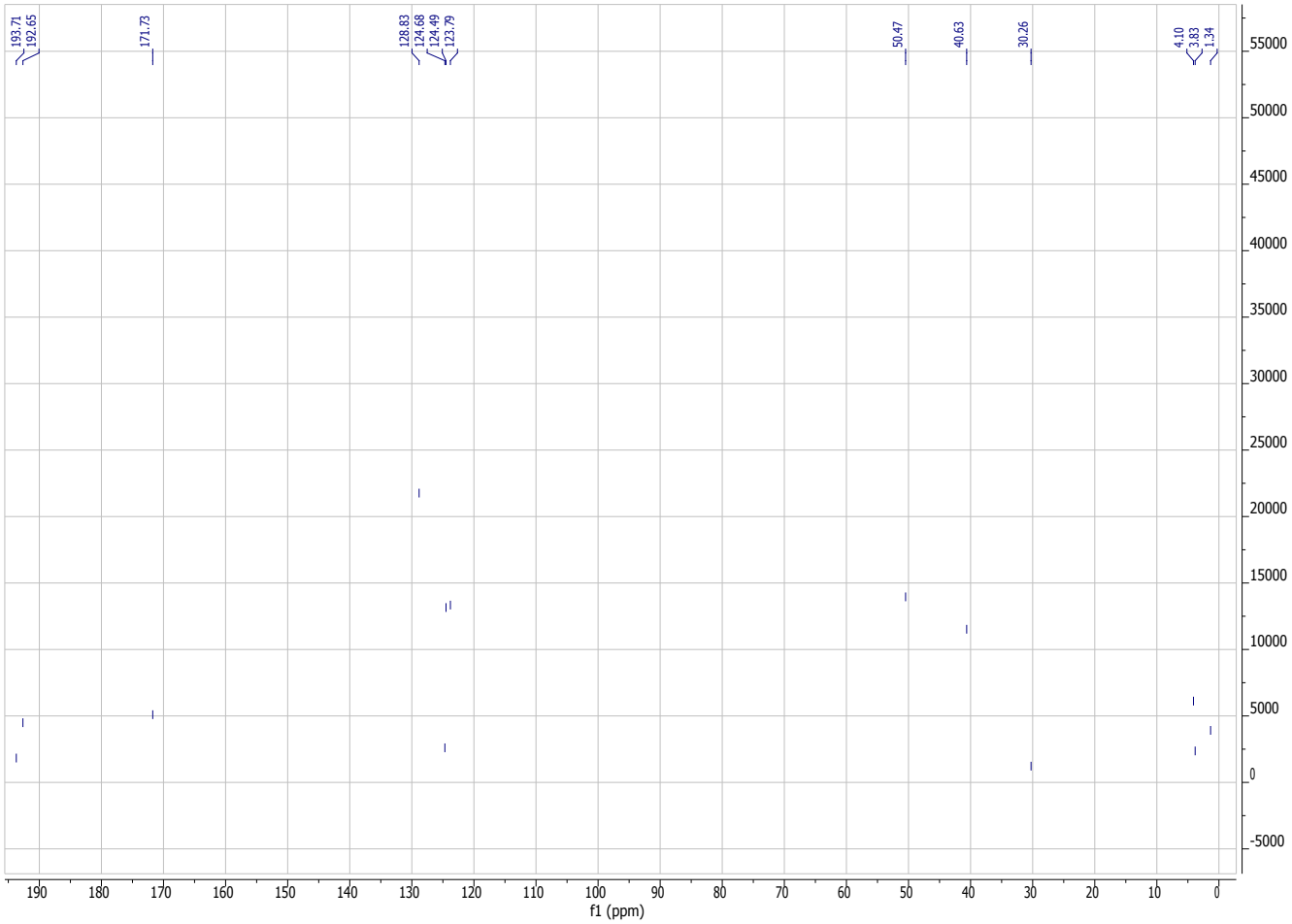

Figure S23. ^{13}C NMR spectrum of compound **1a** in CD_2Cl_2 at 23°C.

***fac*-acetonitrile-tricarbonyl(1,1'-dimethyl-3,3'-propylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (1b)**

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.81 (ddddd, 2H, ^{4}J = 30.0 Hz, ^{3}J = 15.0 Hz, ^{3}J = 12.1 Hz, ^{2}J = 6.1 Hz, ^{2}J = 3.0 Hz, $NCH_2CH_2CH_2N$), 2.38 (s, 3H, $NCCH_3$), 3.74 (dddd, 2H, ^{4}J = 29.3 Hz, ^{3}J = 14.8 Hz, ^{3}J = 12.3 Hz, ^{2}J = 2.8 Hz, $NCHHCH_2CHHN$), 3.99 (dddd, 2H, $NCHHCH_2CHHN$), 4.05 (s, 3H, NCH_3), 4.06 (s, 3H, NCH_3), 7.00 (d, 1H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$), 7.03 (d, 1H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$), 7.15 (d, 1H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$), 7.18 (d, 1H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 3.97 ($NCCH_3$), 34.90 ($NCH_2CH_2CH_2N$), 40.71 ($NCHCHNCH_3$), 41.74 ($NCHCHNCH_3$), 46.38 ($NCH_2CH_2CH_2N$), 47.19 ($NCH_2CH_2CH_2N$), 121.79 ($NCHCHNCH_3$), 122.43 ($NCHCHNCH_3$), 124.56 ($NCCH_3$), 125.42 ($NCHCHNCH_3$), 126.08 ($NCHCHNCH_3$), 173.31 (NCN), 174.78 (NCN), 191.74 ($CO_{cis\text{-}NHC}$), 193.27 ($CO_{trans\text{-}NHC}$) , 193.60 ($CO_{trans\text{-}NHC}$).

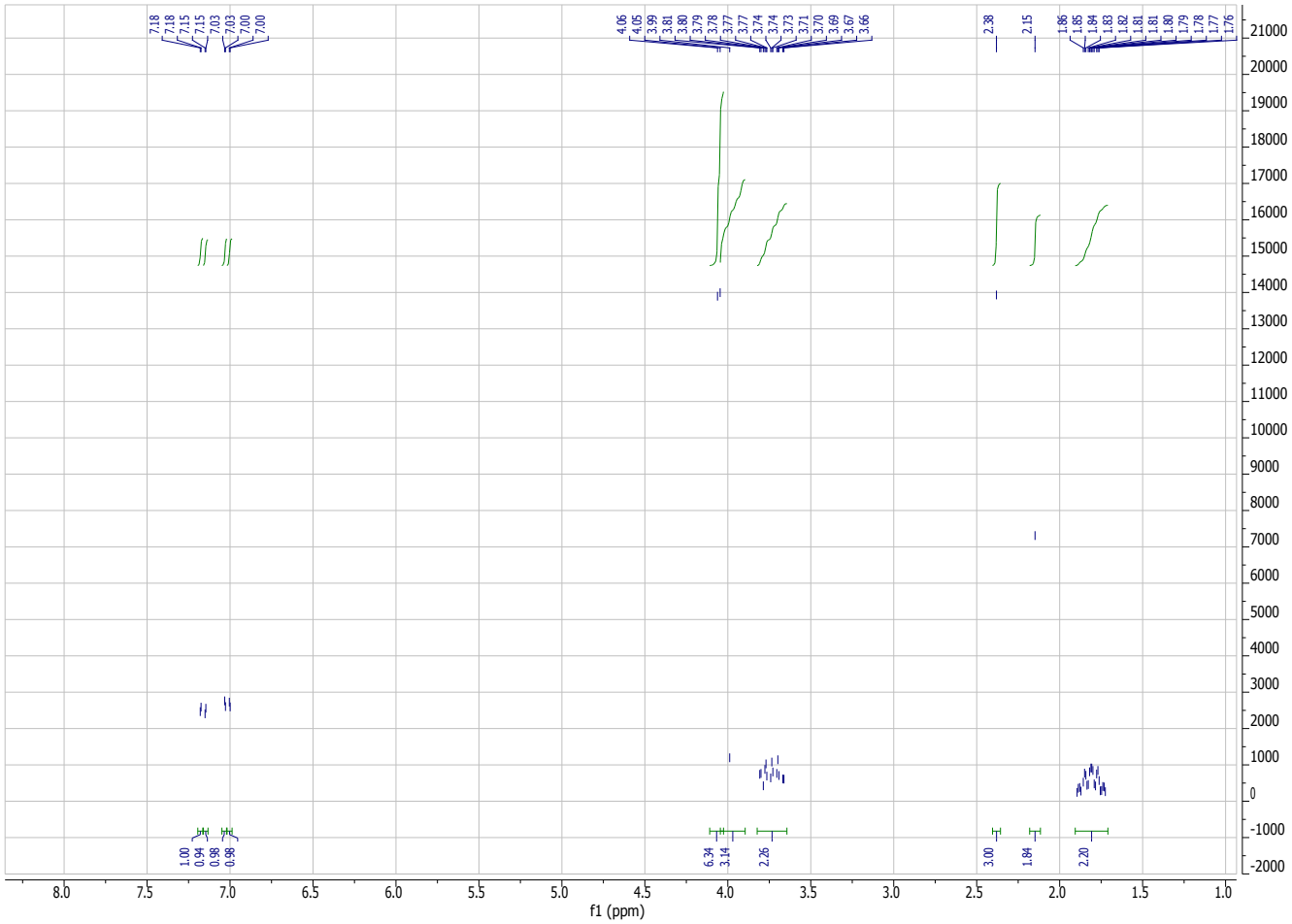

Figure S24. ^{1}H NMR spectrum of compound **1b** in CD_2Cl_2 at 23°C.

