Synthesis of novel dinuclear N-substituted-(4-dimethylaminobenzaldehyde)thiosemicarbazonates of rhenium(I): formation of four- and/or five-membered chelate rings, conformation analysis and reactivity

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Supplementary Information

Content

List of compounds studied in the present work.

Details of the compositions of the solvated crystals are included in Tables S1 and Table List of compounds studied in the present work.

Details of the compositions of the solvated crystals are included in Tables S1 and Table S2

Compound	Abbreviation	Conformer (**C2-N3**-N2-C1(S)-N1)	Characterization	
Free thiosemicarbazone				
HL^A	HL^A	**E**,E,E,Z	Spectroscopic,	X-ray[a]
HL^B	HL^B	**E**,E,E,Z	Spectroscopic,	X-ray
Thiosemicarbazone complexes				
$[ReCl(\kappa^2S,N3\text{-}HL^A)(CO)_3]$		**E**,E,Z,Z	Spectroscopic	
$[ReBr(\kappa^2S,N3\text{-}HL^A)(CO)_3]$		**E**,E,Z,Z	Spectroscopic	
$[ReCl(\kappa^2S,N3\text{-}HL^B)(CO)_3]$		**E**,E,Z,Z	Spectroscopic	
$[ReBr(\kappa^2S,N3\text{-}HL^B)(CO)_3]$		**E**,E,Z,Z	Spectroscopic,	X-ray
Thiosemicarbazonate complexes (dimers)				
$[Re_2(\mu\text{-}\kappa^2S,N2{:}\kappa S\text{-}L^A)_2(CO)_6]$	1A	**E**,E,E,Z	Spectroscopic,	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N2{:}\kappa S\text{-}L^B)_2(CO)_6]$	1B	**E**,E,E,Z	Spectroscopic,	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^A)_2(CO)_6]$	2.1A'	**E**,E,Z,Z	Spectroscopic,[b]	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^A)_2(CO)_6]$	2.2A'	**E**,E,Z,E		X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^B)_2(CO)_6]$	2.2B'	**E**,E,Z,E	Spectroscopic,[c]	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^A)_2(CO)_6]$	2.3A	**Z**,E,Z,E	Spectroscopic,[b]	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^A)_2(CO)_6]$	2.3A'	**Z**,E,Z,E		X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^B)_2(CO)_6]$	2.3B	**Z**,E,Z,E	Spectroscopic,[b]	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^B)_2(CO)_6]$	2.3B'	**Z**,E,Z,E		X-ray
$[Re_2(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^{NO2})_2(CO)_6]$		**Z**,E,Z,E	Spectroscopic,	X-ray
$[Re_2(\mu\text{-}\kappa^2S,N2{:}\kappa S\text{-}L^A)(\mu\text{-}\kappa^2S,N3{:}\kappa S\text{-}L^A)(CO)_6]$		**E**,E,E,Z / **Z**,E,Z,E		X-ray
$[Re_2(\mu\text{-}\kappa^2S,N2{:}\kappa N3\text{-}L^B)_2(CO)_6]$	4B'	**Z**,_,E,Z		X-ray
Thiosemicarbazonate complexes (monomers)				
$[Re(\kappa^2S,N3\text{-}L^A)(py)(CO)_3]$		**Z**,E,Z,E	Spectroscopic,	X-ray

[Re(κ^2S,N2:κS-L^B)(κS-HL^B)(CO)$_3$]		**E**,E,E,Z		X-ray

[a] The X-ray structure is identical to those determined by Y. Yu, L.R. Lin, K.B. Yang, H. Zhang, R.B. Hang, L.S. Zheng, Youji Hoaxue (Chin.) (Chin. J. Org. Chem.) 26 (2006) 933-936.

[b] We were unable to distinguish the presence of one or other form in the isolated solid.

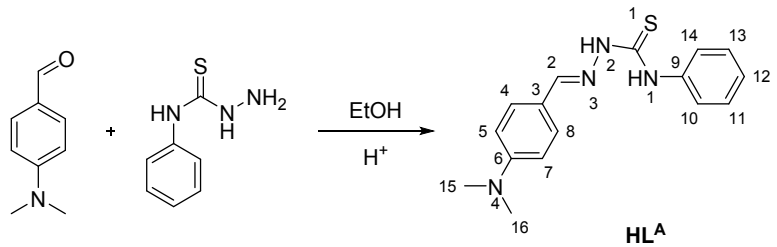
[c] The isolated samples contain traces of NaBr that could not be removed, so elementary analysis consistent with a defined stoichiometry was not obtained.

Synthesis of the ligands

N-phenyl-(4-dimethylaminobenzaldehyde)-thiosemicarbazone (HL^A)

This ligand was synthesized following the method reported by Yu *et al*[1].[34] To a solution of 4-dimethylaminobenzaldehyde (1.06 g: 7.1 mmol) and 4-phenylthiosemicarbazide (1.16 g: 6.9 mmol) in ethanol (40 mL) was added a drop of acetic acid and the mixture was heated under reflux for 3 h. The yellow solution was stirred at r.t. for 16 h. The resulting yellow solid was filtered off and vacuum dried over $CaCl_2$/KOH.

Single crystals of HL^A were obtained after storing a dichloromethane solution at –23 °C.



Yield: 1.84 g (90%). M.p.: 215 °C. $C_{16}H_{18}N_4S$ (298.13): calcd. C 64.3, H 6.1, N 18.8, S 10.7; found. C 64.4, H 6.1, N 18.8, S 10.7%. MS-ESI [*m*/*z* (%)]: 299 (100) |M + H|$^+$. IR data (ATR, ν/cm^{-1}): 3277b ν(NH); 1589s ν(C=N); 752m ν(C=S).

^{1}H NMR (acetone-d_6, ppm): 10.41 (*s*, 1H, N2H), 9.78 (*s*, 1H, N1H), 8.13 (*s*, 1H, C2H), 7.78 (*d*, *J* = 7.5 Hz, 2H, C10H, C14H), 7.68 (*d*, *J* = 8.9 Hz, 2H, C4H, C8H), 7.35 (*t*, *J* = 7.5 Hz, 2H, C11H, C13H), 7.17 (*t*, *J* = 7.5 Hz, 1H, C12H), 6.76 (*d*, *J* = 8.9 Hz, 2H, C5H, C7H), 3.03 (*s*, 6H, C15H, C16H).

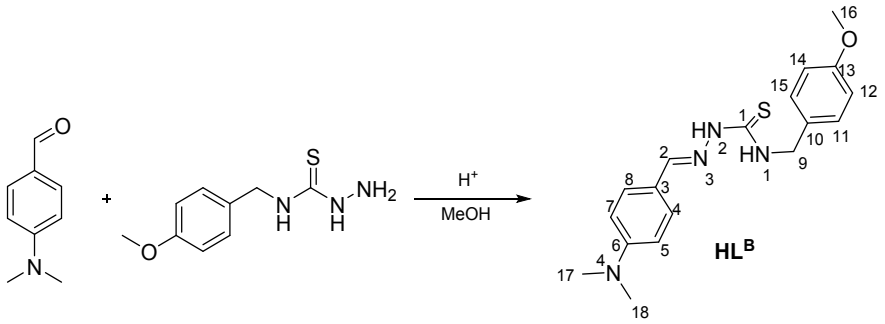
^{1}H NMR (DMSO-d_6, ppm): 11.59 (*s*, 1H, N2H), 9.93 (*s*, 1H, N1H), 8.04 (*s*, 1H, C2H), 7.69 (*d*, *J* = 8.9 Hz, 2H, C4H, C8H), 7.60 (*d*, *J* = 7.5 Hz, 2H, C10H, C14H), 7.36 (*t*, *J* = 7.5 Hz, 2H, C11H, C13H), 7.19 (*t*, *J* = 7.5 Hz, 1H, C12H), 6.72 (*d*, *J* = 8.9 Hz, 2H, C5H, C7H), 2.98 (*s*, 6H, C15H, C16H).

[1] Yu, Y.; Lin, L.R.; Yang, K.B.; Zhang, H.; Hang, R.B.; Zheng, L.S. Synthesis and Chiral Crystal Structure of 1-[4-(Dimethylamino)- benzylidene]-4-phenylthiosemicarbazide. *Youji Hoaxue (Chin.) (Chin. J. Org. Chem.)* **2006**, *26*, 933-936.

N-4-methoxybenzyl-(4-dimethylaminobenzaldehyde)-thiosemicarbazone (HL^B)

A solution of 4-dimethylaminobenzaldehyde (125 mg g: 0.84 mmol), 4-methoxybenzyl thiosemicarbazide (180 mg: 0.85 mmol) and a drop of acetic acid in methanol (20 mL) was heated under reflux for 4 h. The yellow solid was filtered off and vacuum dried over $CaCl_2$/KOH.

Single crystals were obtained after storing a methanol solution at 4 °C.



Yield: 230 mg (80%). M.p.: 170 °C. $C_{18}H_{22}N_4OS$ (342.2): calcd. C 63.1, H 6.5, N 16.4, S 9.3; found. C 62.9, H 6.6, N 16.5, S 8.8%. MS-ESI [*m*/*z* (%)]: 343 (100) $|M + H|^+$. IR data (ATR, ν/cm^{-1}): 3145b ν(NH); 1609m, 1597s ν(C=N); 814m ν(C=S).

^{1}H NMR (acetone-d_6, ppm): 10.18 (*s*, 1H, N2H), 8.46 (*s*, 1H, N1H), 8.05 (*s*, 1H, C2H), 7.55 (*d*, *J* = 8.7 Hz, 2H, C4H, C8H), 7.37 (*d*, *J* = 8.5 Hz, 2H, C11H, C15H), 6.89 (*d*, *J* = 8.5 Hz, 2H, C12H, C14H), 6.72 (*d*, *J* = 8.7 Hz, 2H, C5H, C7H), 4.89 (*d*, *J* = 6.2 Hz, 2H, C9H), 3.78 (*s*, 3H, C16H), 2.99 (*s*, 6H, C17H, C18H).

^{1}H NMR (DMSO-d_6, ppm): 11.28 (*s*, 1H, N2H), 8.75 (*t*, *J* = 6.0 Hz, 1H, N1H), 7.95 (*s*, 1H, C2H), 7.58 (*d*, *J* = 8.7 Hz, 2H, C4H, C8H), 7.30 (*d*, *J* = 8.5 Hz, 2H, C11H, C15H), 6.88 (*d*, *J* = 8.5 Hz, 2H, C12H, C14H), 6.69 (*d*, *J* = 8.7 Hz, 2H, C5H, C7H), 4.75 (*d*, *J* = 6.0 Hz, 2H, C9H), 3.72 (*s*, 3H, C16H), 2.95 (*s*, 6H, C17H, C18H).

Table S1. Crystal data and structure refinement for the $\mathbf{HL^A}$ derivatives.

Structure	**1A**	**2.1A'.2MeOH**	**2.2A'.2C$_3$H$_6$O**	**2.3A**	**2.3A.0.27MeOH**	**2.3A'.4DMSO**	**2.3A/2.3A'.2DMSO**	**3A**	**[Re(L^A)(py)(CO)$_3$]**
CCDC ref.	2011245	2011247	2011246	2011253	2011254	2011243	2011252	2011244	2011256
Empirical formula	$C_{38}H_{34}N_8O_6Re_2S_2$	$C_{40}H_{42}N_8O_8Re_2S_2$	$C_{44}H_{46}N_8O_8Re_2S_2$	$C_{38}H_{34}N_8O_6Re_2S_2$	$C_{39}H_{36.75}N_8O_{6.74}Re_2S_2$	$C_{46}H_{58}N_8O_{10}Re_2S_6$	$C_{59}H_{57}N_{12}O_{10}Re_3S_4$	$C_{38}H_{34}N_8O_6Re_2S_2$	$C_{24}H_{22}N_5O_3ReS$
Formula weight	1135.25	1199.34	1251.40	1135.25	1161.95	1447.76	1781.00	1135.25	646.72
Temperature (K)	293(2)	293(2)	220(2)	100(2)	100(2)	100(2)	100(2)	100(2)	135(2)
λ (Å)	1.54178	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$P4_22_12$	P-1	P-1	P-1	$P2_1/c$	Pbca	P-1	P-1	$P2_1/c$
a (Å)	14.2145(3)	7.6145(11)	7.5900(5)	12.0226(10)	9.5332(10)	19.421(3)	11.5233(7)	10.4956(19)	13.0513(13)
b (Å)	14.2145(3)	11.0875(16)	13.7988(9)	12.9353(10)	24.862(3)	8.9135(12)	14.9606(9)	13.156(2)	11.2495(11)
c (Å)	20.5788(5)	13.984(2)	14.1217(8)	16.5028(14)	17.4984(19)	31.036(4)	19.8454(13)	14.995(3)	16.2346(17)
α(°)	90	66.997(4)	62.188(2)	70.700(3)	90	90	93.141(3)	73.452(5)	90
β(°)	90	88.047(4)	81.634(2)	72.206(3)	104.175(4)	90	99.828(3)	84.772(6)	98.488(3)
γ(°)	90	83.275(4)	84.908(2)	66.019(3)	90	90	109.590(3)	80.429(5)	90
Volume (Å^3)	4158.0(2)	1079.2(3)	1293.87(14)	2169.0(3)	4021.1(7)	5372.6(12)	3152.7(3)	1955.0(6)	2357.5(4)
Z	4	1	1	2	4	4	2	2	4
Density (Mg/m^3)	1.814	1.845	1.606	1.738	1.919	1.790	1.876	1.929	1.822
μ (mm^{-1})	12.601	5.761	4.808	5.724	6.178	4.798	5.944	6.350	5.280
θ range (°)	3.779-71.822	2.694-28.396	2.713-28.335	2.460-26.500	2.203-28.344	2.474-26.436	2.318-26.627	2.367-28.466	2.210-28.347
Indep. Ref. (R_{int})	4075 (0.0811)	8873 (0.0301)	6430 (0.0546)	8957 (0.0502)	10033 (0.0575)	5497(0.0886)	13072(0.0542)	9740(0.0621)	5876(0.0415)
S (F^2)	1.078	1.097	1.092	1.017	1.041	1.295	1.078	1.059	1.044
R1/wR2 [I>2σ(I)]	0.0518/0.1360	0.0354/0.0824	0.0334/0.0549	0.0344/0.0793	0.0354/0.0602	0.0855/0.1496	0.0610/0.1191	0.0450/0.0891	0.0166/0.0426
R1/wR2 (all data)	0.0538/0.1385	0.0408/0.0862	0.0402/0.0562	0.0480/0.0862	0.0571/0.0653	0.1221/0.1607	0.0899/0.1411	0.0731/0.099	0.0202/0.0438
Flack parameter	-0.04(3)								