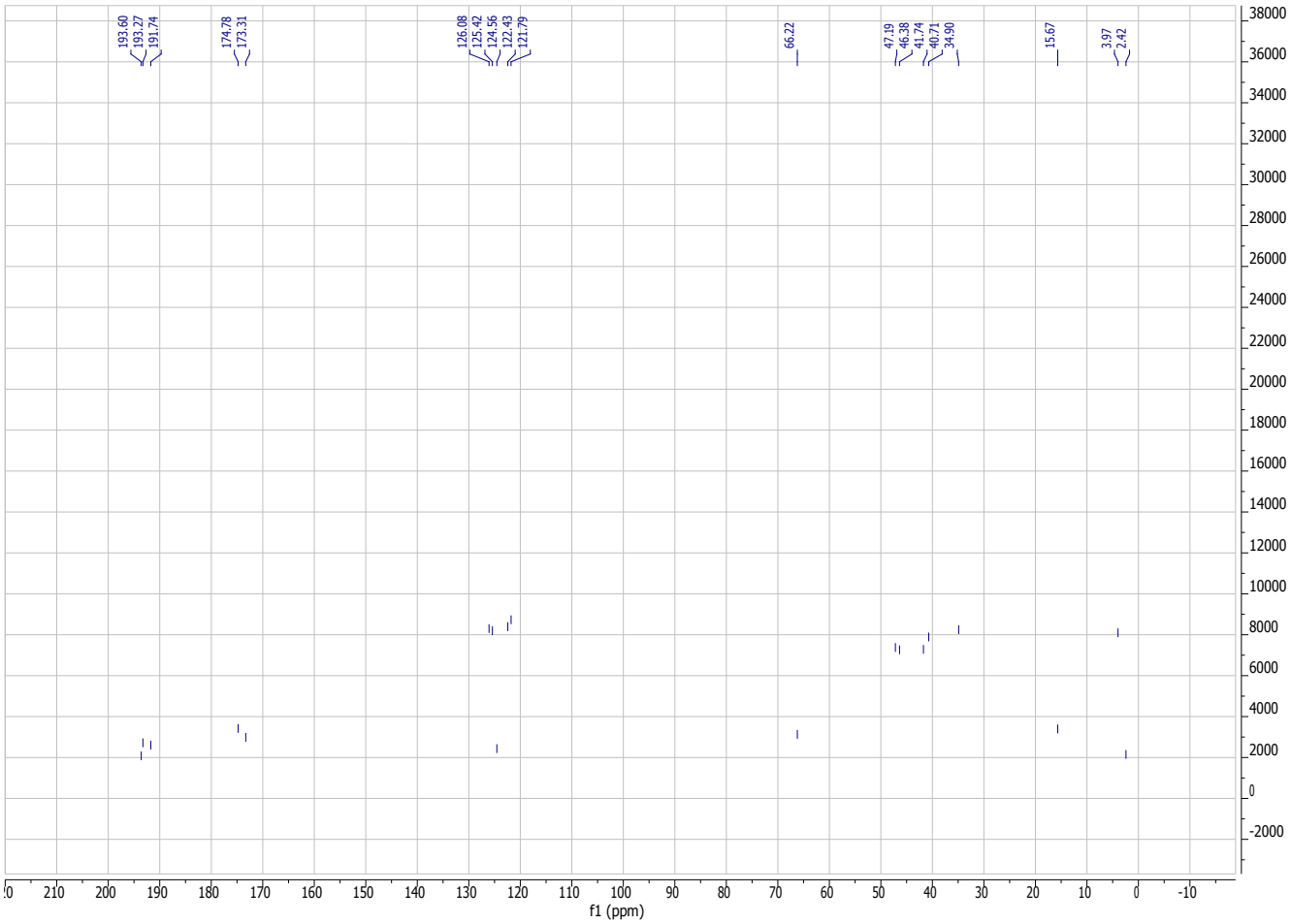

Figure S25. ^{13}C NMR spectrum of compound **1b** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-dimethyl-3,3'-butylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (1c)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.34 (m, 4H, $NCH_2CH_2CH_2CH_2N$), 2.30 (s, 3H, $NCCH_3$), 2.45 (s, 3H, NCH_3), 2.48 (s, 3H, NCH_3), 3.80-4.25 (m, 4H, $NCH_2(CH_2)_2CH_2N$), 7.07 (dd, 2H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$), 7.15 (d, 1H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$), 7.21 (d, 1H, ^{2}J = 1.9 Hz, $NCHCHNCH_3$).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 3.94 ($NCCH_3$), 21.98 ($NCH_2CH_2CH_2CH_2N$), 22.50 ($NCH_2CH_2CH_2CH_2N$), 40.09 ($NCHCHN\text{-}CH_3$), 41.16 ($NCHCHNCH_3$), 47.84 ($NCH_2CH_2CH_2CH_2N$), 48.35 ($NCH_2CH_2CH_2CH_2N$), 121.36 ($NCHCHNCH_3$), 121.73 ($NCHCHNCH_3$), 124.46 ($NCCH_3$), 124.98 ($NCHCHNCH_3$), 125.66 ($NCHCHNCH_3$), 174.08 (NCN), 174.58 (NCN), 191.69 ($CO_{cis\text{-}NHC}$), 191.74 ($CO_{trans\text{-}NHC}$), 192.89 ($CO_{trans\text{-}NHC}$).

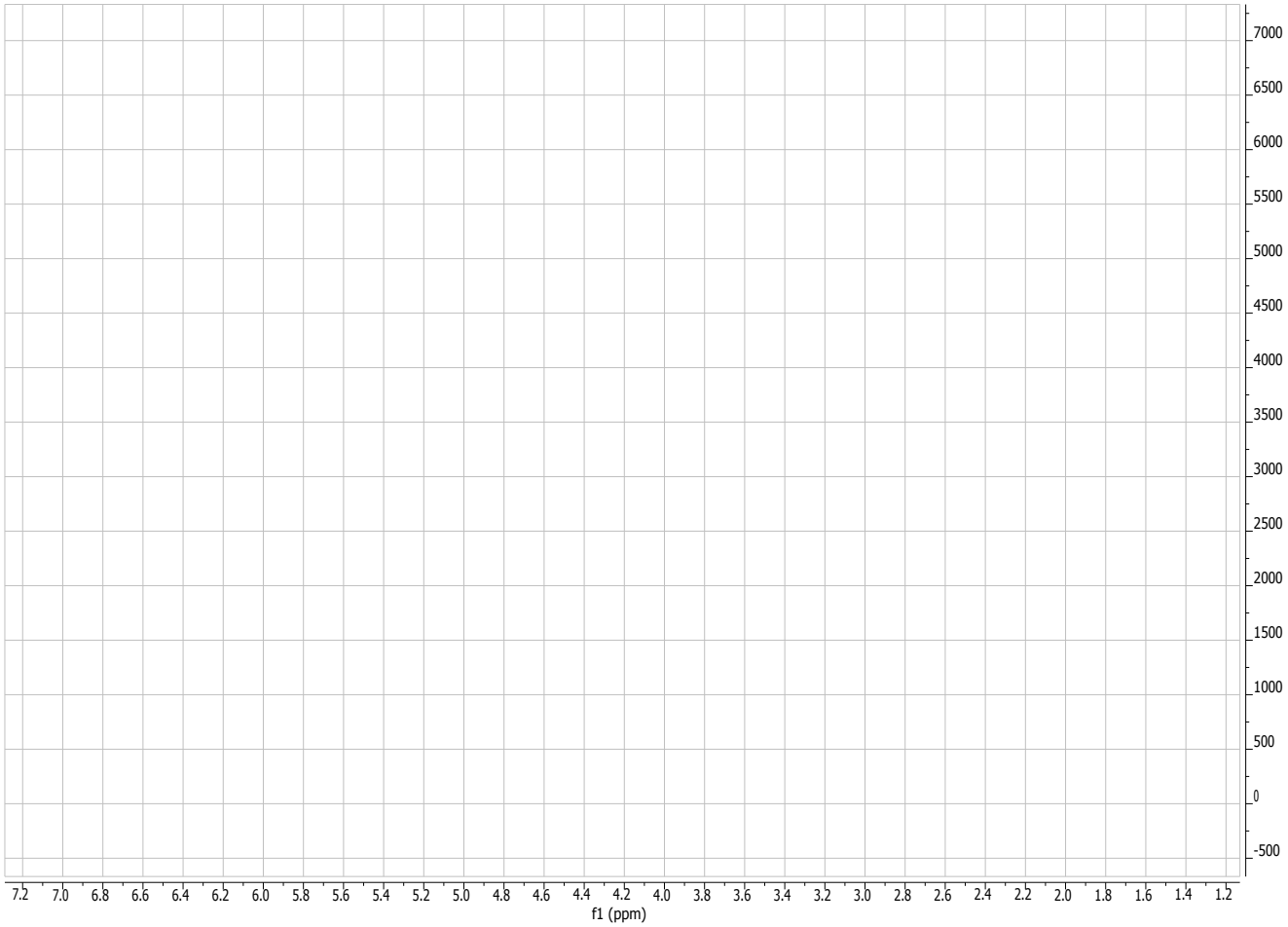

Figure S26. ^{1}H NMR spectrum of compound **1c** in CD_2Cl_2 at 23°C.

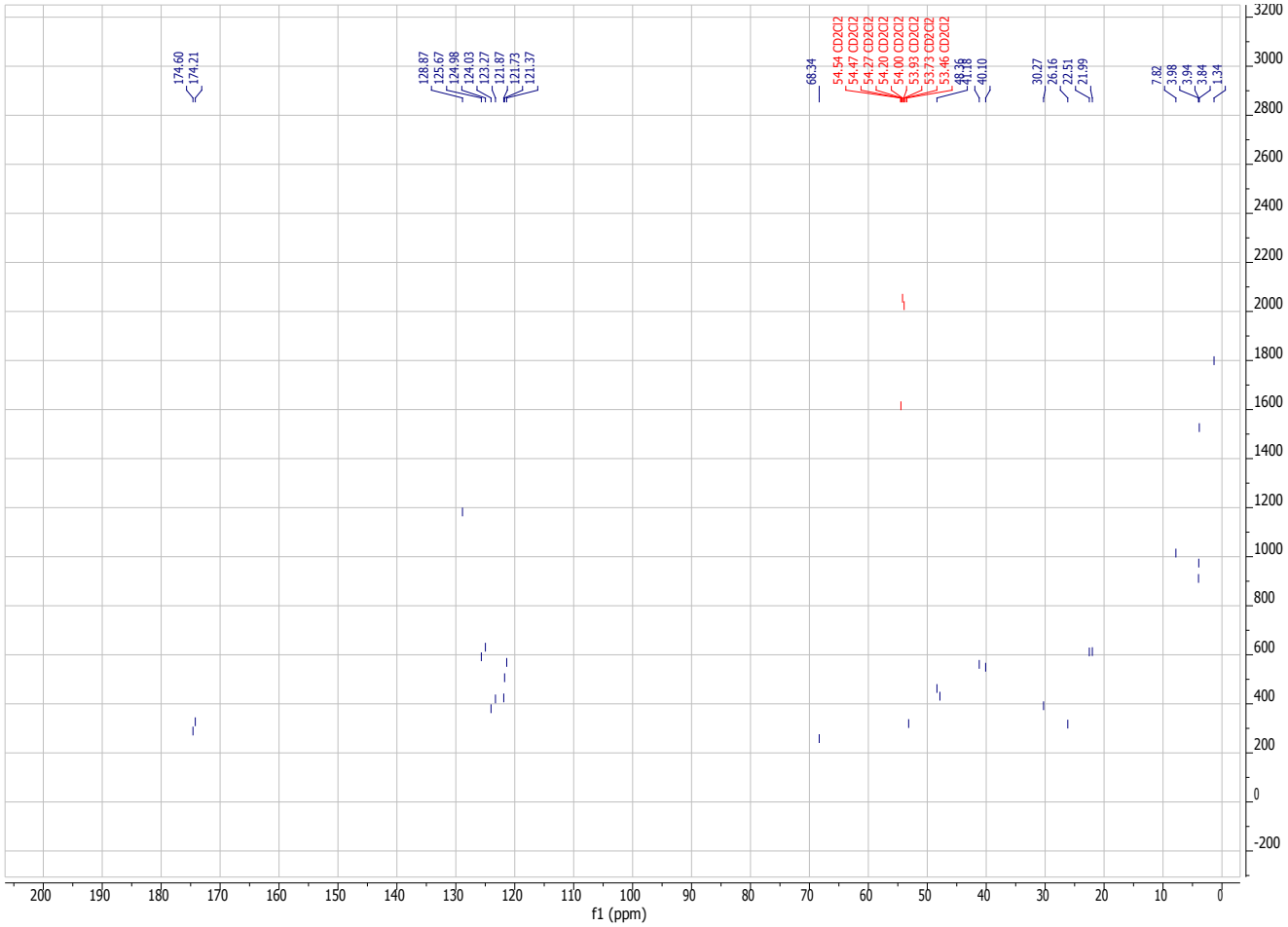

Figure S27. ^{13}C NMR spectrum of compound **1c** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-diisopropyl-3,3'-ethylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (2a)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.47 (s, 3H, CH(C*H*$_3$)$_2$), 1.49 (s, 3H, CH(C*H*$_3$)$_2$), 1.51 (s, 3H, C(C*H*$_3$)$_2$), 1.53 (s, 3H, C(C*H*$_3$)$_2$), 2.43 (s, 3H, NCC*H*$_3$), 4.50 (m, 2H, NCH*H*CH*H*N), 4.86 (m, 2H, NC*H*HC*H*HN), 5.08 (hept, 2H, ^{3}J = 6.6 Hz, C*H*(CH$_3$)$_2$), 7.14 (m, 4H, NC*H*C*H*NC(CH$_3$)$_2$).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.51 (NC*C*H$_3$), 24.54 (C(*C*H$_3$)$_2$), 24.24 (C(*C*H$_3$)$_2$), 50.41 (N*C*H$_2$*C*H$_2$N), 55.29 (*C*H(CH$_3$)$_2$), 123.08 (N*C*HCHNCH(CH$_3$)$_2$), 124.16 (NCH*C*HNCH(CH$_3$)$_2$), 124.90 (N*C*CH$_3$), 170.43 (N*C*N), 184.12 (*C*O$_{cis\text{-}NHC}$), 191.94 (*C*O$_{trans\text{-}NHC}$).

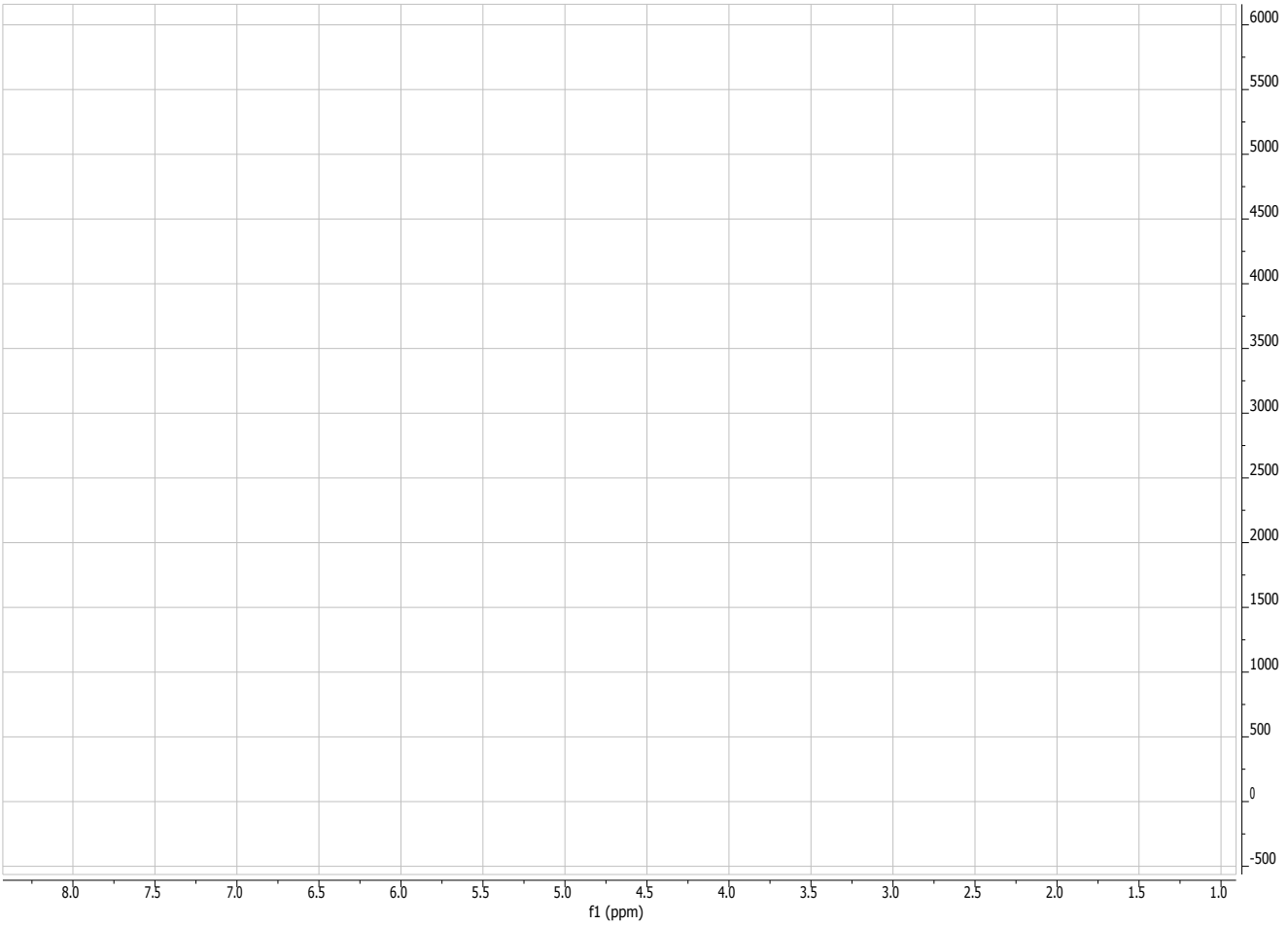

Figure S28. ^{1}H NMR spectrum of compound **2a** in CD_2Cl_2 at 23°C.

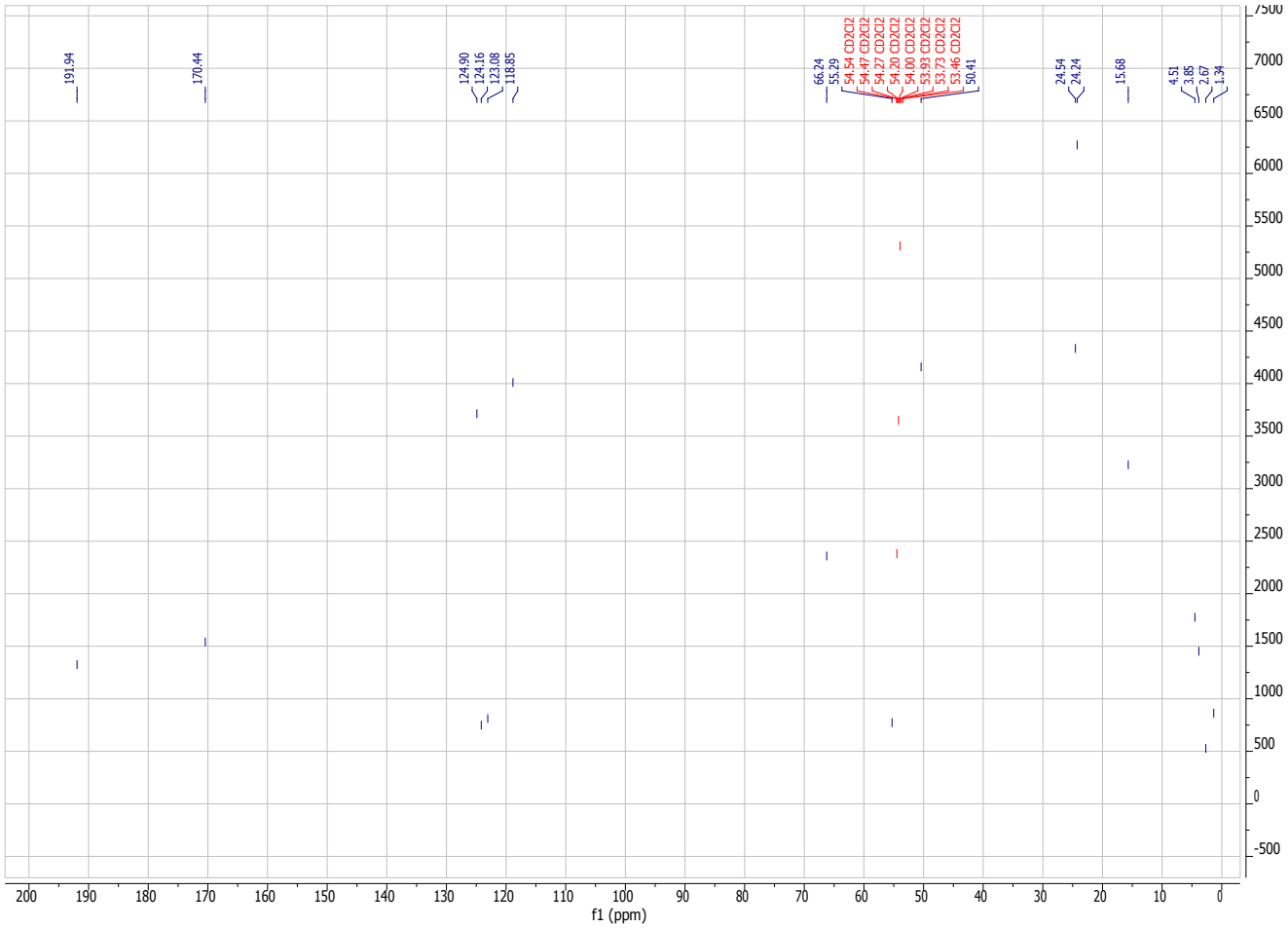

Figure S29. ^{13}C NMR spectrum of compound **2a** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-diisopropyl-3,3'-propylene-diimidazoline-2,2'-diylidene)-rhenium(I)hexafluorophosphate (2b)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.51 (m, 6H, CH(CH_3)$_2$), 1.61, (m, 6H, CH(CH_3)$_2$), 1.79(m, 2H, NCH$_2$CH_2CH$_2$N), 2.39 (s, 3H, NCCH_3), 3.61 (ddd, 1H, ^3J = 14.6 Hz, ^3J = 11.9 Hz, ^2J = 2.9 Hz, NCHHCH$_2$CHHN), 3.74 (ddd, 1H, ^3J = 14.4 Hz, ^3J = 12.1 Hz, ^2J = 3.1 Hz, NCHHCH$_2$CHHN), 3.94 (dt, 1H, ^3J = 14.1 Hz, ^2J = 3.1 Hz, NCHHCH$_2$CHHN), 4.08 (dt, 1H, ^3J = 14.5 Hz, ^2J = 3.2 Hz, NCHHCH$_2$CHHN), 5.31 (hept, 1H, ^3J = 6.7 Hz, CH(CH$_3$)$_2$), 5.43 (hept, 1H, ^3J = 6.7 Hz, CH(CH$_3$)$_2$), 7.08 (d, 1H, ^2J = 2.0 Hz, NCHCHN-^{i}Pr, 7.13 (d, 1H, ^2J = 2.0 Hz, NCHCHNCH(CH$_3$)$_2$), 7.25 (m, 2H, NCHCHNCH(CH$_3$)$_2$).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.00 (NCCH$_3$), 23.71 (CH(CH_3)$_2$), 23.87 (CH(CH_3)$_2$), 25.18 (CH(CH_3)$_2$), 25.23 (CH(CH_3)$_2$), 35.18 (NCH$_2$CH_2CH$_2$N), 46.45 (NCH_2CH$_2$CH$_2$N), 47.35 (NCH$_2$CH$_2$CH_2N), 54.08 (CH(CH$_3$)$_2$), 54.80 (CH(CH$_3$)$_2$), 120.25 (NCHCHNCH(CH$_3$)$_2$), 120.60 (NCHCHNCH(CH$_3$)$_2$), 122.89 (NCHCHNCH(CH$_3$)$_2$), 123.49 (NCHCHNCH(CH$_3$)$_2$), 124.19 (NCCH$_3$), 172.65 (NCN), 173.50 (NCN), 191.22 (C$O_{cis\text{-}NHC}$), 192.76 (C$O_{trans\text{-}NHC}$) , 193.62 (C$O_{trans\text{-}NHC}$).

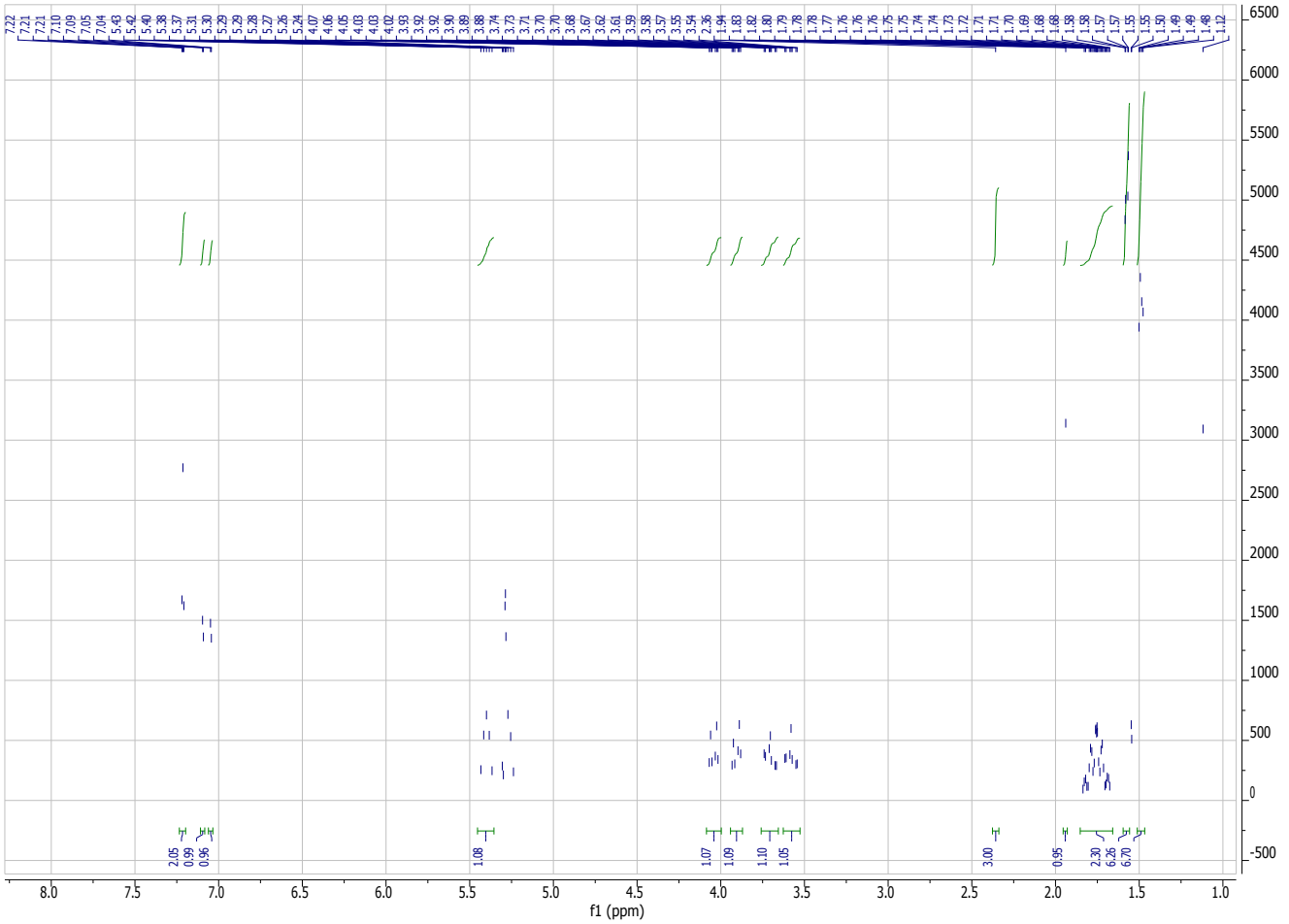

Figure S30. ^{1}H NMR spectrum of compound **2b** in CD_2Cl_2 at 23°C.