Table S2. Selected bond distances and angles $\mathbf{HL^A}$ derivatives

	1A	**2.1A'.2MeOH**	**2.2A'.2C_3H_6O**	**2.3A[(a)]**	**2.3A.0.27MeOH[b]**	**2.3A'.4DMSO**	**2.3A/2.3A'.2DMSO**		**3A**		**[Re(L^A)(py)$(CO)_3$]**
Coordination mode	μ-κ^2S,N2:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS		μ-κ^2S,N2:κS	μ-κ^2S,N3:κS	κ^2S,N3
Conformation of the ligand(*)	*EEEZ*	*EEZZ*	*EEZE*	*ZEZE*	*ZEZE*	*ZEZE*	*ZEZE*		*EEEZ*	*ZEZE*	*ZEZE*
(Pseudo)symmetry dimer	2	-1	-1	2	2	-1	2 [b]	-1	2		
X =	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$		N_{py}
Re(1)-S(1)	2.527(3)	2.4651(13)	2.4587(9)	2.4568(1)	2.4616(8)	2.459(3)	2.445(2)	2.480(3)	2.5377(17)[(b)]	2.4338(17)	2.4477(5)
Re(1)-N(2)	2.182(11)								2.182(5) [(b)]		
Re(1)-N(3)		2.199(5)	2.218(3)	2.182(4)	2.187(3)	2.171(10)	2.197(68)	2.176(8)		2.206(5)	2.1855(16)
Re(1)-X	2.537(3)	2.5404(15)	2.5417(9)	2.544(1)	2.5536(8)	2.528(3)	2.550(2)	2.532(3)	2.5412(19) [(b)]	2.559(2)	2.2346(17)
S(1)-C(1)	1.762(11)	1.771(6)	1.783(4)	1.793(4)	1.788(3)	1.797(13)	1.801(8)	1.861(11)	1.764(6) [(b)]	1.791(6)	1.746(2)
N(1)-C(1)	1.348(16)	1.362(7)	1.360(4)	1.343(6)	1.363(4)	1.341(17)	1.328(10)	1.266(15)	1.346(8) [(b)]	1.367(8)	1.366(3)
N(2)-C(1)	1.334(15)	1.297(7)	1.283(5)	1.294(6)	1.289(4)	1.292(16)	1.314(9)	1.365(14)	1.304(8) [(b)]	1.265(8)	1.313(3)
N(3)-N(2)	1.355(15)	1.417(7)	1.423(4)	1.387(5)	1.405(4)	1.408(13)	1.411(8)	1.375(11)	1.406(7) [(b)]	1.386(8)	1.399(2)
N(3)-C(2)	1.270(17)	1.311(8)	1.299(5)	1.300(6)	1.302(4)	1.306(14)	1.300(9)	1.313(14)	1.283(9) [(b)]	1.316(9)	1.307(3)
N(2)-Re(1)-S(1)	64.6(3)								63.86(15) [(b)]		
N(3)-Re(1)-S(1)		78.76(13)	78.31(8)	78.57(9)	78.70(7)	77.6(3)	78.3(1)	77.0(2)		78.29(16)	78.95(5)
S(1)-Re(1)-X	81.82(10)	81.02(5)	81.29(3)	81.59(4)	81.81(3)	82.47(11)	82.49(6)	81.92(10)	79.49(6) [(b)]	81.11(6)	86.21(5)
N(2)-Re(1)-X	87.3(2)								86.99(16) [(b)]		
N(3)-Re(1)-X		85.31(14)	87.97(8)	90.12(9)	90.45(7)	83.0(3)	92.2(2)	81.9(2)		89.43(17)	82.38(6)
N(2)-C(1)-S(1)	109.0(9)	124.7(4)	125.7(3)	125.2(4)	126.0(2)	123.8(10)	122.8(6)	116.7(9)	109.1(5) [(b)]	126.4(5)	127.01(16)
N(1)-C(1)-S(1)	129.3(9)	119.7(4)	112.6(3)	112.6(3)	112.6(2)	112.8(10)	113.8(6)	114.2(8)	128.1(5) [(b)]	109.8(5)	114.33(15)
N(2)-C(1)-N(1)	121.7(11)	115.6(5)	121.7(3)	122.2(4)	121.4(3)	123.3(12)	123.4(7)	128.4(10)	122.7(6) [(b)]	123.8(6)	118.65(18)
C(1)-N(2)-N(3)	113.4(10)	117.4(5)	116.2(3)	116.1(4)	115.8(3)	115.5(10)	116.8(6)	119.0(9)	114.8(5) [(b)]	115.6(5)	114.76(16)
C(2)-N(3)-N(2)	116.6(10)	108.1(5)	109.2(3)	115.6(4)	113.8(3)	114.1(10)	114.4(6)	115.4(9)	114.2(6) [(b)]	115.8(5)	114.96(16)

[a] Average values of the two molecules of the asymmetric unit .

[b] Average values between the two monomers that constitute the asymmetric unit.

(*) Corresponding to the TSC arm bonds, respectively: C2-N3/N3-N2/N2-C1/C1-N1.

Table S3. Crystal data and structure refinement for the **HL^B** derivatives.

Structure	**HL^B**	**$[ReBr(HL^B)(CO)_3]$**	**1B**	**$2.2B'.2(CHCl_3)$**	**2.3B**	**2.3B.2(DMSO)**	**2.3B'**	**4B'.2(THF)**	**$4B'.2(C_3H_6O)$**	**$[Re(L^B)(HL^B)(CO)_3]$**
CCDC ref.	2011258	2011248	2011249	2011255	2011259	2011242	2011251	2011257	2011250	2011240
Empirical formula	$C_{18}H_{22}N_4OS$	$C_{21}H_{22}BrN_4O_4ReS$	$C_{42}H_{42}N_8O_8Re_2S_2$	$C_{44}H_{44}Cl_6N_8O_8Re_2S_2$	$C_{42}H_{42}N_8O_8Re_2S_2$	$C_{44}H_{54}N_8O_{10}Re_2S_2$	$C_{42}H_{42}N_8O_8Re_2S_2$	$C_{50}H_{58}N_8O_{10}Re_2S_2$	$C_{48}H_{54}N_8O_{10}Re_2S_2$	$C_{39}H_{43}N_8O_5ReS_2$
Formula weight	342.5	692.59	1223.35	1462.09	1223.35	1379.58	1223.35	1367.56	1339.51	954.13
Temperature (K)	100.0(2)	293(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	102(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	C2/c	P-1	P-1	$P2_1/n$	P-1	P-1	P-1	P-1
a (Å)	10.6294(8)	7.0656(5)	29.6962(17)	11.2793(11)	11.6523(9)	13.6065(17)	6.8986(4)	8.5426(10)	8.5511(6)	12.7270(9)
b (Å)	12.3275(9)	12.4131(9)	11.1984(6)	11.6949(10)	12.9299(10)	20.412(3)	9.1803(6)	12.0341(13)	11.6605(7)	17.1075(12)
c (Å)	15.6410(11)	15.2623(11)	28.1259(15)	12.0534(11)	15.3926(11)	19.884(3)	17.7604(12)	13.4890(15)	14.1617(10)	19.8217(15)
α(°)	105.280(2)	109.761(2)	90	71.047(3)	96.490(2)	90	83.875(2)	76.479(3)	98.204(2)	76.626(2)
β(°)	95.715(2)	100.467(2)	105.918(2)	62.221(3)	102.894(2)	105.642(4)	85.443(2)	76.178(4)	107.182(2)	80.578(2)
γ(°)	112.174(2)	98.649(2)	90	84.981(3)	90.487(3)	90	72.918(2)	85.682(4)	92.458(2)	71.506(2)
Volume ($Å^3$)	1784.8(2)	1205.92(15)	8994.6(9)	1326.6(2)	2244.8(3)	5317.9(12)	1067.66(12)	1308.9(3)	1329.83(16)	3962.7(5)
Z	4	2	8	1	2	4	1	1	1	4
Density (Mg/m^3)	1.274	1.907	1.807	1.830	1.810	1.723	1.903	1.735	1.673	1.599
μ (mm^{-1})	0.194	6.816	5.531	4.996	5.541	4.766	5.825	4.764	4.687	3.226
θ range (°)	2.483-26.635	2.706-28.403	2.344-28.330	2.254-28.339	2.487-28.353	2.331-24.798	2.330-26.435	2.456-28.414	2.519-28.332	2.258-28.341
Indep. Ref. (R_{int})	7373(0.0585)	6041(0.0219)	11184(0.0435)	6603(0.0505)	11185(0.050)	9089(0.1012)	4382(0.1116)	6550(0.0333)	6604(0.0494)	19714(0.0600)
S (F^2)	1.090	1.122	1.096	1.104	1.025	1.116	1.017	1.052	1.048	1.030
R1/wR2 [I>2σ(I)]	0.0590/0.1170	0.0165/0.0380	0.0285/0.0522	0.0363/0.0770	0.0347/0.0709	0.0578/0.1218	0.0434/0.0909	0.0182/0.0394	0.0250/0.0503	0.0419/0.0830
R1/wR2 (all data)	0.0880/0.1271	0.0193/0.0390	0.0373/0.0551	0.0514/0.0833	0.0514/0.0764	0.1092/0.1572	0.0610/0.0977	0.0216/0.0404	0.0322/0.0522	0.0655/0.0935

Table S4. Selected bond distances and angles HL^B derivatives

	HL^B [a]	**[ReBr(HL^B)($CO)_3$]**	**1B[b]**	**2.2B'.2($CHCl_3$)**	**2.3B[b]**	**2.3B.2(DMSO)[b]**	**2.3B'**	**4B'.2(THF)**	**4B'.2(C_3H_6O)**	**[Re(L^B)(HL^B)($CO)_3$]**
Coordination mode	--	κ^2S,N3	μ-κ^2S,N2:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N3:κS	μ-κ^2S,N2:κN3	μ-κ^2S,N2:κN3	κ^2S,N2/κS
Conformation of the ligand(*)	EEEZ	EEZZ	*EEEZ*	*EEZE*	*ZEZE*	*ZEZE*	*ZEZE*	*ZZEZ*	*ZZEZ*	*EEEZ*
(Pseudo)symmetry dimer	--	--	2	-1	2	2	-1	-1	-1	--
X =	--	Br	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$S^{\#1}$	$N3^{\#1}$	$N3^{\#1}$	S
Re(1)-S(1)	__	2.4466(6)	2.5448(6)	2.4720(11)	2.4642(7)	2.451(2)	2.4698(16)	2.5409(6)	2.5275(8)	2.5565(8)
Re(1)-N(2)	__		2.195(2)					2.1651(17)	2.163(2)	2.187(3)
Re(1)-N(3)	__	2.2485(17)		2.214(4)	2.193(3)	2.178(7)	2.184(6)			
Re(1)-X	__	2.6467(3)	2.5406(6)	2.5461(12)	2.5486(8)	2.549(2)	2.5338(18)	2.2115(17)	2.213(2)	2.5229(8)
S(1)-C(1)	1.695(2)	1.686(2)	1.767(2)	1.788(5)	1.777(3)	1.781(8)	1.791(7)	1.745(2)	1.745(3)	1.730(4)[d] 1.728(4)[e]
N(1)-C(1)	1.333(2)	1.333(3)	1.338(3)	1.354(5)	1.311(4)	1.354(11)	1.346(8)	1.329(3)	1.321(4)	1.312(4)[d] 1.283(4)[e]
N(2)-C(1)	1.357(2)	1.333(3)	1.315(3)	1.288(6)	1.295(4)	1.302(11)	1.299(8)	1.320(3)	1.328(4)	1.322(4)[d] 1.303(4)[e]
N(3)-N(2)	1.381(2)	1.399(2)	1.403(3)	1.428(5)	1.391(4)	1.406(10)	1.393(7)	1.427(2)	1.429(3)	1.389(4)[d] 1.386(4)[e]
N(3)-C(2)	1.287(2)	1.296(3)	1.290(4)	1.297(6)	1.309(4)	1.325(11)	1.311(9)	1.297(3)	1.291(4)	1.288(4)[d] 1.280(4)[e]
N(2)-Re(1)-S(1)	--		64.07(6)					64.28(5)	64.82(6)	64.20(7)
N(3)-Re(1)-S(1)	--	79.95(5)		78.57(10)	78.41(7)	78.9(2)	76.99(15)			
S(1)-Re(1)-X	--	86.965(18)	81.13(2)	81.04(4)	82.76(3)	82.27(7)	83.64(6)	87.64(5)	86.47(6)	87.38(3)
N(2)-Re(1)-X	--		88.34(7)					79.10(6)	80.18(9)	81.51(7)
N(3)-Re(1)-X	--	84.92(5)		86.65(10)	91.04(8)	90.5(2)	83.69(16)			
N(2)-C(1)-S(1)	118.4(1)	122.06(16)	109.6(1)	125.8(3)	126.0(2)	125.40(7)	125.7(5)	110.06(16)	110.3(2)	111.0(2)[c] 122.9(2)[d]

	HL^{B} (a)	**[ReBr(HL^{B})$(CO)_3$]**	**1B(b)**	**2.2B'.2($CHCl_3$)**	**2.3B(b)**	**2.3B.2(DMSO)(b)**	**2.3B'**	**4B'.2(THF)**	**4B'.2(C_3H_6O)**	**[Re(L^{B})(HL^{B})$(CO)_3$]**
N(1)-C(1)-S(1)	125.5(1)	120.70(17)	123.7(2)	115.6(4)	115.8(2)	115.2(6)	115.2(5)	125.42(16)	125.4(2)	125.2(3) (c) 121.7(2) (d)
N(2)-C(1)-N(1)	116.1(1)	117.2(2)	126.7(2)	118.6(4)	118.2(3)	119.4(8)	119.1(6)	124.5(2)	124.3(3)	123.8(3) (c) 115.5(3) (d)
C(1)-N(2)-N(3)	120.53(1)	123.81(18)	115.1(2)	116.4(4)	115.9(2)	115.7(7)	113.6(6)	118.21(17)	117.7(2)	116.1(3) (c) 124.1(3) (d)
C(2)-N(3)-N(2)	115.4(1)	111.66(17)	113.4(2)	109.0(4)	113.6(3)	113.4(7)	115.6(6)	117.08(17)	118.6(2)	113.9(3) (c) 116.2(3) (d)

[a] Average values of the two molecules of the asymmetric unit .

[b] Average values between the two monomers that constitute the asymmetric unit.

(c) Corresponding to bidentate (κ^2S,N2) ligand

(d) Corresponding to monodentate (κS) ligand.

(*) Corresponding to the TSC arm bonds, respectively: C2-N3/N3-N2/N2-C1/C1-N1.

Table S5. Crystal data and structure refinement for the $\mathbf{HL^{NO2}}$ derivative.

Structure	$\mathbf{[Re_2(L^{NO2})_2(CO)_6]}$
CCDC reference	2011241
Empirical formula	$C_{38}H_{32}N_{10}O_{10}Re_2S_2$
Formula weight	1225.25
Temperature (K)	100.0(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	18.8431(15)
b (Å)	15.6643(12)
c (Å)	14.9377(12)
α(°)	90
β(°)	110.277(3)
γ(°)	90
Volume (Å^3)	4135.8(6)
Z	4
Density (Mg/m^3)	1.968
μ (mm^{-1})	6.020
θ range (°)	2.304-28.366
Indep. Ref. (R_{int})	5158(0.0696)
S (F^2)	1.032
R1/wR2 [I>2σ(I)]	0.0252/0.0405
R1/wR2 (all data)	0.0384/0.0432

Table S6. Selected bond distances and angles $\mathbf{HL^B}$ derivatives

	$\mathbf{[Re_2(L^{NO2})_2(CO)_6]}$
Coordination mode	μ-κ^{2}S,N2:κN3
Conformation of the ligand(*)	*ZEZE*
(Pseudo)symmetry dimer	2
X =	$S^{\#1}$

Re(1)-S(1)	2.4602(7)
Re(1)-N(3)	2.190(2)
Re(1)-X	2.5520(8)
S(1)-C(1)	1.784(3)
N(1)-C(1)	1.365(4)
N(2)-C(1)	1.292(4)
N(3)-N(2)	1.406(3)
N(3)-C(2)	1.302(4))
N(3)-Re(1)-S(1)	78.02(7)
S(1)-Re(1)-X	82.56(2)
N(3)-Re(1)-X	91.80(7)
N(2)-C(1)-S(1)	125.8(2)
N(1)-C(1)-S(1)	113.4(2)
N(2)-C(1)-N(1)	120.8(2)
C(1)-N(2)-N(3)	115.0(2)
C(2)-N(3)-N(2)	115.2(2)

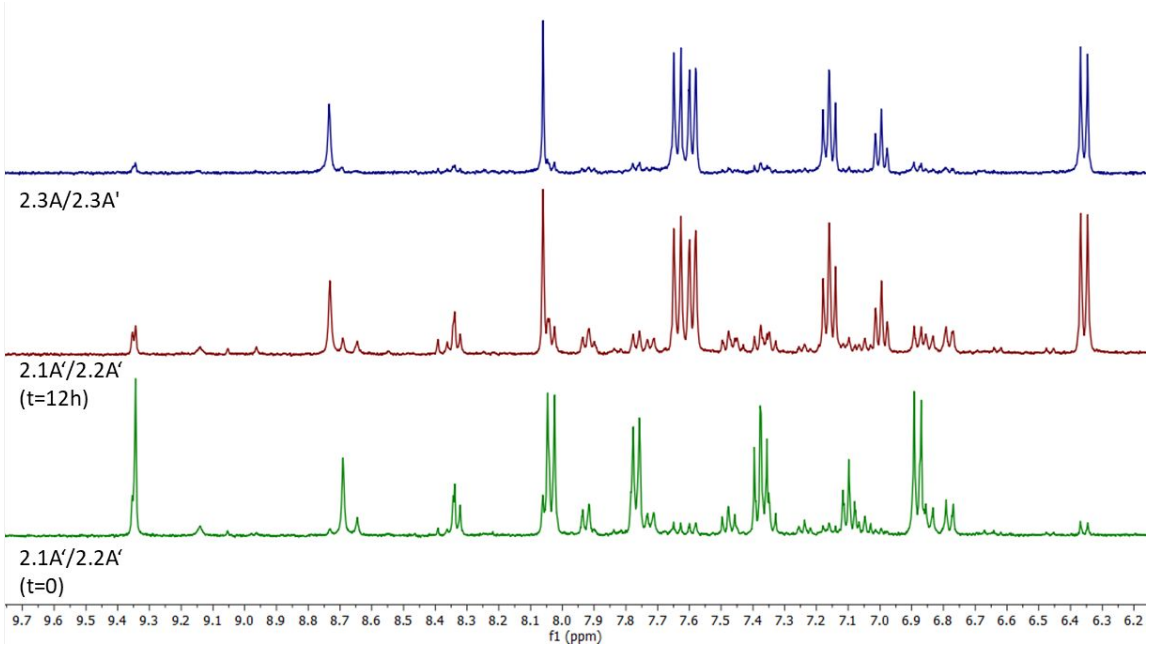


Figure S1. ^{1}H-NMR spectra in acetone-d_6 of the dimers **2.1A'/2.2A'** and **2.3A/2.3A'** and their time evolution.