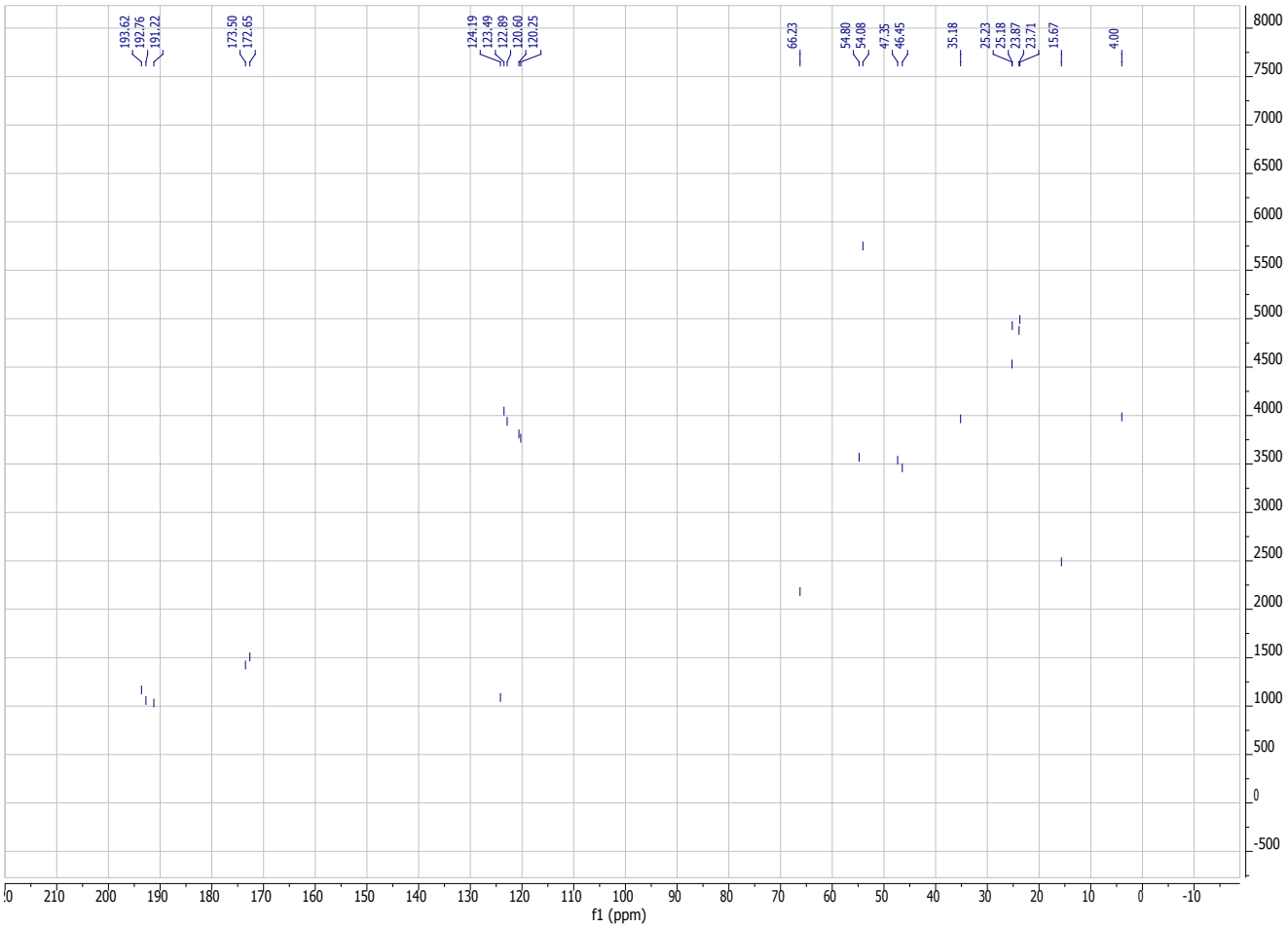

Figure S31. ^{13}C NMR spectrum of compound **2b** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-dimesityl-3,3'-ethylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (3a)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.97 (s, 6H, *ortho*-CH_3), 2.01 (s, 6H, *ortho*-CH_3), 2.32 (s, 6H, *para*-CH_3), 2.35 (s, 3H, NCCH_3), 4.54 (dd, 2H, ^{3}J = 7.7 Hz, ^{2}J = 15.7 Hz, NCH*H*CH*H*N), 4.88 (dd, 2H, ^{3}J = 7.7 Hz, ^{2}J = 15.7 Hz, NC*H*HC*H*HN), 6.92 (d, 2H, ^{3}J = 1.9 Hz, NC*H*CHNC-Mes), 6.98 (s, 4H, *meta*-C*H*), 7.28 (d, 2H, ^{3}J = 1.9 Hz, NCHC*H*N-Mes).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.13 (NC*C*H$_3$), 18.39 (*ortho*-*C*H$_3$), 18.57 (*ortho*-*C*H$_3$), 26.12 (*para*-*C*H$_3$), 52.84 (N*C*H$_2$*C*H$_2$N), 123.43 (N*C*HCHN-Mes), 123.78 (N*C*CH$_3$), 123.85 (N*C*HCHN-Mes), 124.29 (NCH*C*HN-Mes), 125.22 (NCH*C*HN-Mes), 129.68 (*C*-*ortho*-CH$_3$), 129.91 (*C*-*ortho*-CH$_3$), 136.64 (*meta*-*C*), 137.67 (*ipso*-*C*N), 140.49 (*C*-*para*-CH$_3$), 173.62 (N*C*N), 189.36 (*C*O$_{trans\text{-}NHC}$), 193.00 (*C*O$_{cis\text{-}NHC}$).

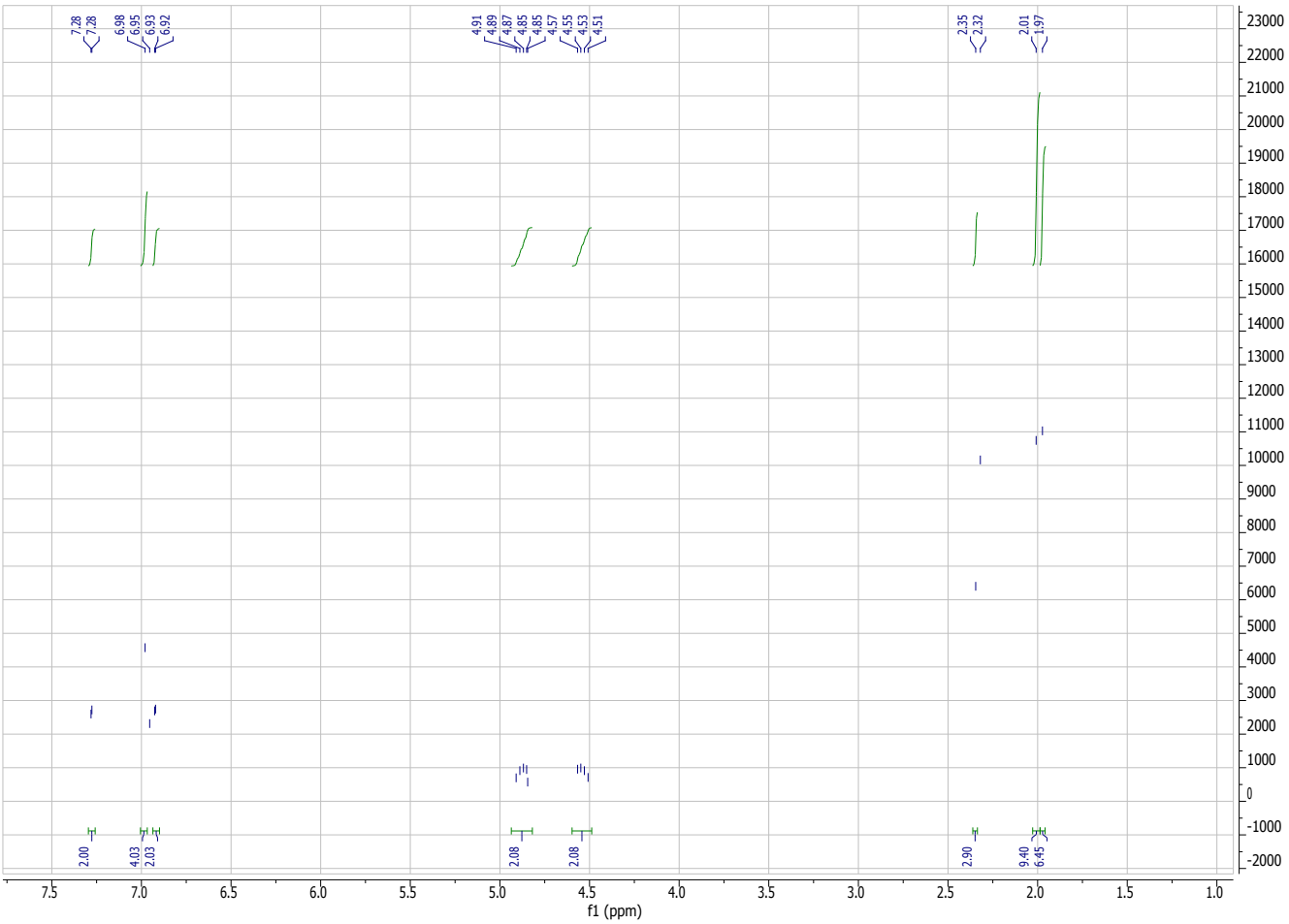

Figure S32. ^{1}H NMR spectrum of compound **3a** in CD_2Cl_2 at 23°C.

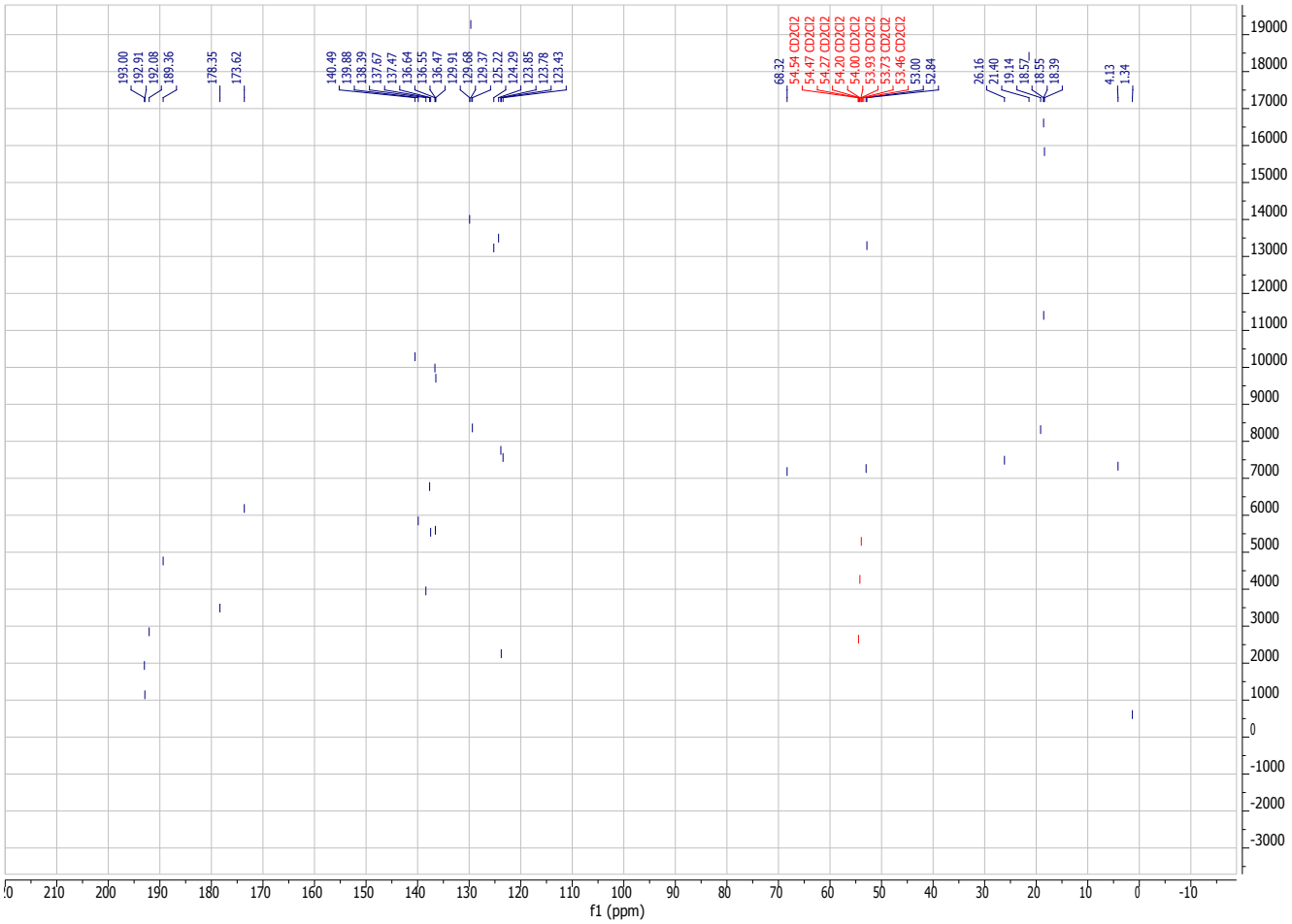

Figure S33. ^{13}C NMR spectrum of compound **3a** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-dimesityl-3,3'-butylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (3c)

^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm): 1.59 (m, 2H, $NCH_2CHHCHHCH_2N$), 1.96 (s, 3H, *ortho*-CH_3), 1.98 (s, 3H, *ortho*-CH_3), 2.02 (m, 2H, $NCH_2CHHCHHCH_2N$), 2.12 (s, 3H, *ortho*-CH_3), 2.14 (s, 3H, *ortho*-CH_3), 2.32 (s, 3H, $NCCH_3$), 2.35 (s, 3H, *para*-CH_3), 2.36 (s, 3H, *para*-CH_3), 4.02 (m, 1H, $NCHH(CH_2)_2CHHN$), 4.15 (m, 1H, $NCHH(CH_2)_2CHHN$), 4.38 (m, 1H, $NCHH(CH_2)_2CHHN$), 4.64 (m, 1H, $NCHH(CH_2)_2CHHN$), 6.93 (m, 1H, *meta*-CH), 6.99 (m, 1H, *meta*-CH), 7.03 (m, 1H, *meta*-CH), 7.03 (m, 1H, *meta*-CH), 7.06 (m, 2H, NCHCHN-Mes), 7.36 (d, 1H, ^{3}J = 1.9 Hz, NCHCHN-Mes), 7.41 (d, 1H, ^{3}J = 2.0 Hz, NCHCHN-Mes).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 3.98 ($NCCH_3$), 18.66 (*ortho*-CH_3), 18.68 (*ortho*-CH_3), 18.72 (*ortho*-CH_3), 18.91 (*ortho*-CH_3), 21.41 (*para*-CH_3), 21.43 (*para*-CH_3), 22.05 ($NCH_2CH_2CH_2CH_2N$), 22.41 ($NCH_2CH_2CH_2CH_2N$), 47.95 ($NCH_2(CH_2)_2CH_2N$), 48.77 ($NCH2(CH2)_2CH_2N$), 122.63 (NCHCHN-Mes), 123.00 (NCHCHN-Mes), 123.04 ($NCCH_3$), 125.57 (NCHCHN-Mes), 125.92 (NCHCHN-Mes), 129.08 (*C-ortho*-CH_3), 129.78 (*C-ortho*-CH_3), 130.04 (*C-ortho*-CH_3), 130.48 (*C-ortho*-CH_3), 135.50 (*meta-C*), 135.81 (*meta-C*), 136.77 (*ipso-C*N), 137.28 (*meta-C*), 137.31 (*ipso-C*N), 137.89 (*meta-C*), 140.42 (*C-para*-CH_3), 140.78 (*C-para*-CH_3), 176.49 (NCN), 177.54 (NCN), 189.28 ($CO_{trans\text{-}NHC}$), 189.85 ($CO_{trans\text{-}NHC}$), 192.30 ($CO_{cis\text{-}NHC}$).

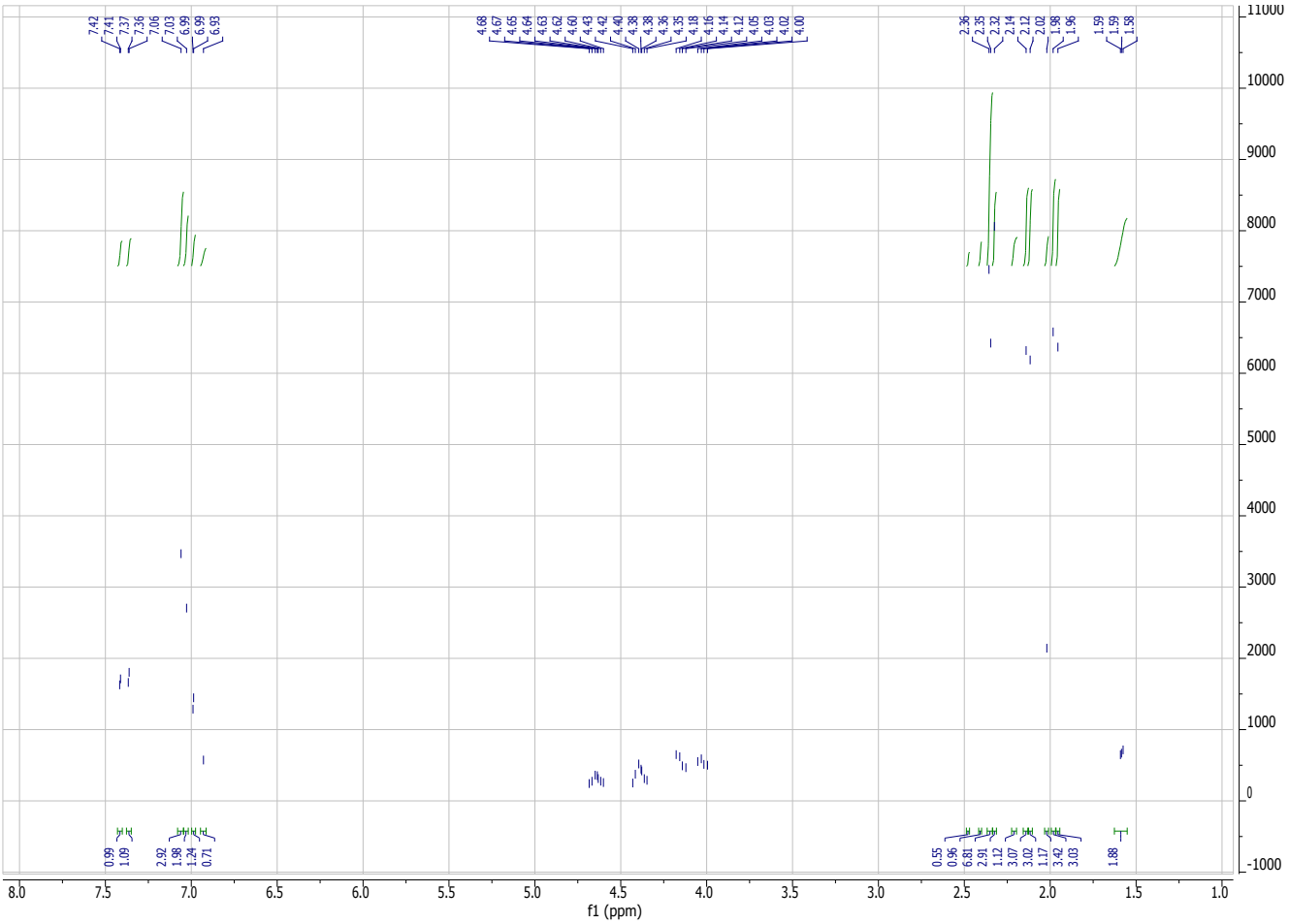

Figure S34. ^{1}H NMR spectrum of compound **3c** in CD_2Cl_2 at 23°C.

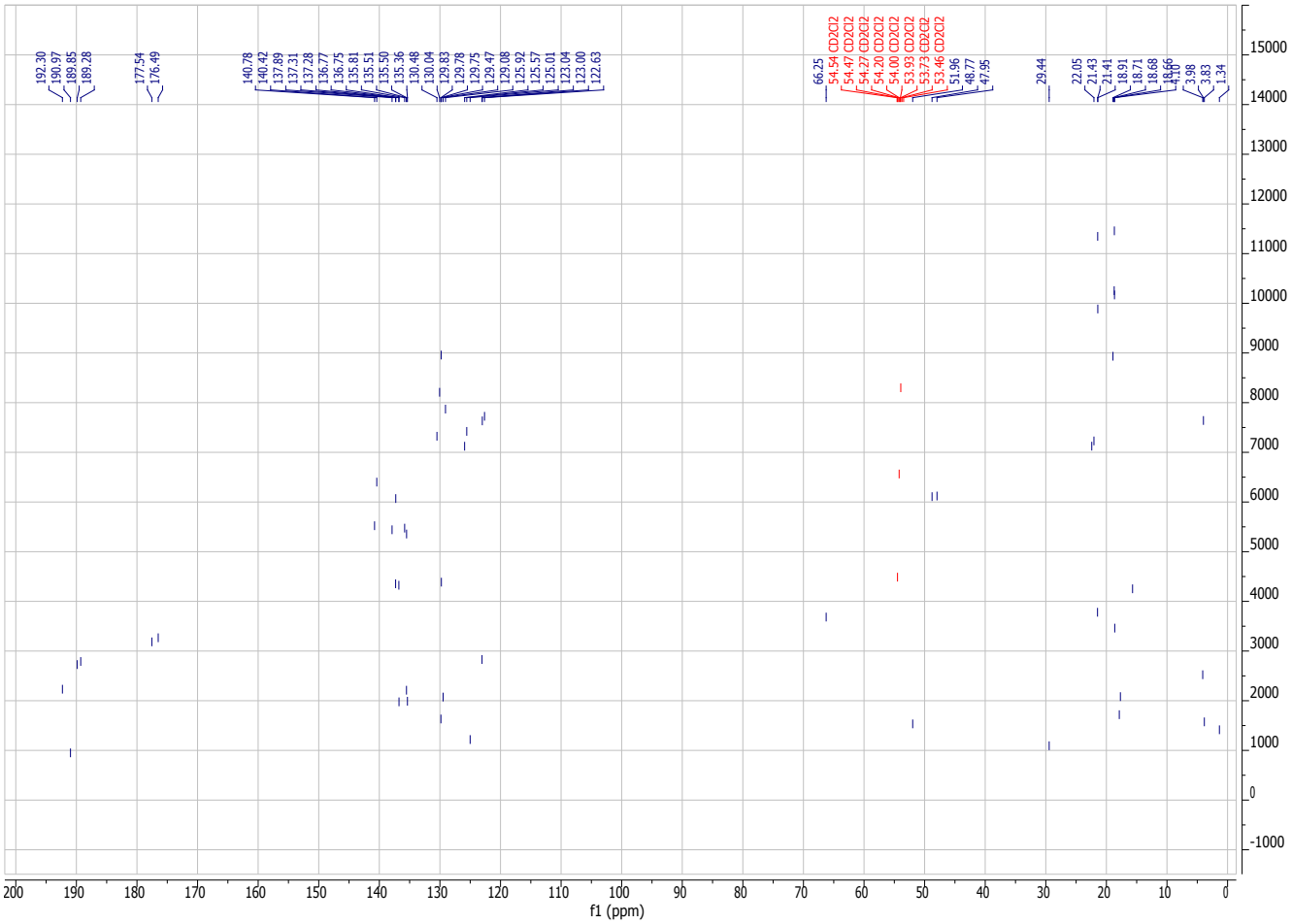

Figure S35. ^{13}C NMR spectrum of compound **3c** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-diisopropylphenyl-3,3'-ethylene-diimidazoline-2,2'-diylidene)rhenium(I)-hexafluorophosphate (4)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.05 (d, 6H, ^{3}J = 6.8 Hz, $CH(CH_3)_2$), 1.11 (d, 6H, ^{3}J = 6.8 Hz, $CH(CH_3)_2$), 1.21 (d, 6H, ^{3}J = 2.5 Hz, $CH(CH_3)_2$), 1.23 (d, 6H, ^{3}J = 2.3 Hz, $CH(CH_3)_2$), 2.34 (s, 3H, $NCCH_3$), 2.34 (m, 2H, $CH(CH_3)_2$, 2.56 (m, 2H, $CH(CH_3)_2$, 4.67 (m, 2H, NCHCHN), 4.78 (m, 2H, NCHHCHN), 6.99 (d, 2H, ^{3}J = 1.9 Hz, NCHCHNC-Dipp), 7.29 (d, 2H, ^{3}J = 1.7 Hz, NCHCHN- Dipp), 7.29 (m, 4H, *ortho-H*), 7.50 (t, 2H, ^{3}J = 7.8 Hz, *para-H*).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.25 ($NCCH_3$), 22.74 ($CH(CH_3)_2$), 22.83 ($CH(CH_3)_2$), 26.31 ($CH(CH_3)_2$), 26.39 ($CH(CH_3)_2$), 28.87 (NCH_2CH_2N), 29.18 (NCH_2CH_2N), 123.93 ($NCCH_3$), 124.35 ($NCHCHN\text{-}CH(CH_3)_2$), 124.95 ($NCHCHN\text{-}CH(CH_3)_2$), 126.13 (*ortho-C*), 131.59 (*meta-C*), 137.97 (*ipso-C*N), 147.07 (*para-C*), 173.96 (NCN), 188.82 ($CO_{trans\text{-}NHC}$), 192.85 ($CO_{cis\text{-}NHC}$).