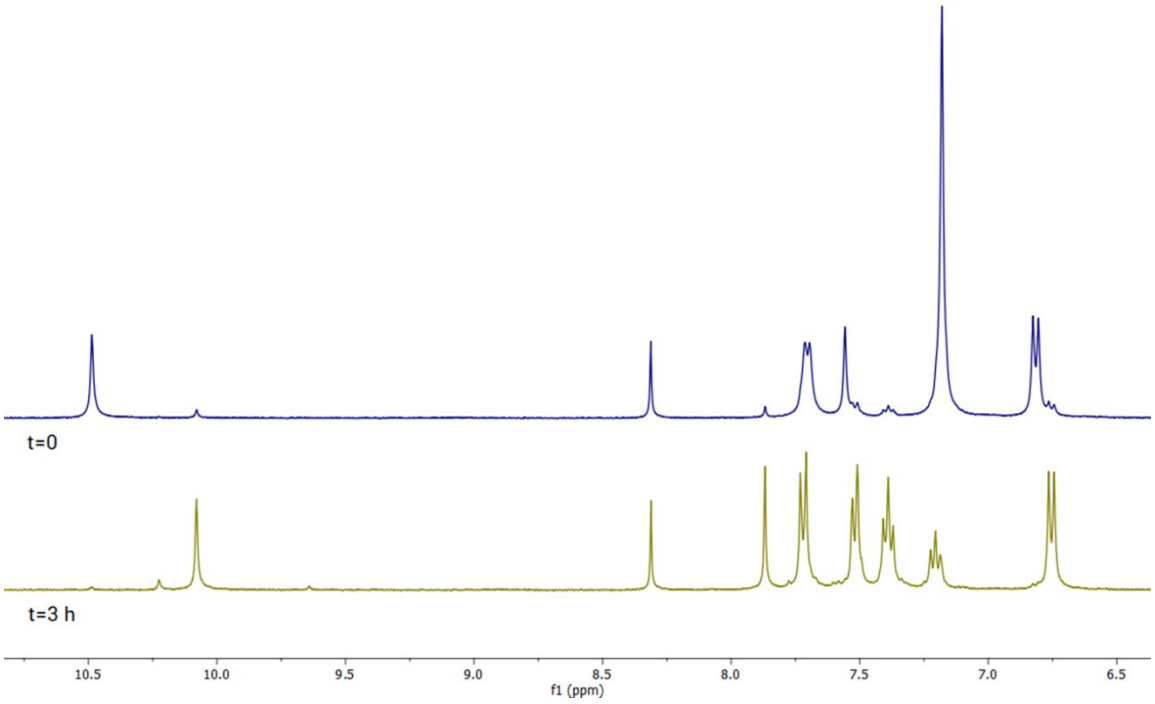


Figure S2. ^{1}H-NMR spectra in dmso-d_6 of the dimer **1A**. The original structure evolves (top) completely in 3 h (bottom).

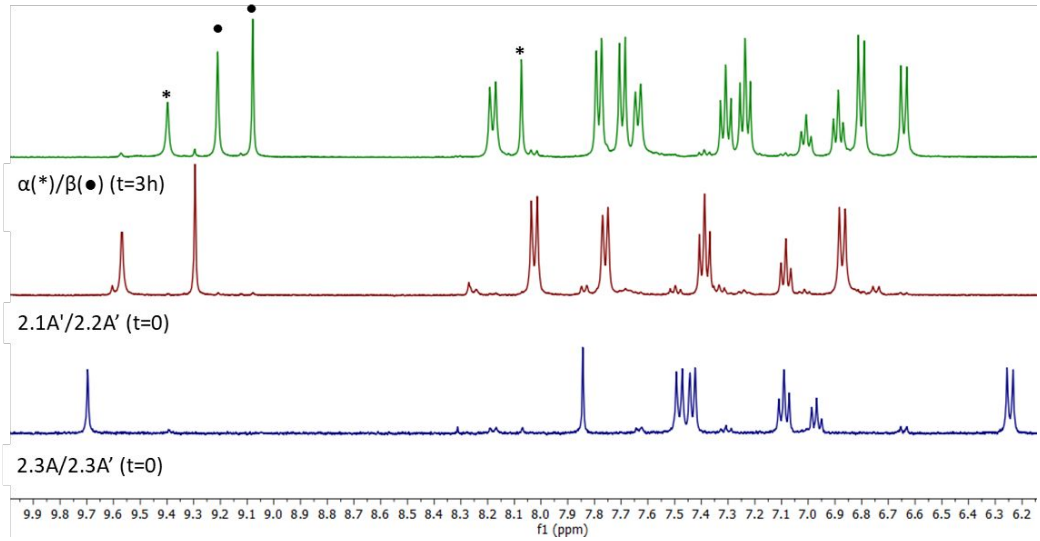


Figure S3. ^{1}H-NMR spectra in dmso-d_6 of freshly prepared solutions of the dimers **2.1A'/2.2A'** and **2.3A/2.3A'**. Both complexes evolve to the named α/β species whose more representative signals corresponding to the N1-H and C2-H protons, respectively. They are identified in the spectrum (top).

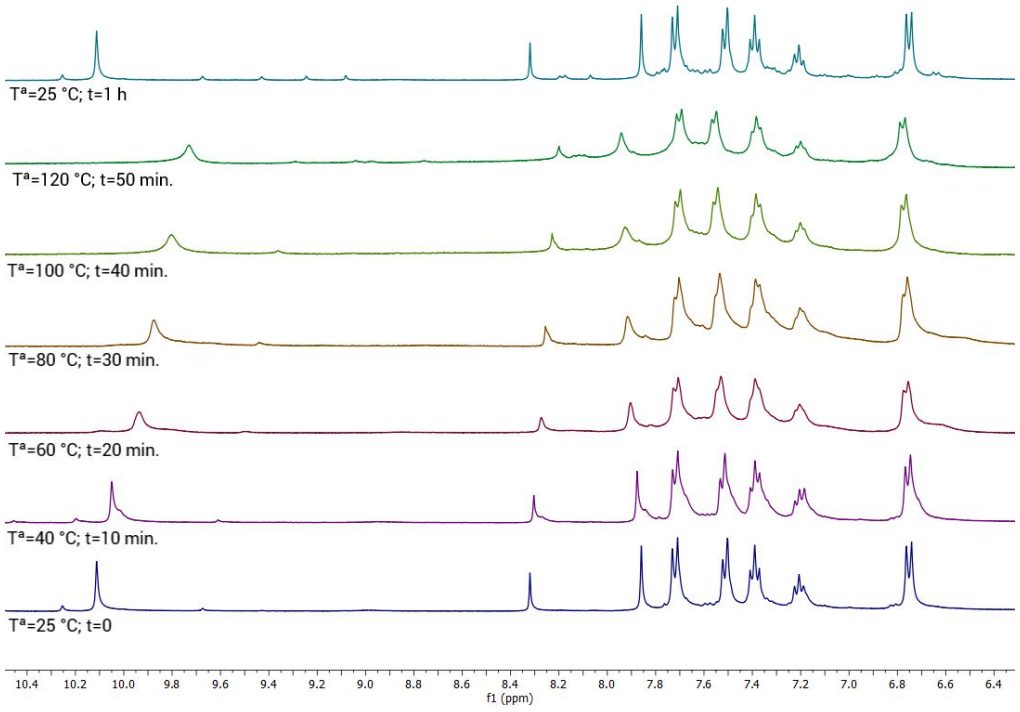


Figure S4. ^{1}H-NMR spectra of the dmso-d_6 solutions of **1A** (after 3h of its dissolution) subjected to a heating cycle (25-120 °C).

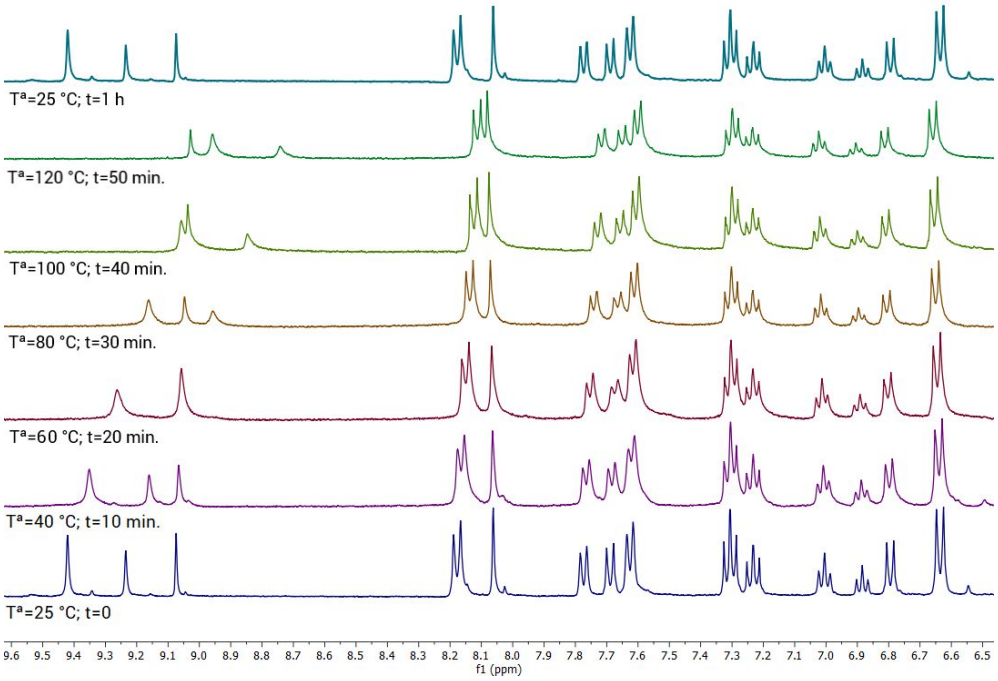


Figure S5. ^{1}H-NMR spectra of the dmso-d_6 solutions of **2.3A/2.3A'** (after 3h of its dissolution) subjected to a heating cycle (25-120°C).

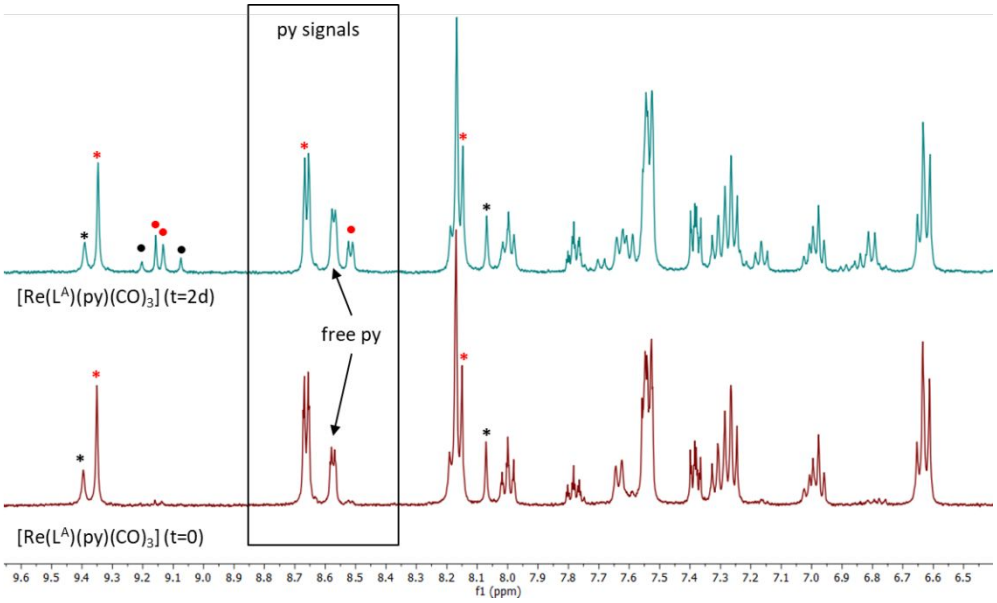


Figure S6. ^{1}H-NMR of a DMSO-d_6 solution of crystals of the complex **[Re(L^{A})(py)(CO)$_3$]** immediately after dissolved (bottom) and after two days at r.t. (top). Black marked signals are attributed to the DMSO solvate (α/β species) while red marked signals are due to analog species of the pyridine complex.

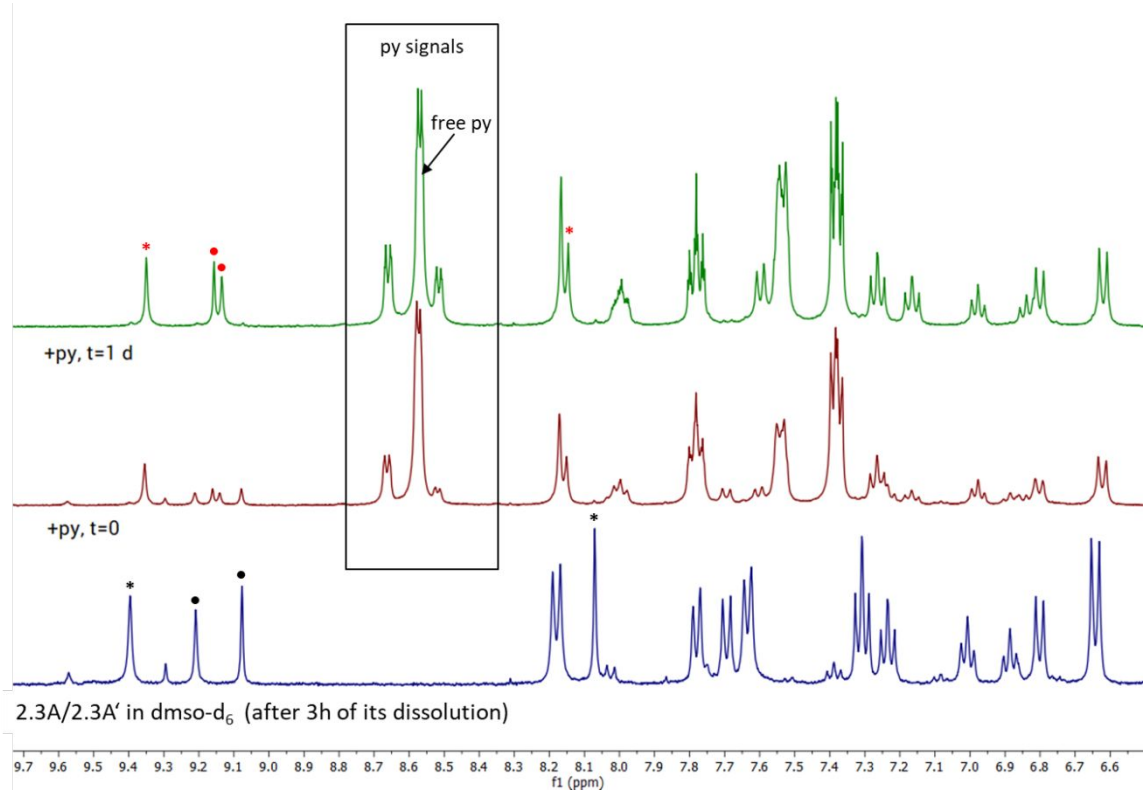


Figure S7. ^{1}H-NMR spectra monitoring of the reaction of **2.3A/2.3A'** with pyridine (excess) in dmso-d_6. Both complexes evolve to the named α/β species whose more representatives signals corresponding to the N1-H and C2-H protons are identified in the spectrum (top). The signals of the α/β species disappear when an excess the pyridine is added but analogs signals of the complex **[Re(κ^{2}S,N-L^A)(py)(CO)$_3$]** are now observed (top).

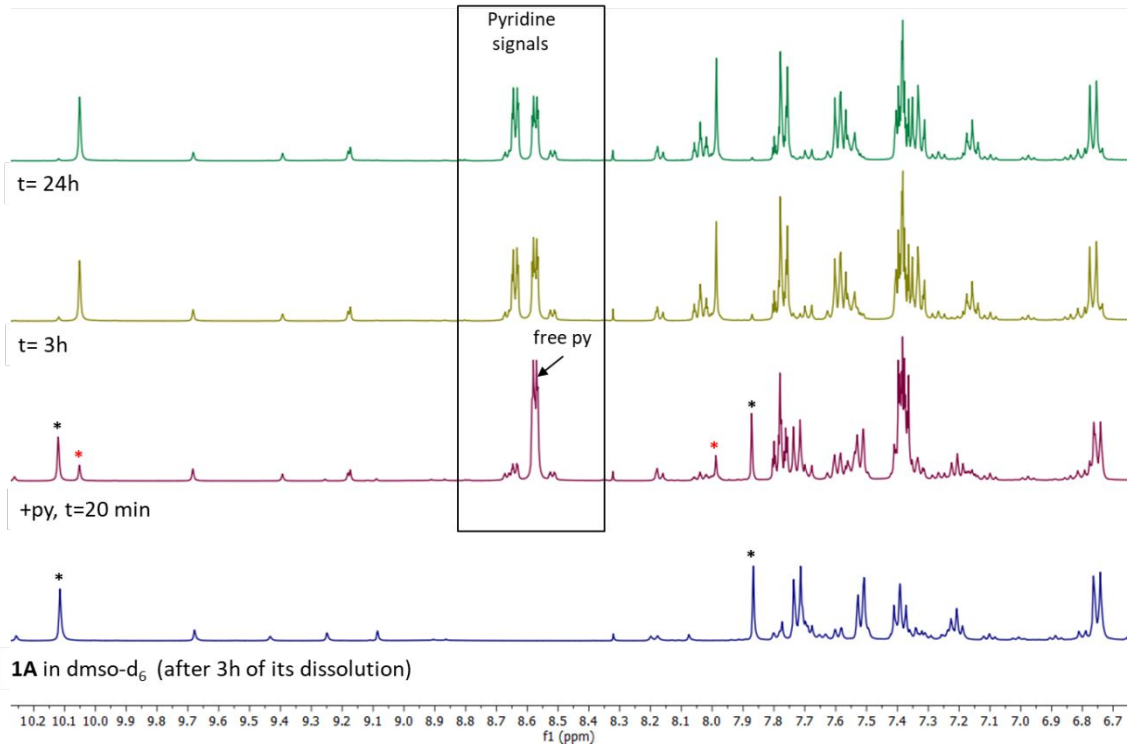


Figure S8. ^{1}H-NMR spectra monitoring of the reaction of **1A** with pyridine (excess) in dmso-d_6. The original specie (whose N1-H and C2-H protons are identified in the spectrum with black asterisks) has practically evolved to a single specie (red asterisks) after 3 h of addition of pyridine. No evolution of the solution is observed after 24 h.

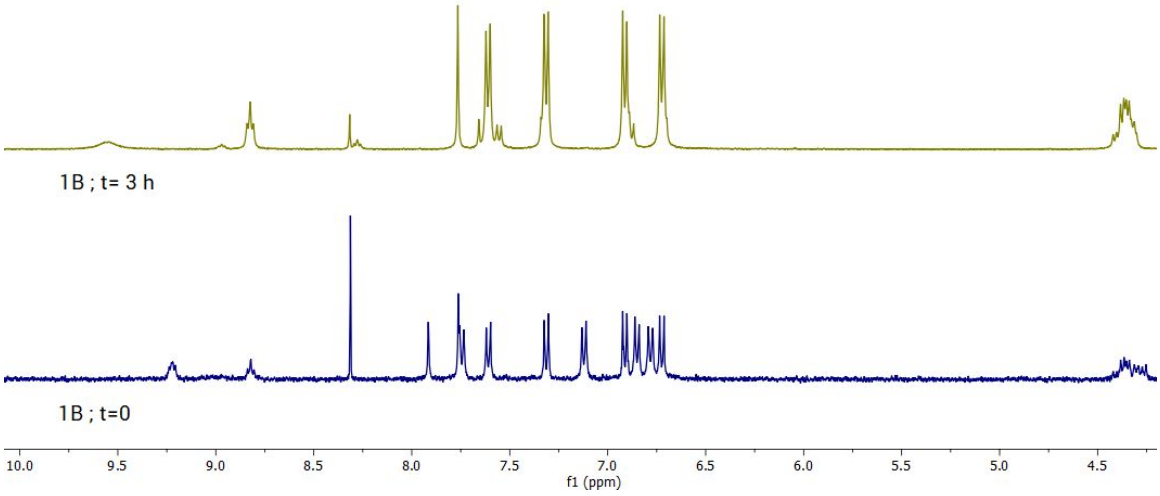


Figure S9. ^{1}H-NMR spectra in dmso-d_6 of the dimer **1B**. The original structure evolves (bottom) completely in 3 h (top).

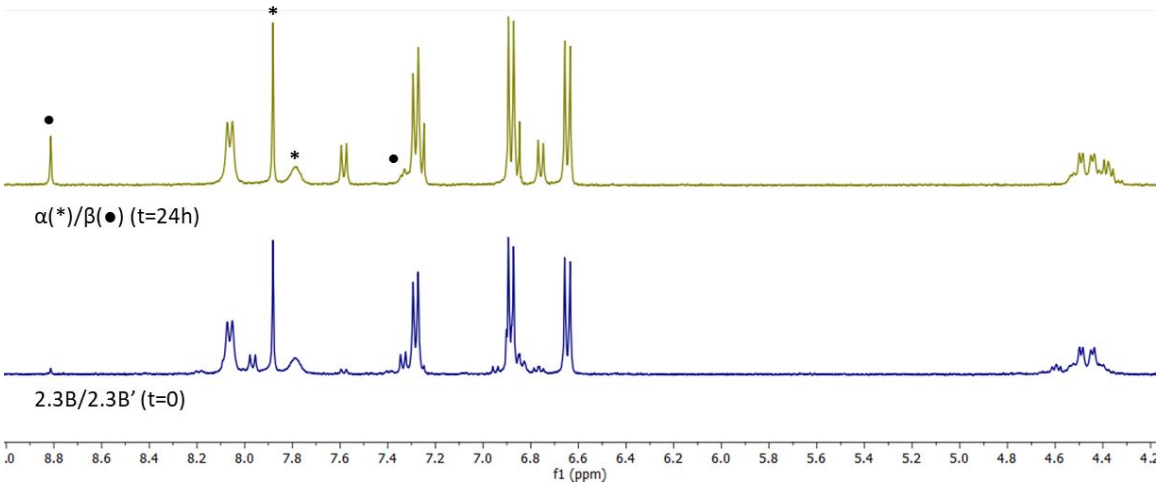
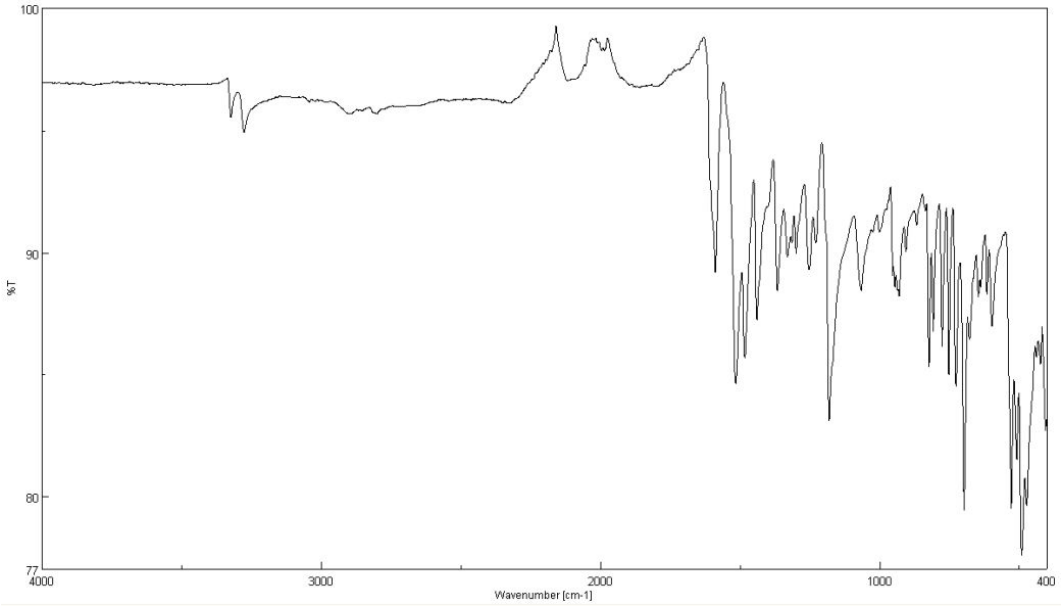


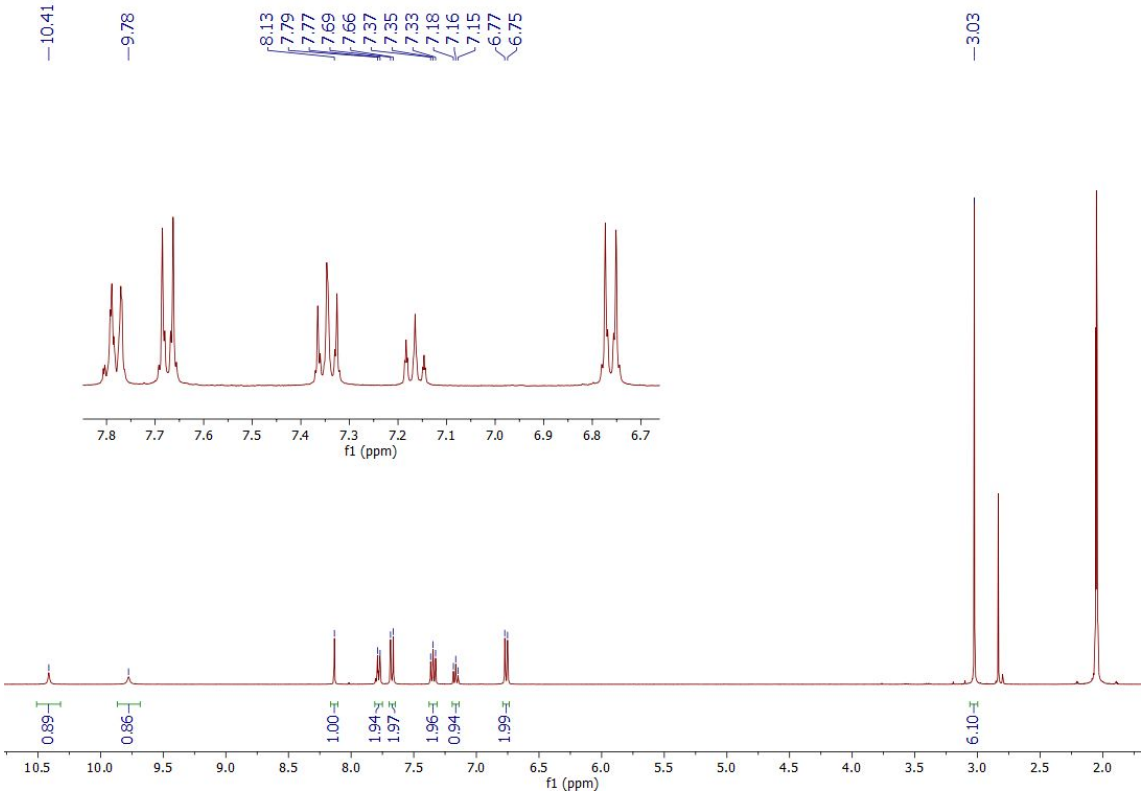
Figure S10. ^{1}H-NMR spectra monitoring of the DMSO-d_6 solutions of **2.3B/2.3B'**. The initial spectrum (t = 0) shows only traces of the dimeric structure. The set of species α/β are observed after 24 h at r.t.

Spectroscopic characterization of **HL^{A}** and its derivatives

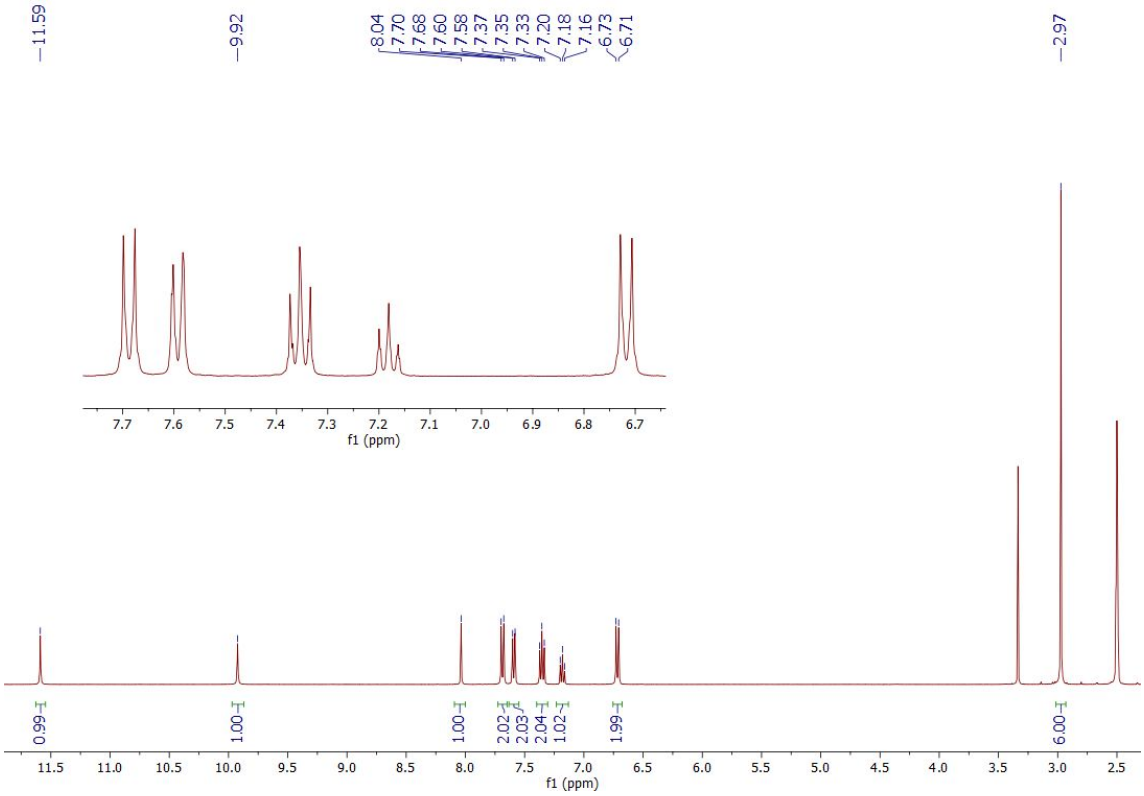
Spectroscopic characterization of **HL^{A}**