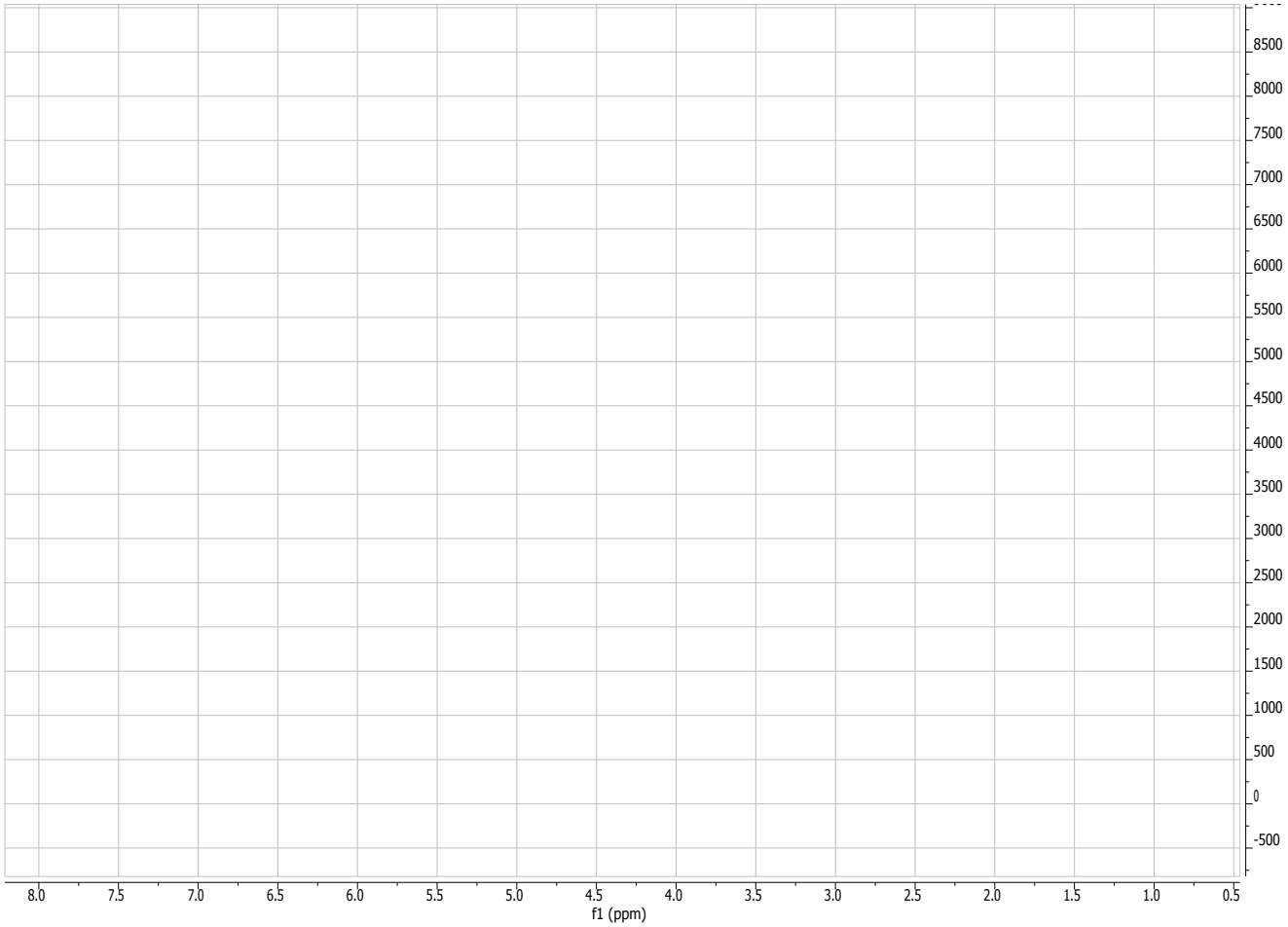

Figure S36. ^{1}H NMR spectrum of compound **4** in CD_2Cl_2 at 23°C.

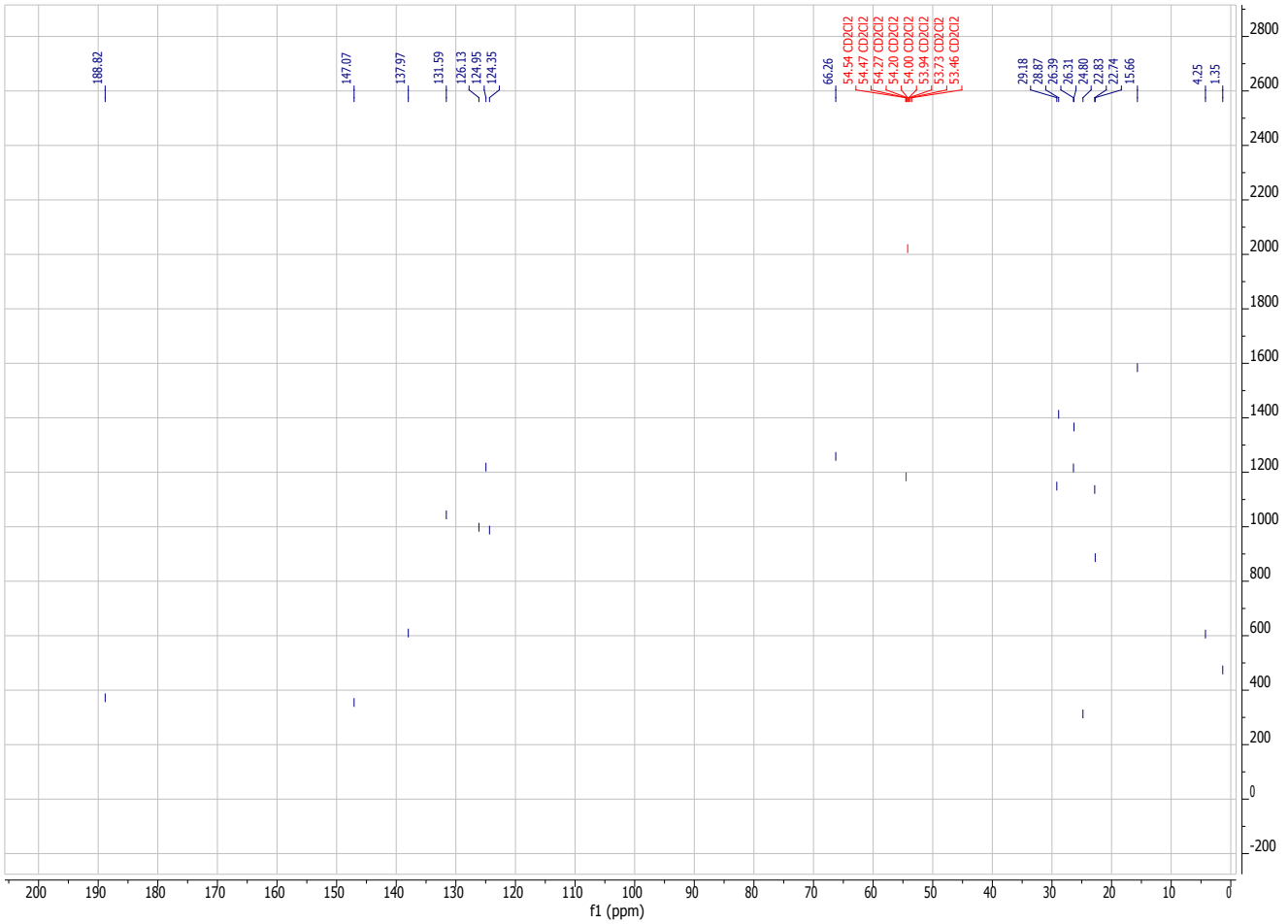

Figure S37. ^{13}C NMR spectrum of compound **4** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-dimesityl-3,3'-ethylene-diimidazoline-2,2'-diylidene)rhenium(I)-[Al(OC(CF$_3$)$_3$)$_4$] (5a)

^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm): 1.97 (s, 6H, *ortho*-CH_3), 1.99 (s, 6H, *ortho*-CH_3), 2.26 (s, 3H, NCCH_3), 2.33 (s, 6H, *para*-CH_3), 4.64 (m, 4H, N(CH_2)$_2$N), 6.97 (d, 2H, ^3J = 1.9 Hz, NC*H*CHNC-Mes), 7.02 (s, 4H, *meta*-C*H*), 7.20 (d, 2H, ^3J = 1.9 Hz, NCHC*H*N-Mes).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.31 (NC*C*H$_3$), 18.31 (*ortho*-*C*H$_3$), 18.58 (*ortho*-*C*H$_3$), 21.39 (*para*-*C*H$_3$), 52.57 (N*C*H$_2$*C*H$_2$N), 120.41 (N*C*HCHN-Mes), 122.88 (N*C*CH$_3$), 123.32 (N*C*HCHN-Mes), 124.69 (NCH*C*HN-Mes), 124.92 (NCH*C*HN-Mes), 129.59 (*C*-*ortho*-CH$_3$), 130.28 (*C*-*ortho*-CH$_3$), 135.95 (*meta*-*C*), 136.76 (*meta*-*C*), 137.30 (*ipso*-*C*N), 140.94 (*C*-*para*-CH$_3$), 173.98 (N*C*N), 188.96 (*C*O$_{trans\text{-}NHC}$), 192.56 (*C*O$_{cis\text{-}NHC}$).

Figure S38. ^{1}H NMR spectrum of compound **5a** in CD_2Cl_2 at 23°C.