IR spectrum

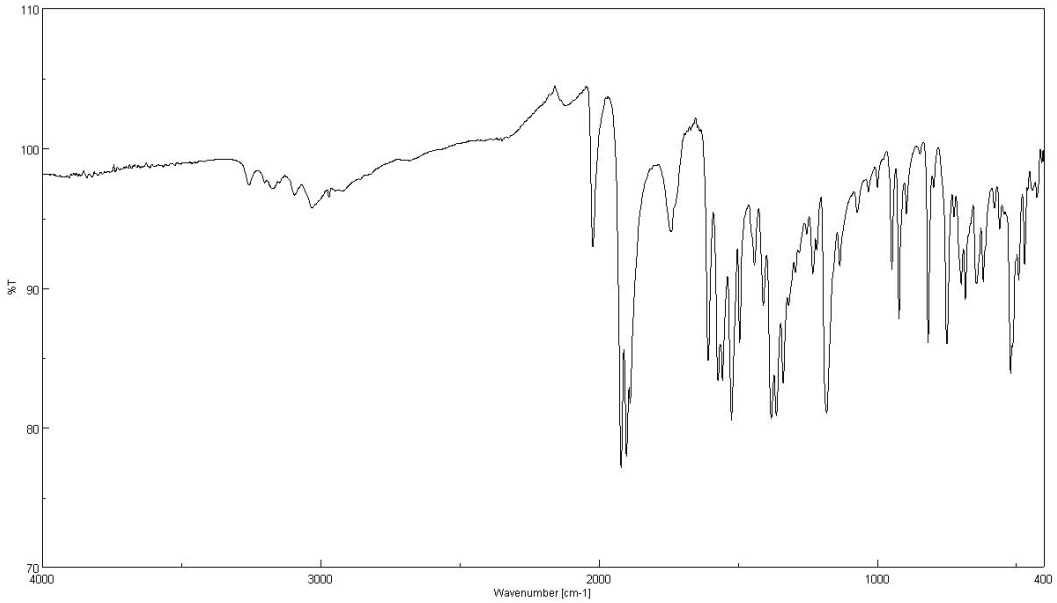


^{1}H-NMR spectrum in acetone-d_6

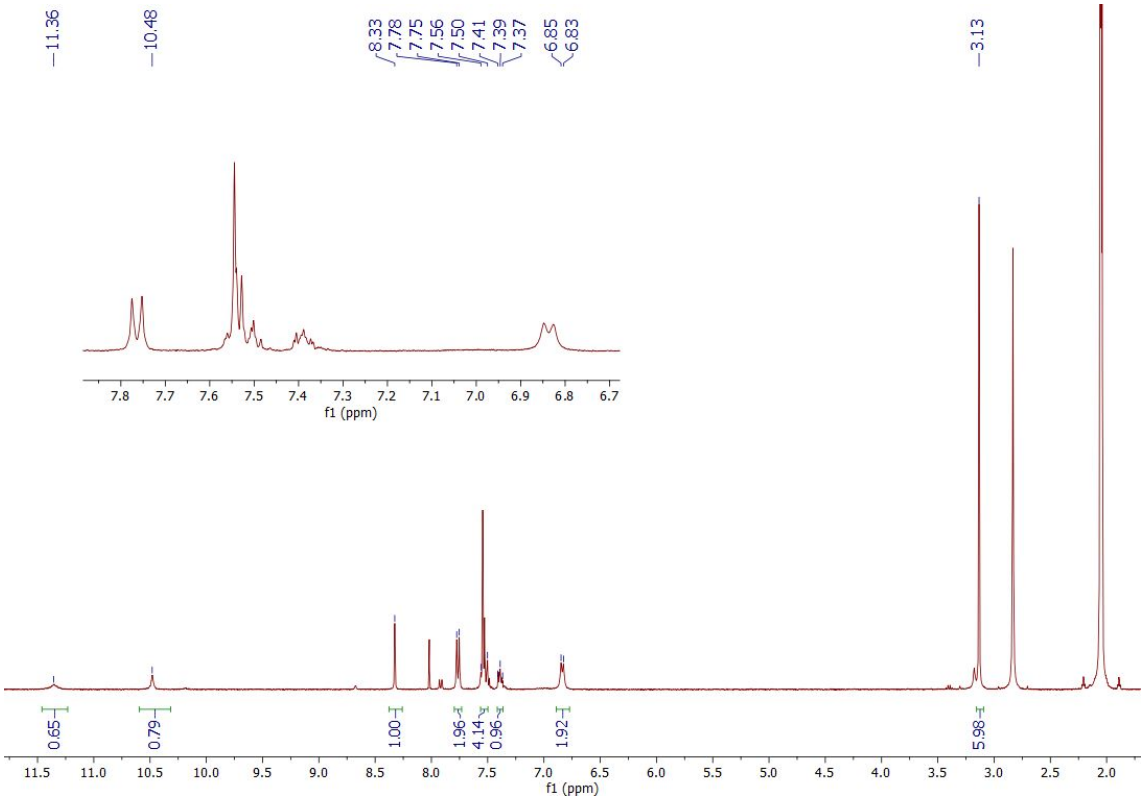


^{1}H-NMR spectrum in DMSO-d_6

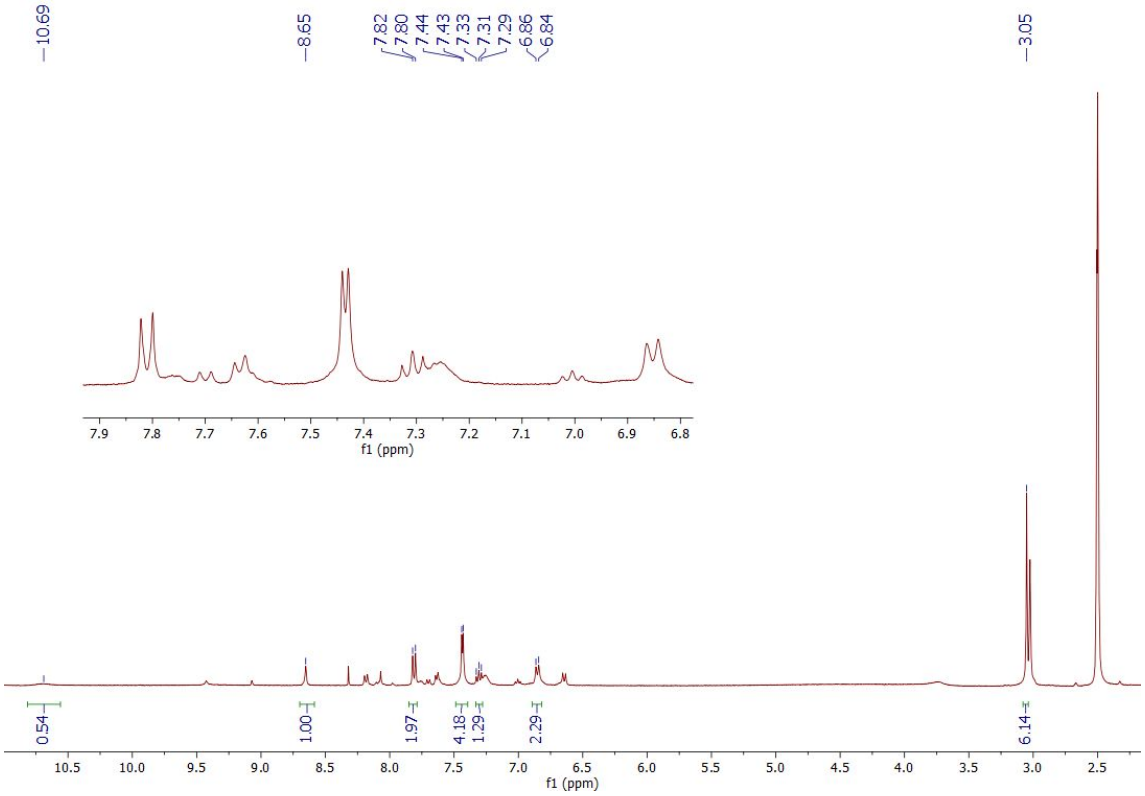
Spectroscopic characterization of **[ReBr(κ²*S*,*N*3-HL^{A})(CO)$_3$]**



IR spectrum

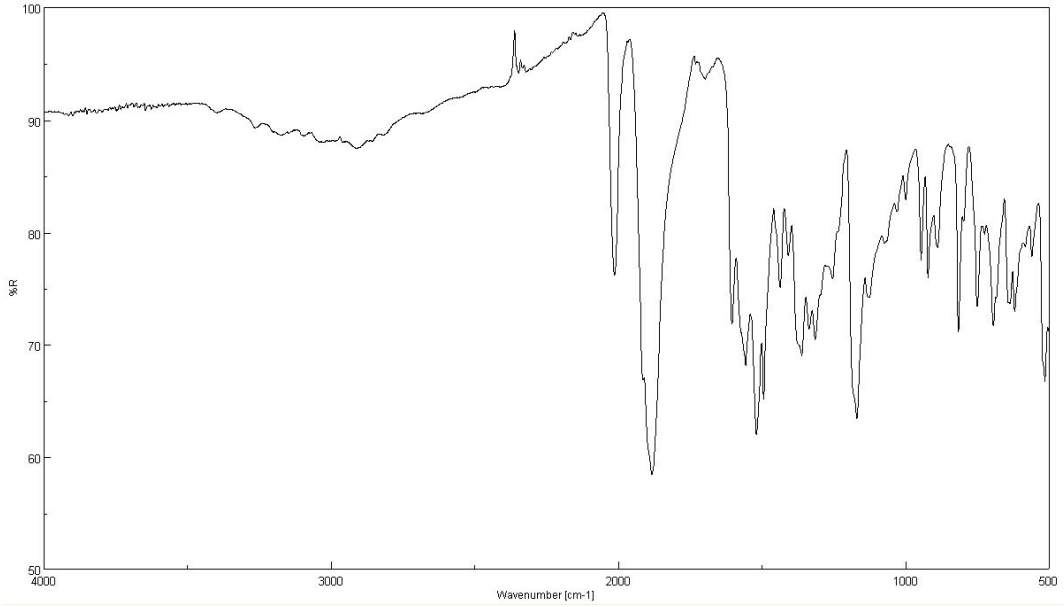


^{1}H-NMR in acetone-d$_6$

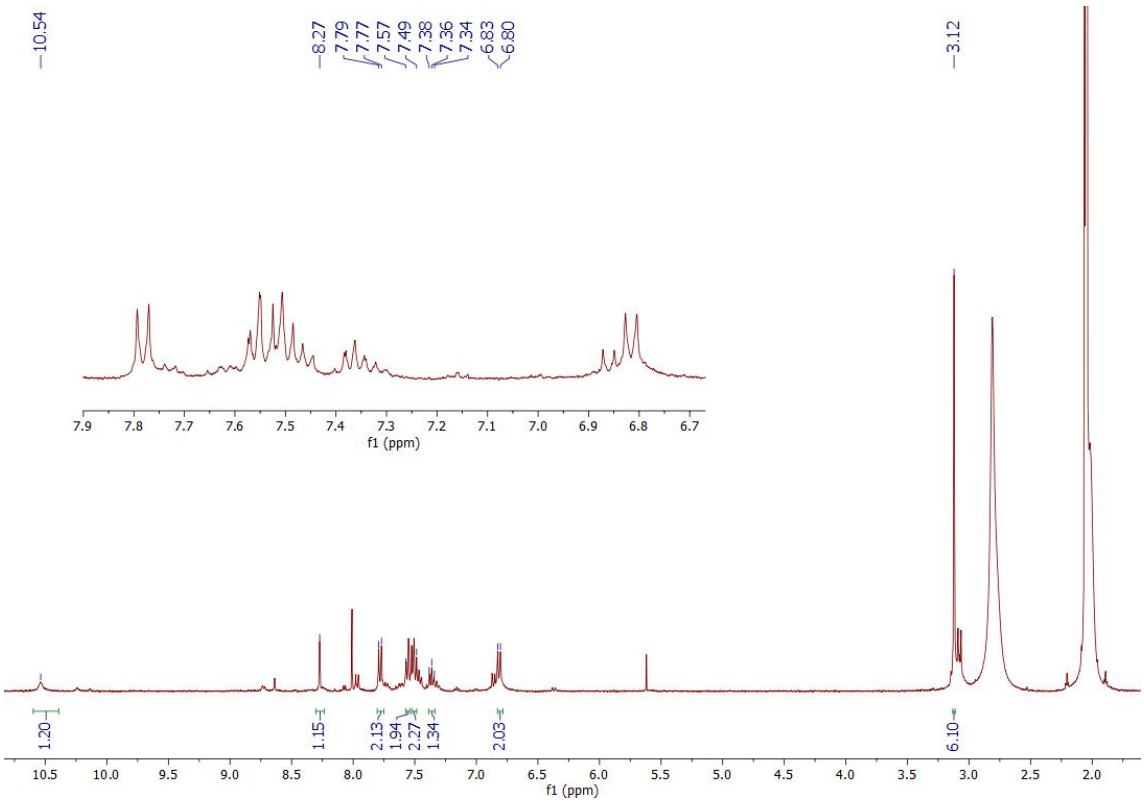


^{1}H-NMR in DMSO-d_6

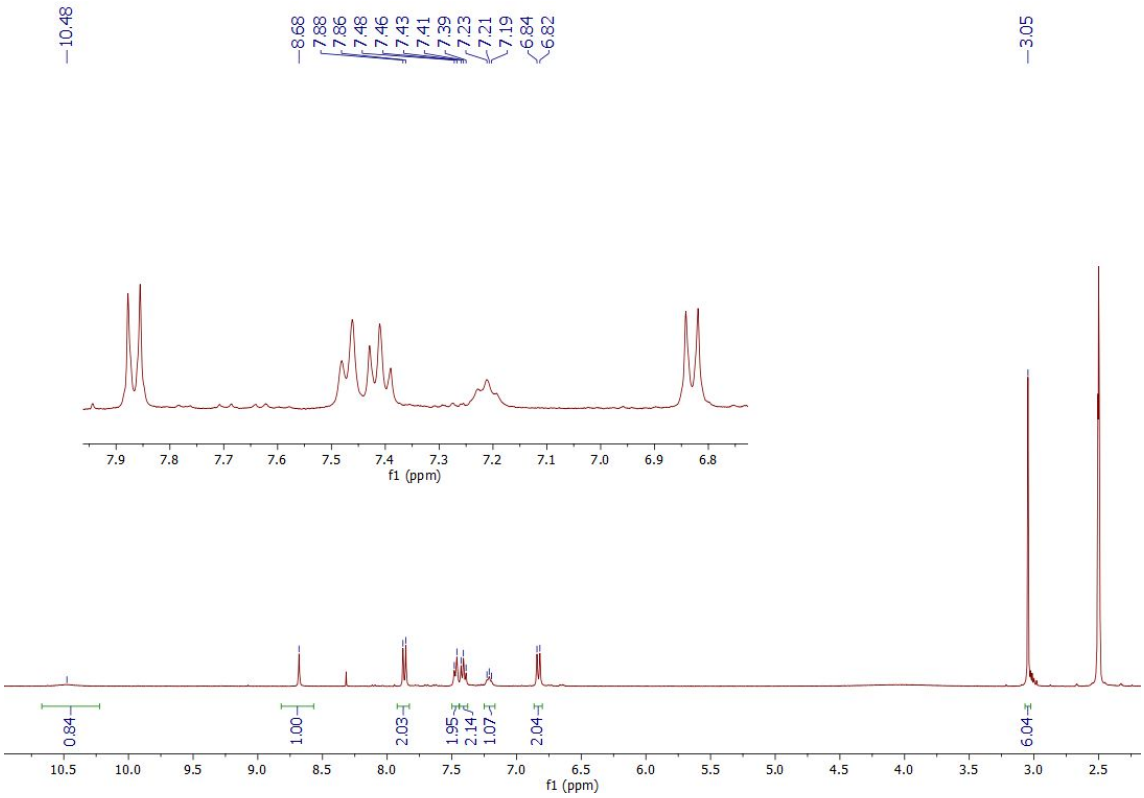
Spectroscopic characterization of **[ReCl(κ²*S*,*N*3-HL^{A})(CO)$_3$]**



IR spectrum

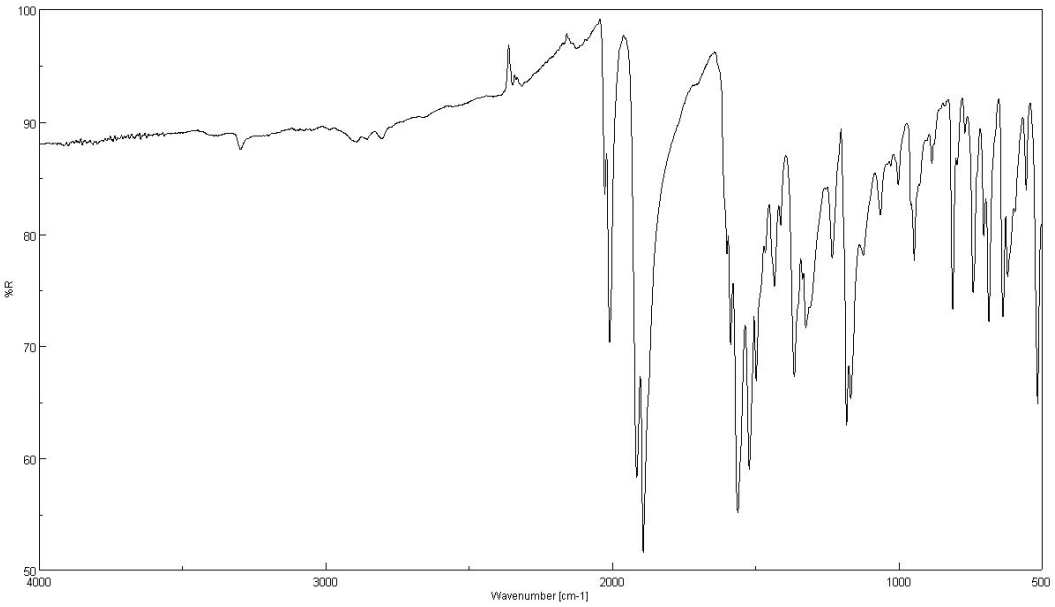


^{1}H-NMR spectrum in acetone-d$_6$

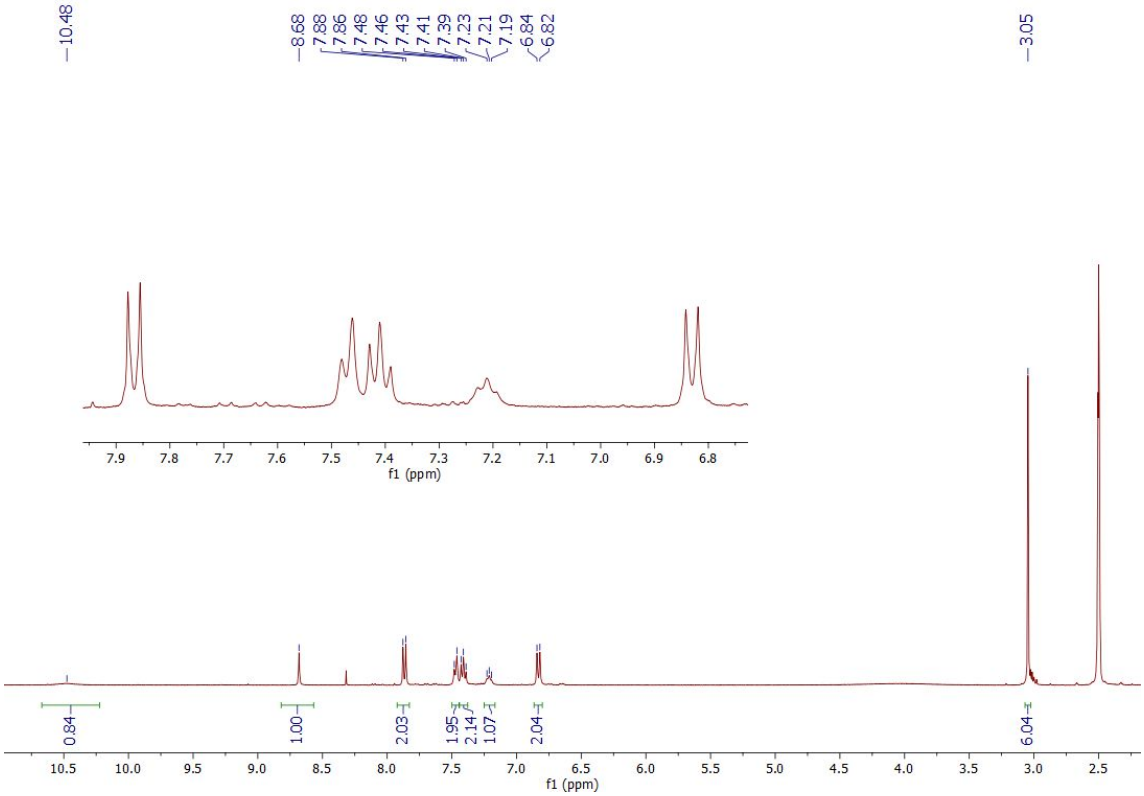


^{1}H-NMR spectrum in DMSO-d_6

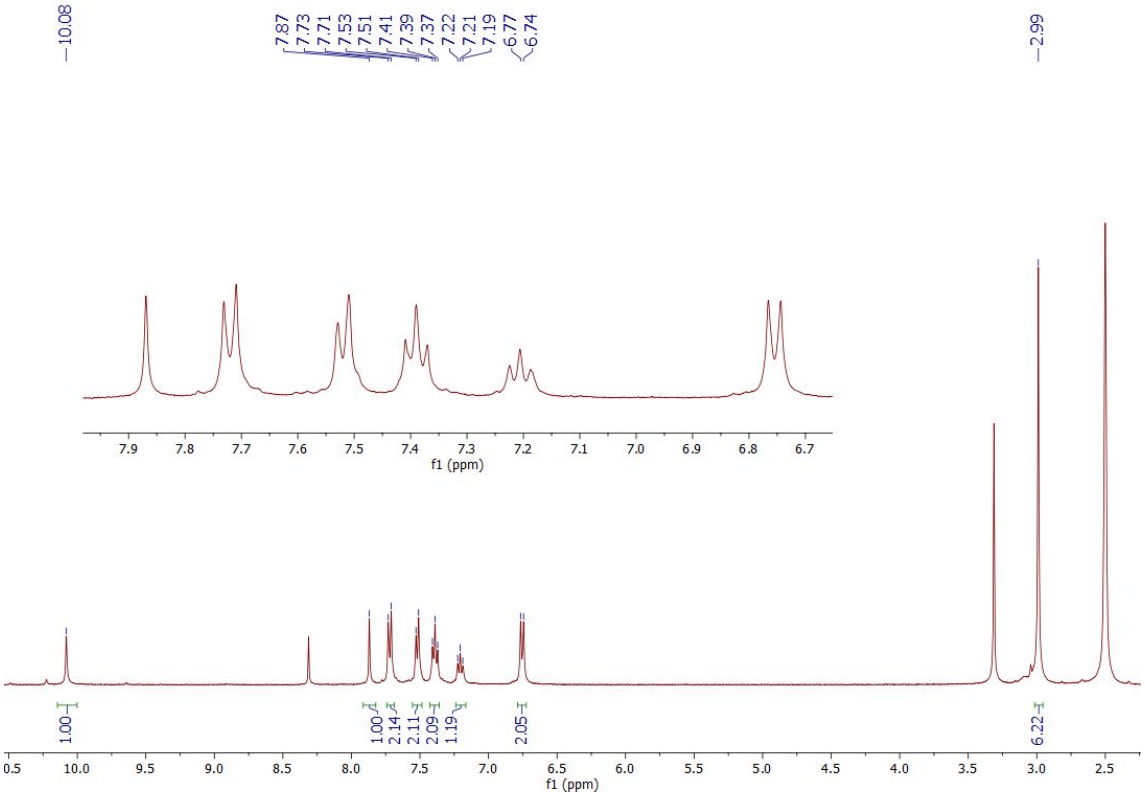
Spectroscopic characterization of **[Re_2(μ-κ^2*S,N2*:κ*S*-L^A)$_2$(CO)$_6$]**
(Structure 1A)



IR spectrum

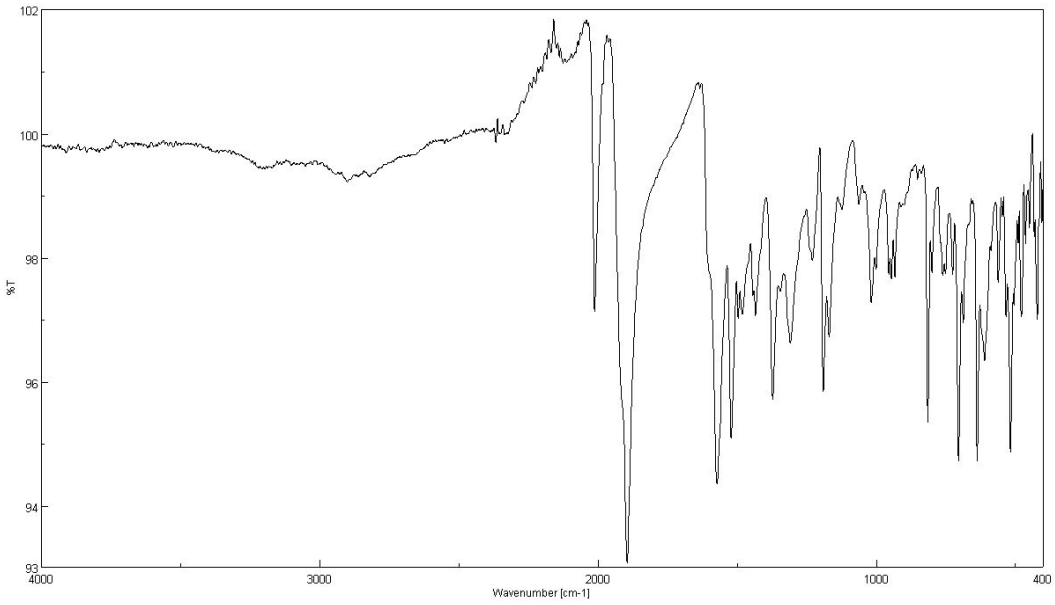


^{1}H-NMR spectrum in DMSO-d_6 (freshly prepared solution).

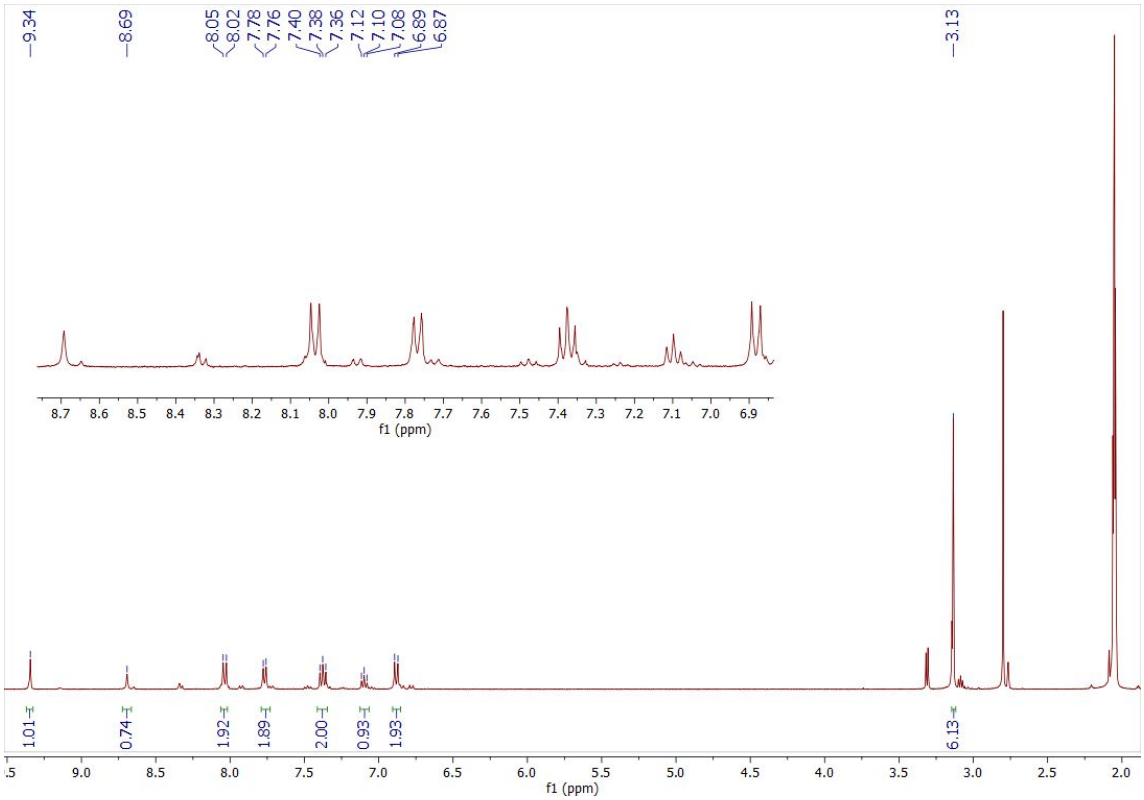


^{1}H-NMR spectrum in DMSO-d_6 (after 5 h).

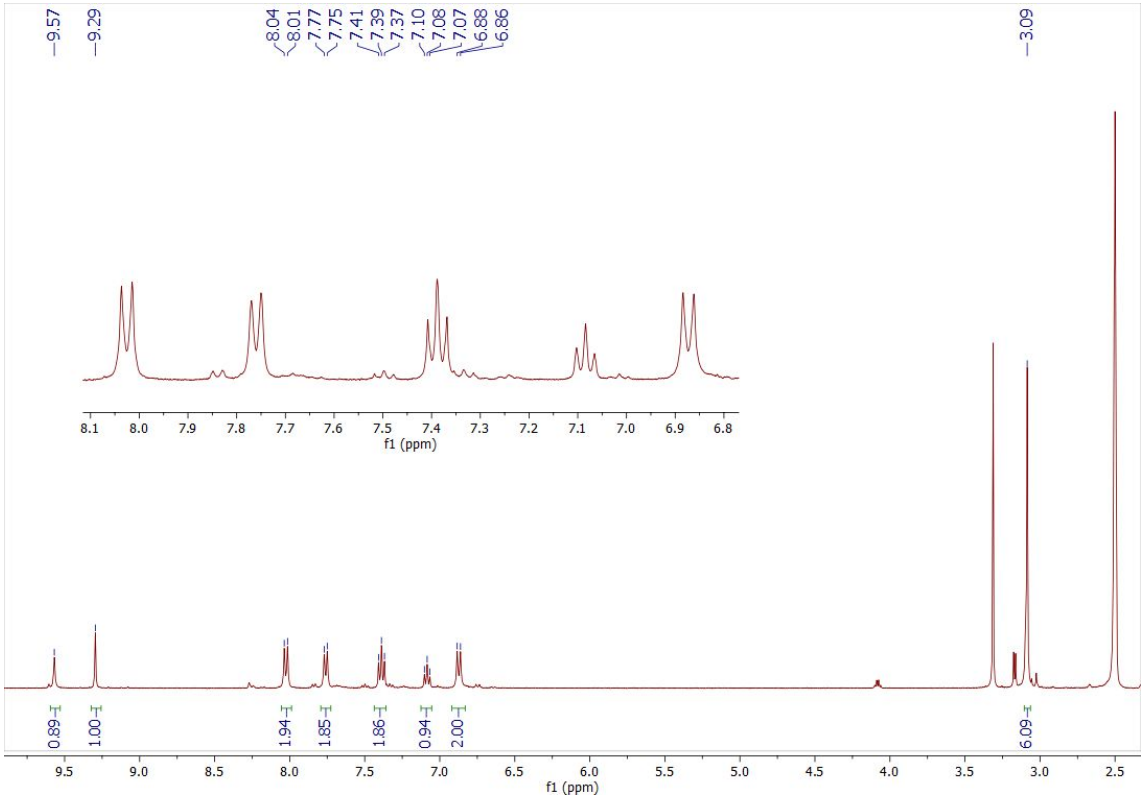
Spectroscopic characterization of **[Re_2(μ-κ^2*S*,*N3*:2κ*S*-L^A)$_2$(CO)$_6$]**
(E configuration in C2-N3 bond - Structures 2.1A'/2.2A')