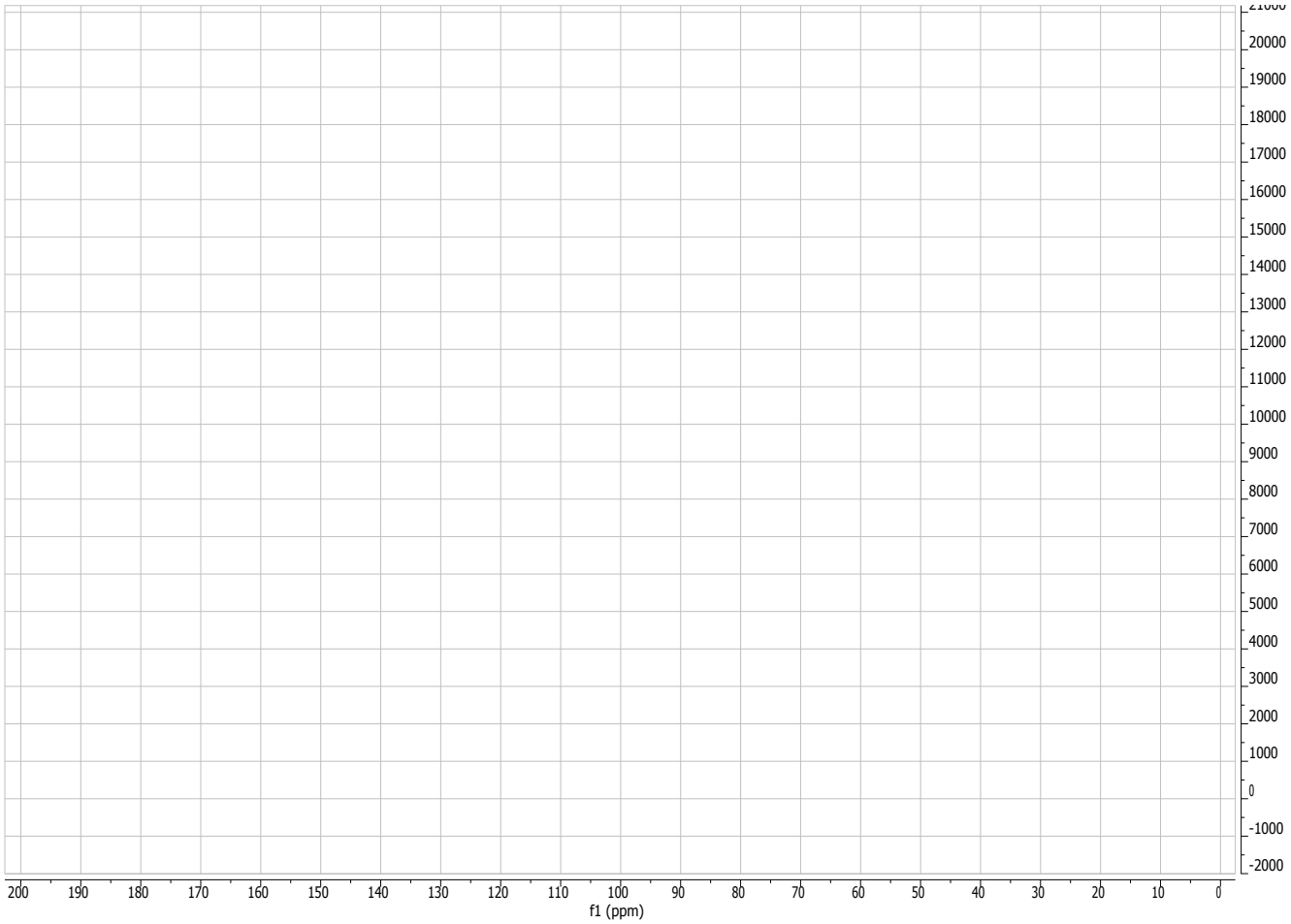

Figure S39. ^{13}C NMR spectrum of compound **5a** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-dimesityl-3,3'-propylene-diimidazoline-2,2'-diylidene)rhenium(I)- [Al(OC(CF$_3$)$_3$)$_4$] (5b)

^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm): 1.96 (s, 3H, *ortho*-CH_3), 1.97 (s, 3H, *ortho*-CH_3), 2.05 (s, 3H, *ortho*-CH_3), 2.07 (m, 2H, NCH$_2$CH_2CH$_2$N), 2.10 (s, 3H, *ortho*-CH_3), 2.28 (s, 3H, NCCH_3), 2.34 (s, 3H, *para*-CH_3), 2.35 (s, 3H, *para*-CH_3), 4.13 (m, 4H, NCH_2CH$_2$CH_2N), 6.99 (m, 1H, *meta*-C*H*), 7.01 (m, 1H, *meta*-C*H*), 7.04 (d, 1H, ^3J = 1.9 Hz, NCHC*H*N-Mes), 7.04 (m, 1H, *meta*-C*H*), 7.05 (m, 1H, *meta*-C*H*), 7.07 (d, 2H, ^3J = 1.9 Hz, NCHC*H*N-Mes), 7.22 (d, 1H, ^3J = 1.9 Hz, NC*H*CHN-Mes), 7.24 (d, 1H, ^3J = 1.9 Hz, NC*H*CHN-Mes).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.16 (NC*C*H$_3$), 18.39 (*ortho*-*C*H$_3$), 18.48 (*ortho*-*C*H$_3$), 18.56 (*ortho*-*C*H$_3$), 18.82 (*ortho*-*C*H$_3$), 21.41 (*para*-*C*H$_3$), 21.41 (*para*-*C*H$_3$), 34.26 (NCH$_2$*C*H$_2$CH$_2$N), 46.57 (NCH$_2$CH$_2$*C*H$_2$N), 47.16 (N*C*H$_2$CH$_2$CH$_2$N), 122.46 (N*C*CH$_3$), 123.21 (N*C*HCHN-Mes), 123.31 (N*C*HCHN-Mes), 126.17 (NCH*C*HN-Mes), 126.21 (NCH*C*HN-Mes), 129.21 (*C*-*ortho*-CH$_3$), 130.05 (*C*-*ortho*-CH$_3$), 130.10 (*C*-*ortho*-CH$_3$), 130.72 (*C*-*ortho*-CH$_3$), 135.19 (*meta*-*C*), 136.14 (*meta*-*C*), 136.56 (*meta*-*C*), 137.22 (*ipso*-*C*N), 137.35 (*ipso*-*C*N), 137.75 (*meta*-*C*), 140.88 (*C*-*para*-CH$_3$), 141.13 (*C*-*para*-CH$_3$), 175.28 (N*C*N), 177.21 (N*C*N), 188.44 (*C*O$_{trans\text{-}NHC}$), 188.72 (*C*O$_{trans\text{-}NHC}$), 192.50 (*C*O$_{cis\text{-}NHC}$).

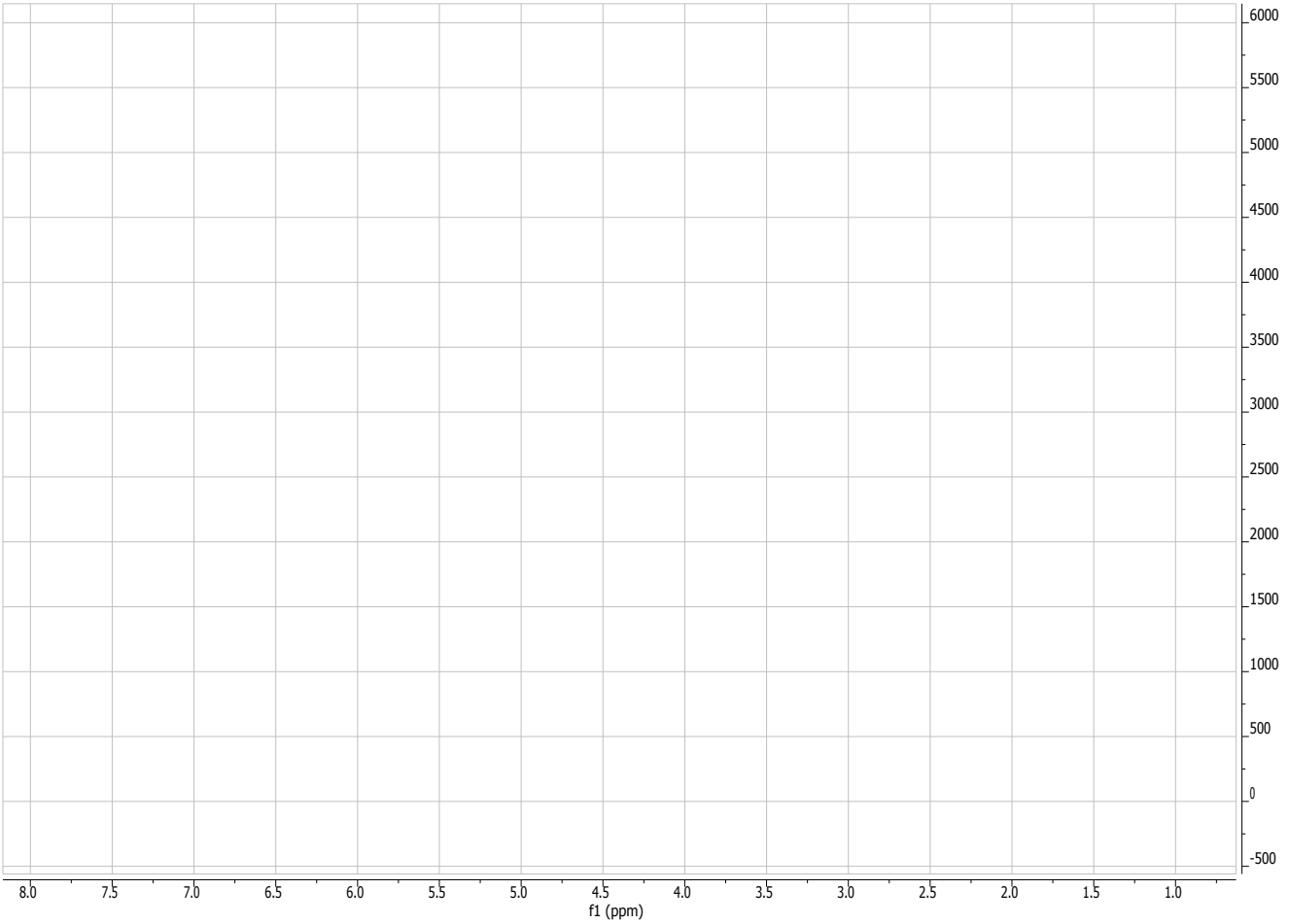

Figure S40. ^{1}H NMR spectrum of compound **5b** in CD_2Cl_2 at 23°C.

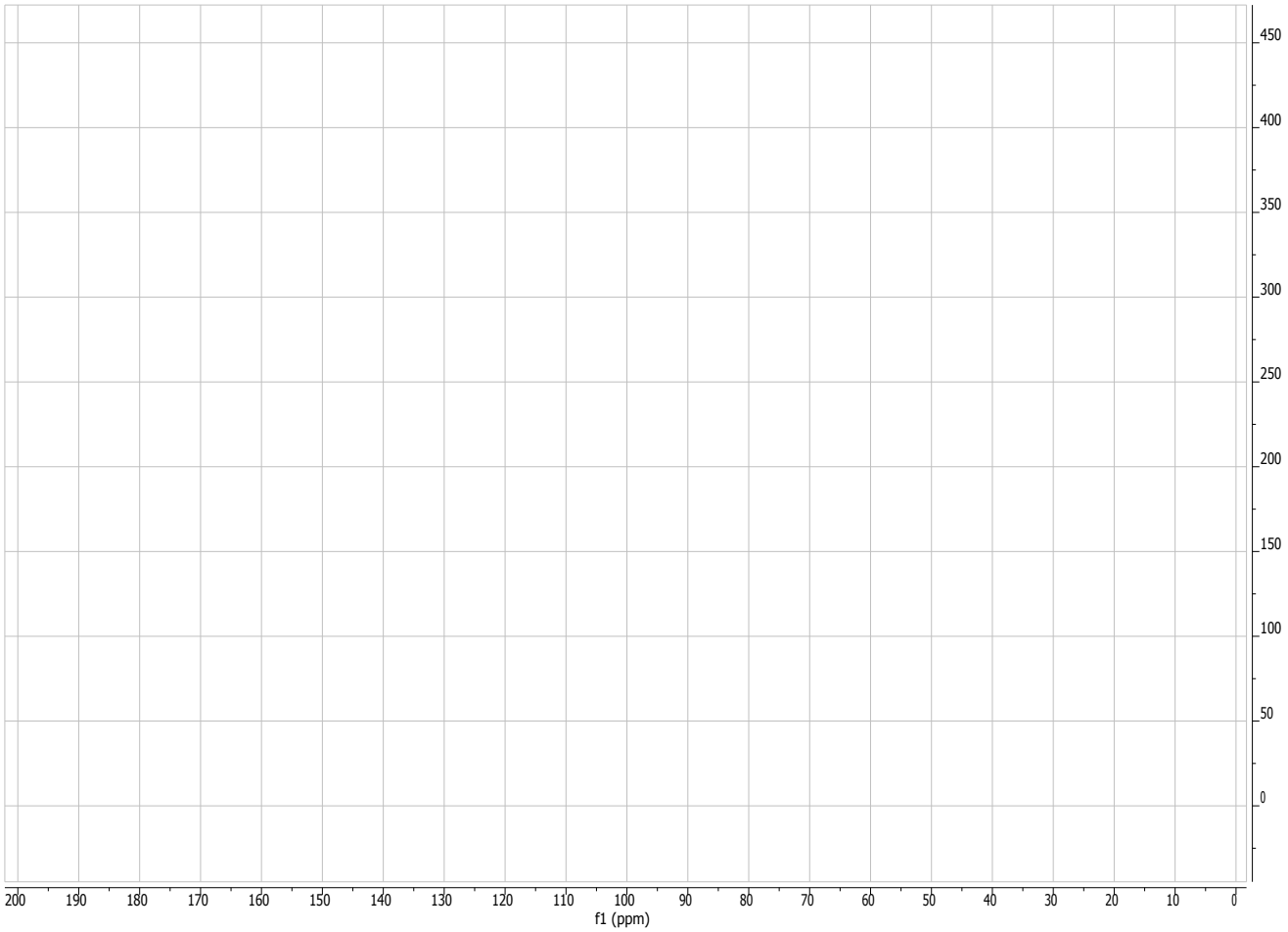

Figure S41. ^{13}C NMR spectrum of compound **5b** in CD_2Cl_2 at 23°C.