IR spectrum

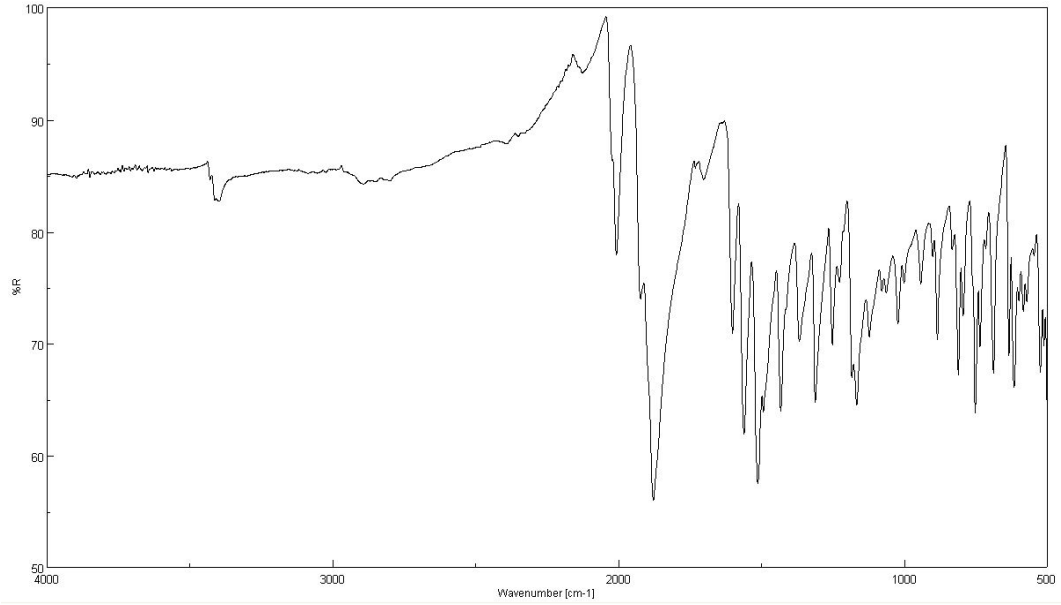


^{1}H-NMR spectrum in acetone-d_6

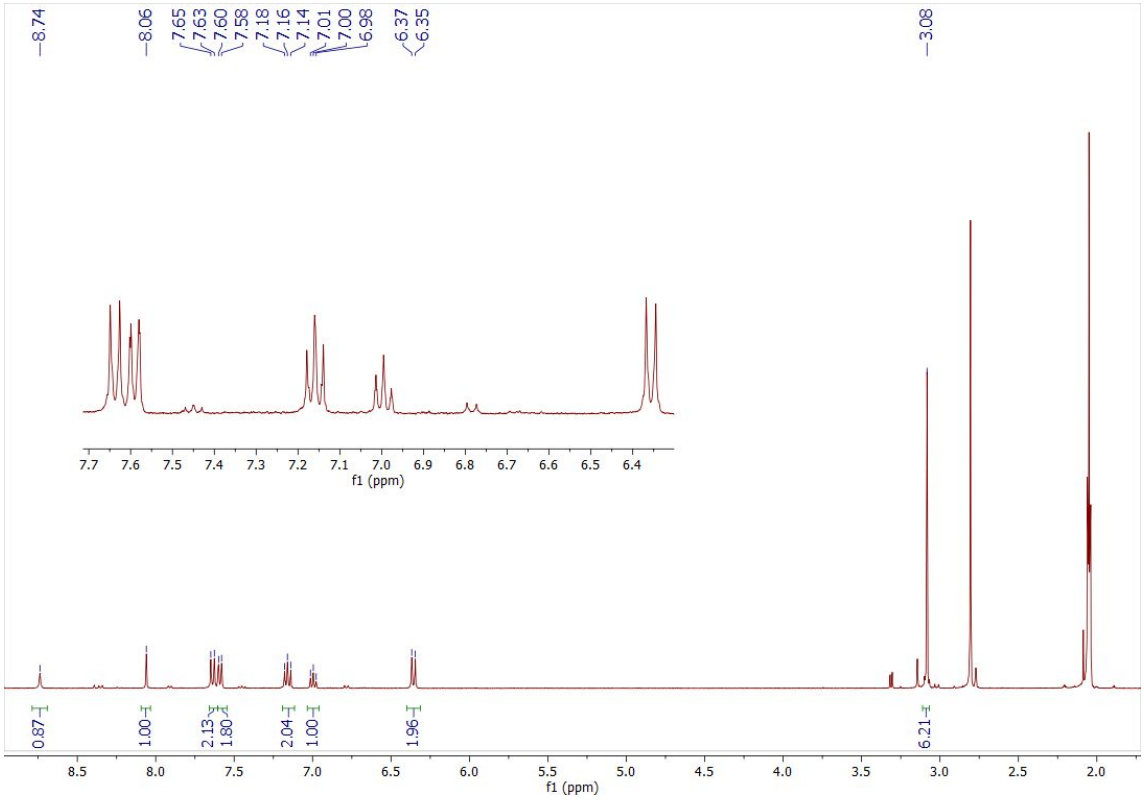


^{1}H-NMR spectrum in DMSO-d_6

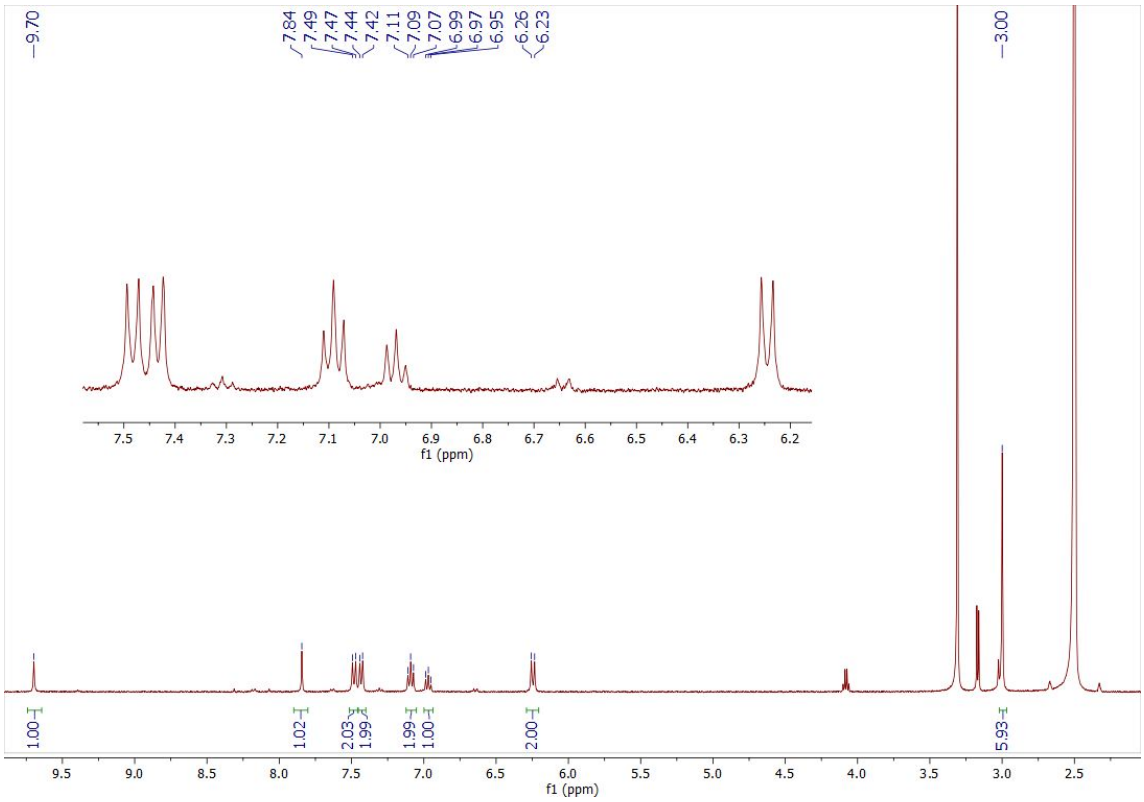
Spectroscopic characterization of **[Re_2(μ-1κ^2*S,N3*:2κ*S*-L^A)$_2$(CO)$_6$]**
(Z configuration in C2-N3 bond - Structures 2.3A and 2.3A')



IR spectrum.

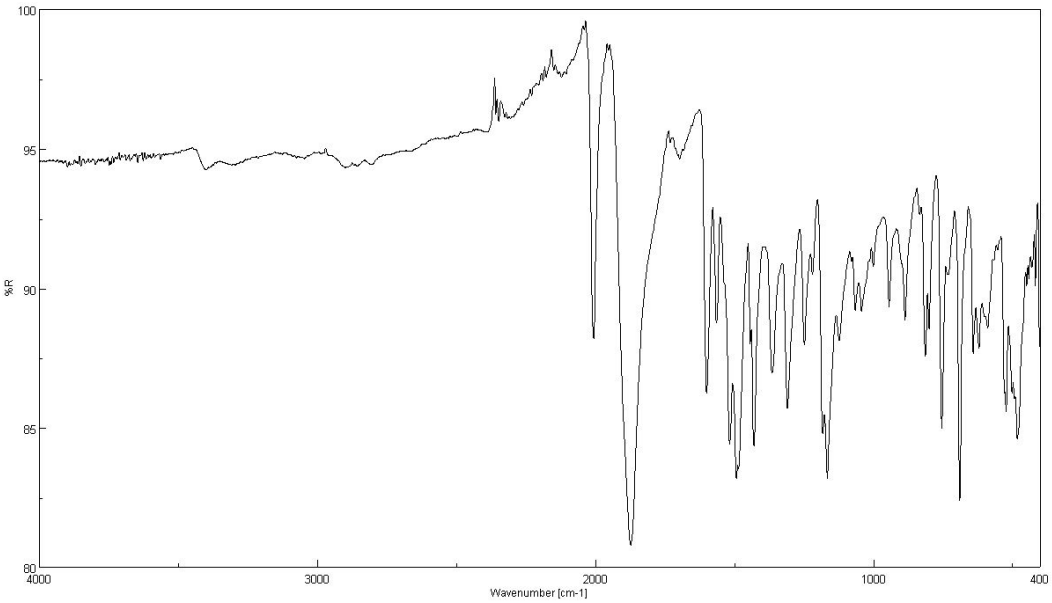


^{1}H-NMR spectrum in acetone-d_6

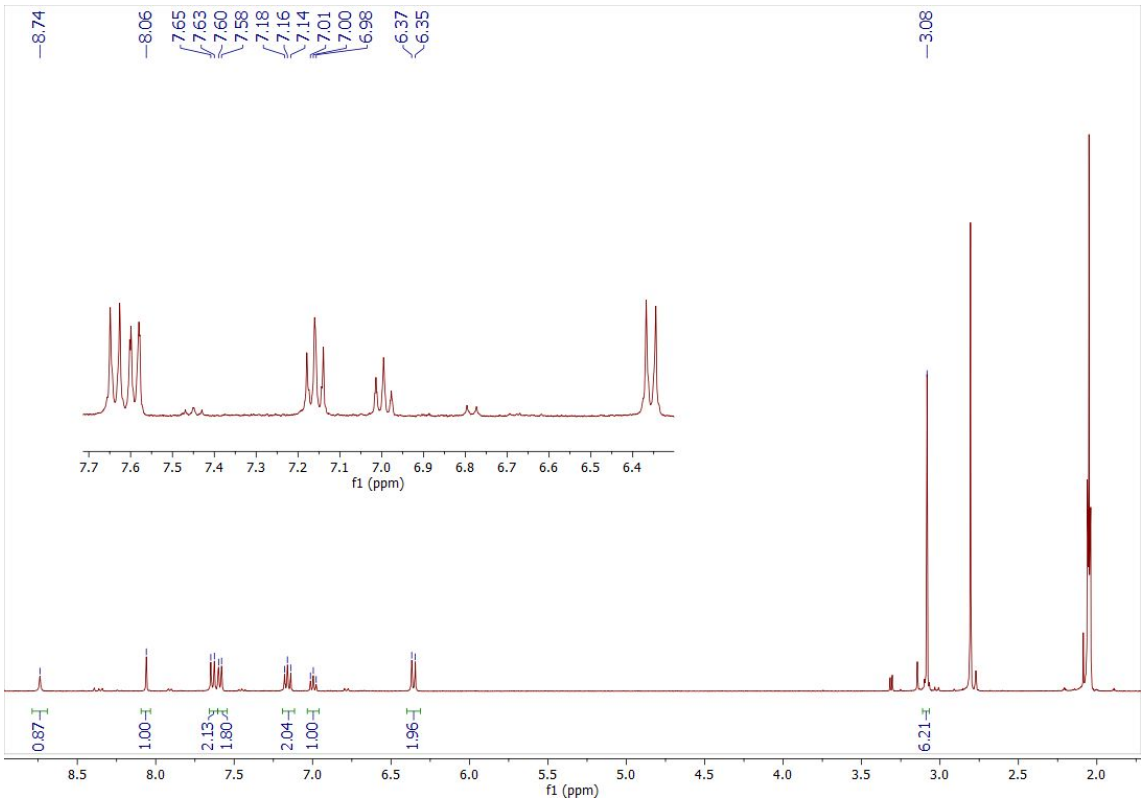


^{1}H-NMR spectrum in DMSO-d_6

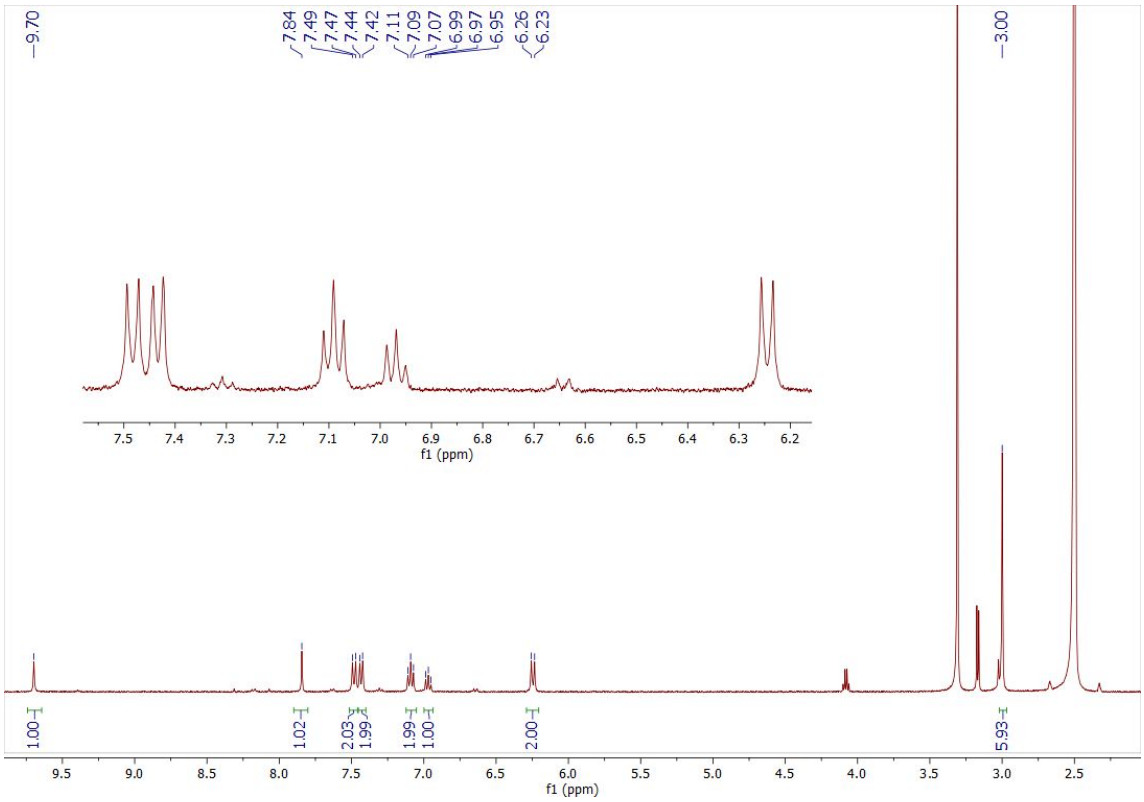
Spectroscopic characterization of ***fac*-[Re(κ²*S*,*N*3-L^{A})(py)(CO)$_3$]**