fac-acetonitrile-tricarbonyl(1,1'-dimesityl-3,3'-butylene-diimidazoline-2,2'-diylidene)rhenium(I)-[Al(OC(CF$_3$)$_3$)$_4$] (5c)

^{1}H-NMR (400 MHz, CD_2Cl_2): δ (ppm): 1.59 (m, 2H, $NCH_2(CH_2)_2CH_2N$), 1.94 (s, 3H, *ortho*-CH_3), 2.00 (s, 3H, *ortho*-CH_3), 2.08 (s, 3H, *ortho*-CH_3), 2.14 (s, 3H, *ortho*-CH_3), 2.22 (m, 2H, $NCH_2CHCHCHCH_2N$), 2.27 (s, 3H, $NCCH_3$), 2.35 (s, 3H, *para*-CH_3), 2.36 (s, 3H, *para*-CH_3), 3.94 (m, 1H, $NCH(CH_2)_2CHHN$), 4.04 (m, 1H, $NCHH(CH_2)_2CHHN$), 4.45 (m, 1H, $NCH(CH_2)_2CHHN$), 4.63 (m, 1H, $NCHH(CH_2)_2CHN$), 7.00 (m, 2H, *meta*-CH), 7.06 (m, 2H, *meta*-CH), 7.07 (m, 1H, *meta*-CH), 7.07 (m, 1H, $NCHCHN$-Mes), 7.10 (d, 1H, ^3J = 2.0 Hz, $NCHCHN$-Mes), 7.32 (d, 1H, ^3J = 2.0 Hz, $NCHCHN$-Mes), 7.34 (d, 1H, ^3J = 2.0 Hz, $NCHCHN$-Mes).

^{13}C-NMR (101 MHz, CD_2Cl_2, 298 K): δ (ppm): 4.17 ($NCCH_3$), 18.60 (*ortho*-CH_3), 18.65 (*ortho*-CH_3), 18.69 (*ortho*-CH_3), 18.93 (*ortho*-CH_3), 21.42 (*para*-CH_3), 21.42 (*para*-CH_3), 21.98 ($NCH_2CH_2CH_2CH_2N$), 22.47 ($NCH_2CH_2CH_2CH_2N$), 48.04 ($NCH_2(CH_2)_2CH_2N$), 48.72 ($NCH2(CH2)_2CH_2N$), 120.40 ($NCHCHN$-Mes), 126.08 ($NCCH_3$), 122.32 ($NCHCHN$-Mes), 122.63 ($NCHCHN$-Mes), 123.31 ($NCHCHN$-Mes), 128.93 (*C-ortho*-CH_3), 130.02 (*C-ortho*-CH_3), 130.13 (*C-ortho*-CH_3), 130.84 (*C-ortho*-CH_3), 134.87 (*meta*-*C*), 135.77 (*meta*-*C*), 136.23 (*ipso*-*C*N), 136.88 (*meta*-*C*), 137.07 (*ipso*-*C*N), 138.12 (*meta*-*C*), 140.78 (*C-para*-CH_3), 141.08 (*C-para*-CH_3), 176.35 (NCN), 178.21 (NCN), 188.98 ($CO_{trans\text{-}NHC}$), 189.54 ($CO_{trans\text{-}NHC}$), 191.82 ($CO_{cis\text{-}NHC}$).

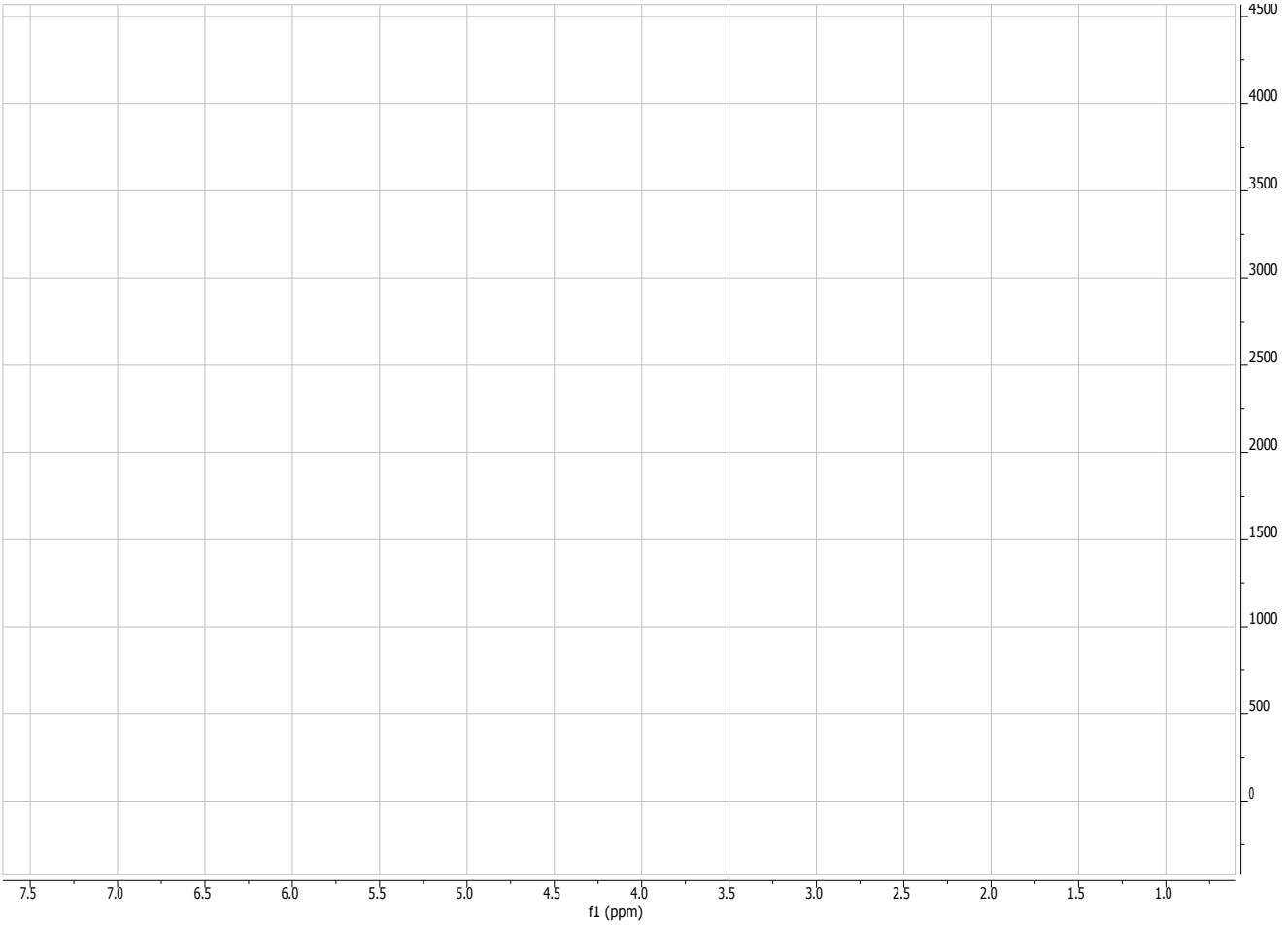

Figure S42. ^{1}H NMR spectrum of compound **5c** in CD_2Cl_2 at 23°C.

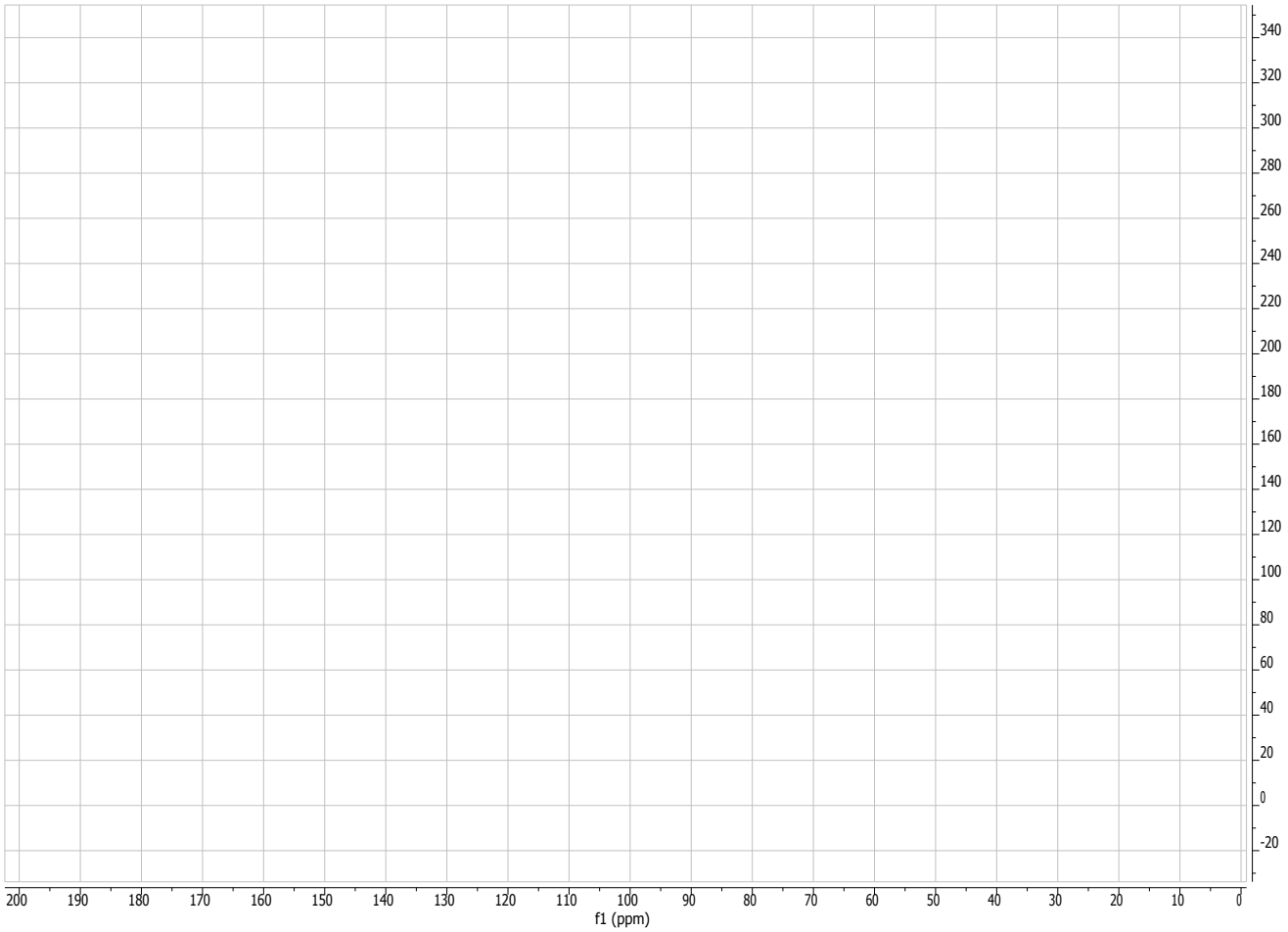

Figure S43. ^{13}C NMR spectrum of compound **5c** in CD_2Cl_2 at 23°C.

5. References

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, Moliterni A. G. G.; A.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. "**SIR97**", A New Tool for Crystal Structure Determination and Refinement; *J. Appl. Crystallogr.* **1999**, *32*, 115-119.
[3a] Sheldrick, G. M. "**SHELXS-97**", Program for Crystal Structure Solution, Göttingen, (1997).
[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.
[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).
[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).
[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.
[8] Huebschle, C. B., Sheldrick, G. M. & Dittrich, B. "**SHELXLE**", *J. Appl. Cryst.* **2011**, *44*, 1281-1284.

Complete Reference **22** from manuscript:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., "**Gaussian 09"** Revision B.1, Wallingford CT: Gaussian Inc..