IR spectrum

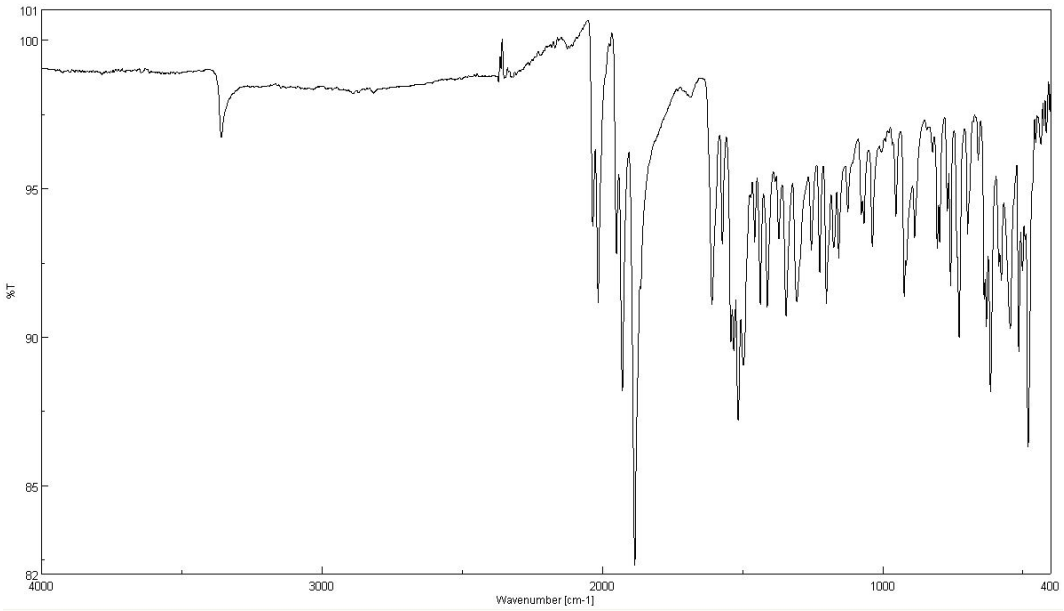


^{1}H-NMR spectrum in acetone-d$_6$

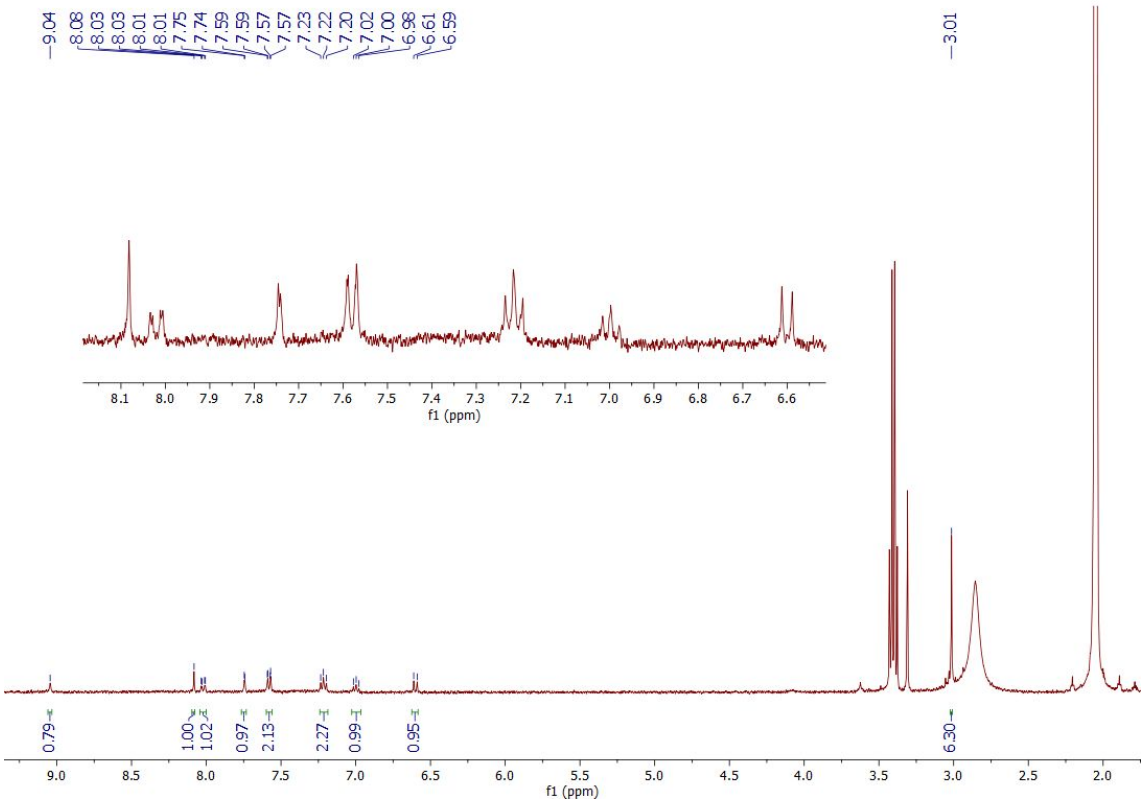


^{1}H-NMR spectrum in DMSO-d_6

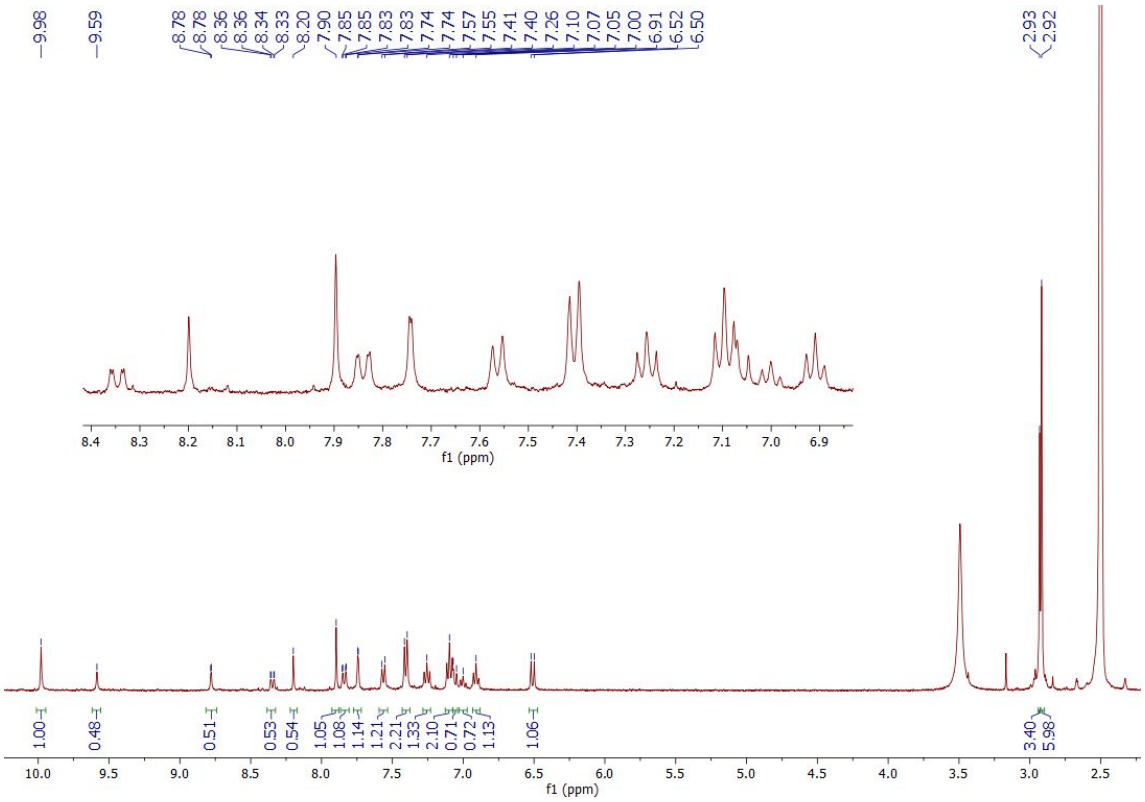
Spectroscopic characterization of **[Re_2(μ-κ²*S*,*N3*:κS-L^{NO2})$_2$(CO)$_6$]**



IR spectrum



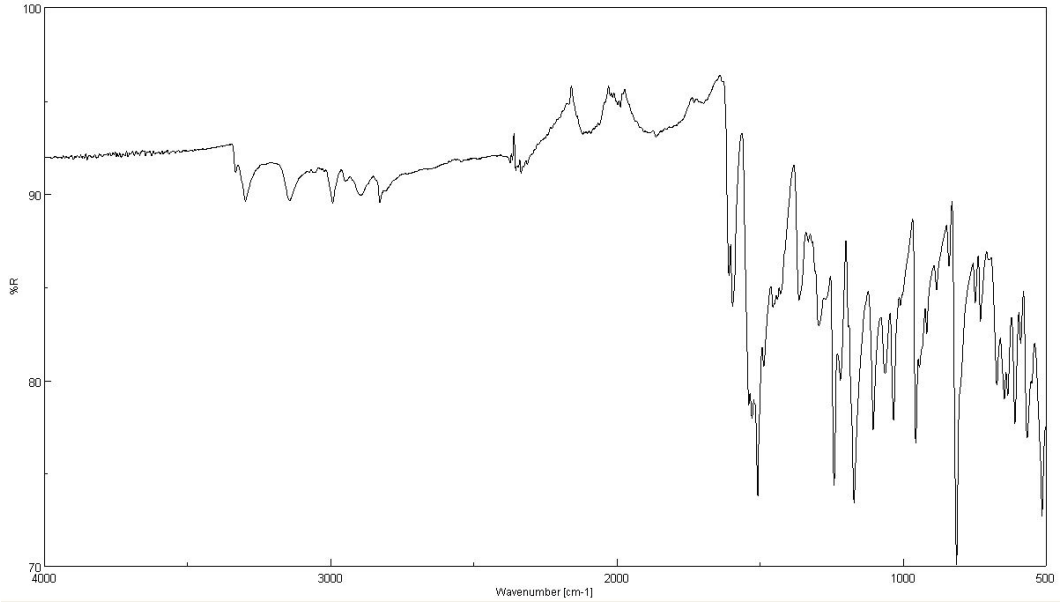
^{1}H-NMR spectrum in acetone-d_6



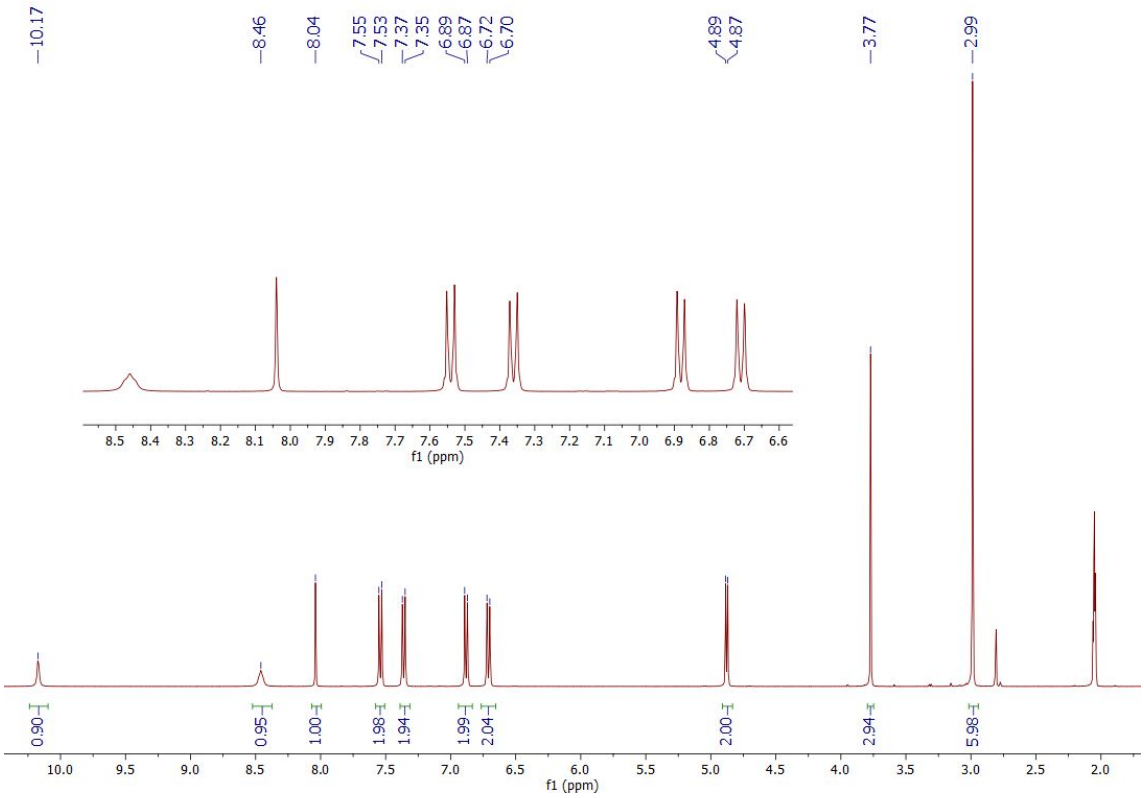
^{1}H-NMR spectrum in DMSO-d_6

Spectroscopic characterization of **HL^{B}** and its derivatives

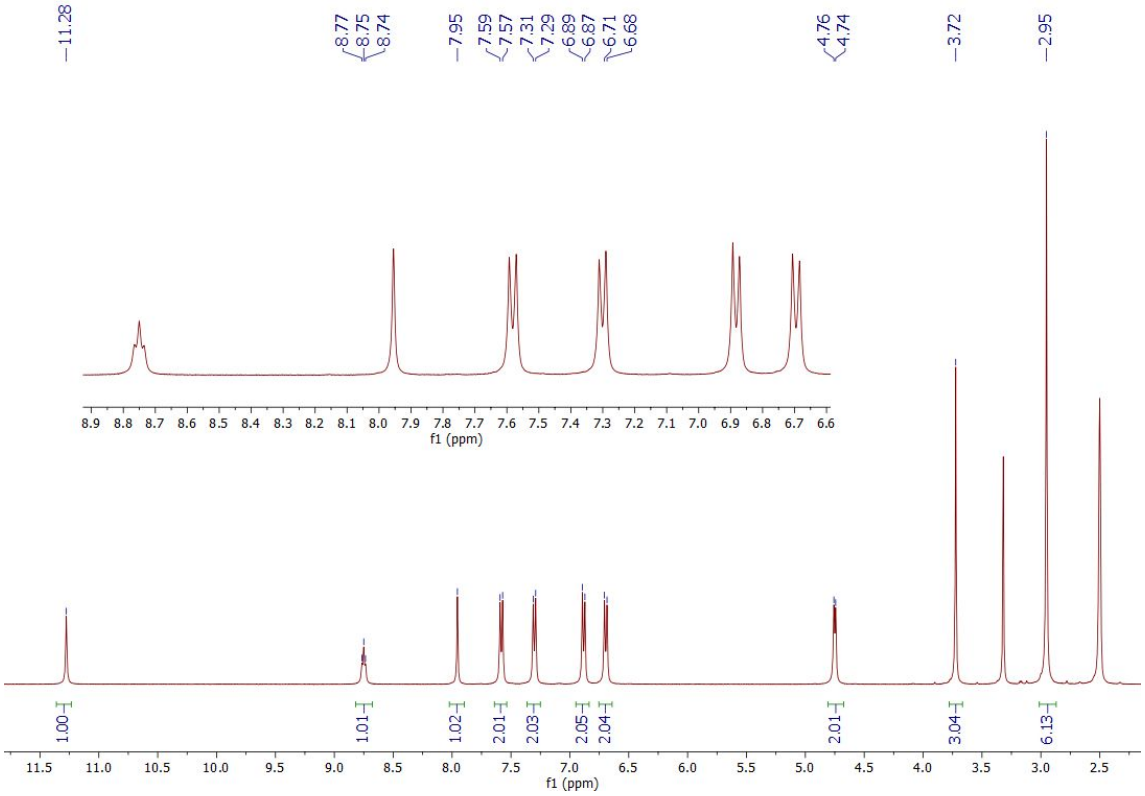
Spectroscopic characterization of **HL^{B}**



IR spectrum

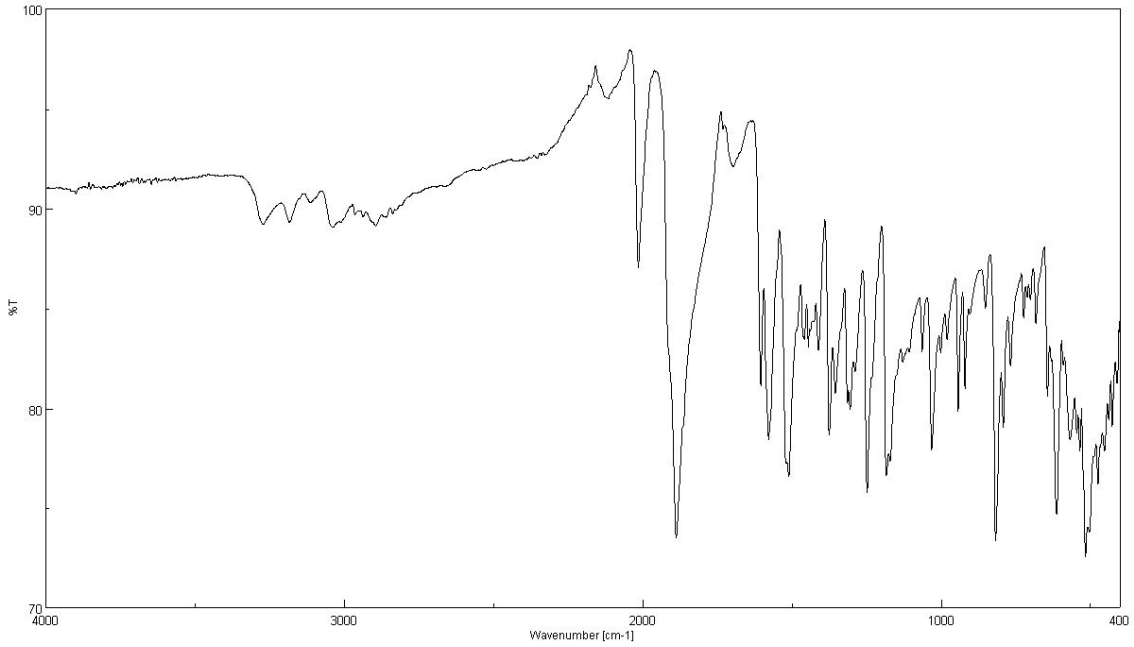


^{1}H-NMR spectrum in acetone-d_6

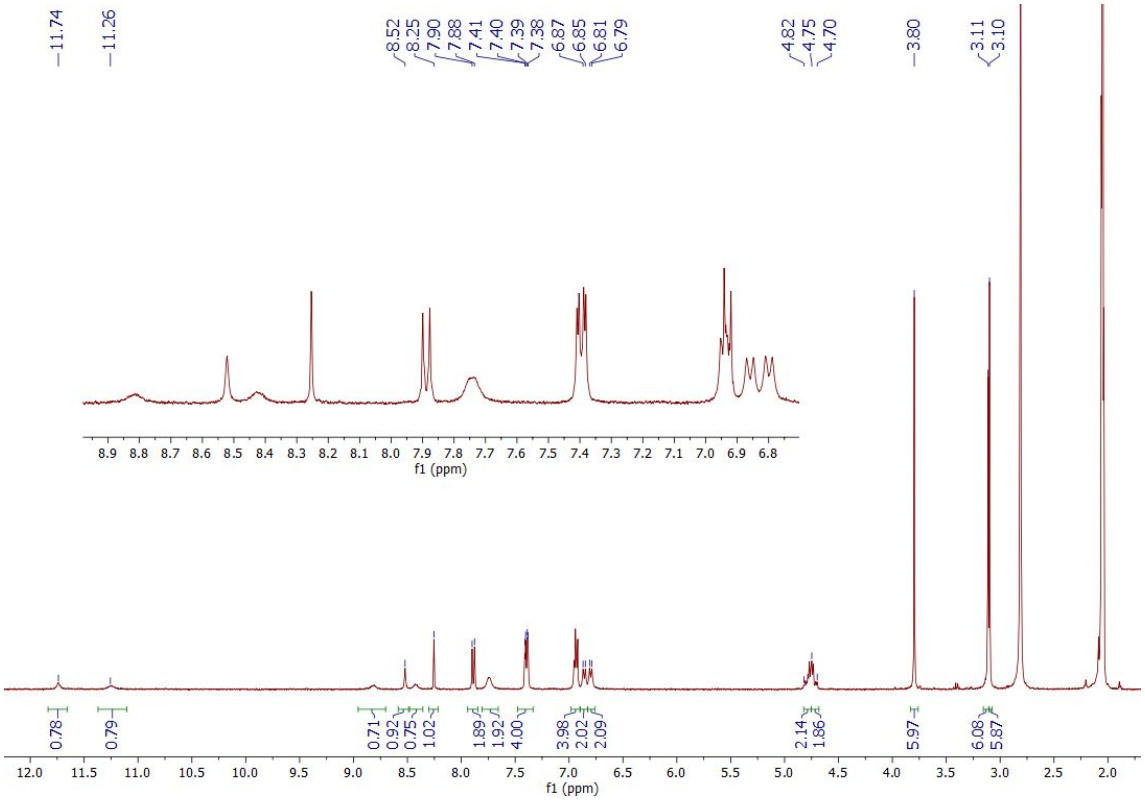


^{1}H-NMR spectrum in DMSO-d_6

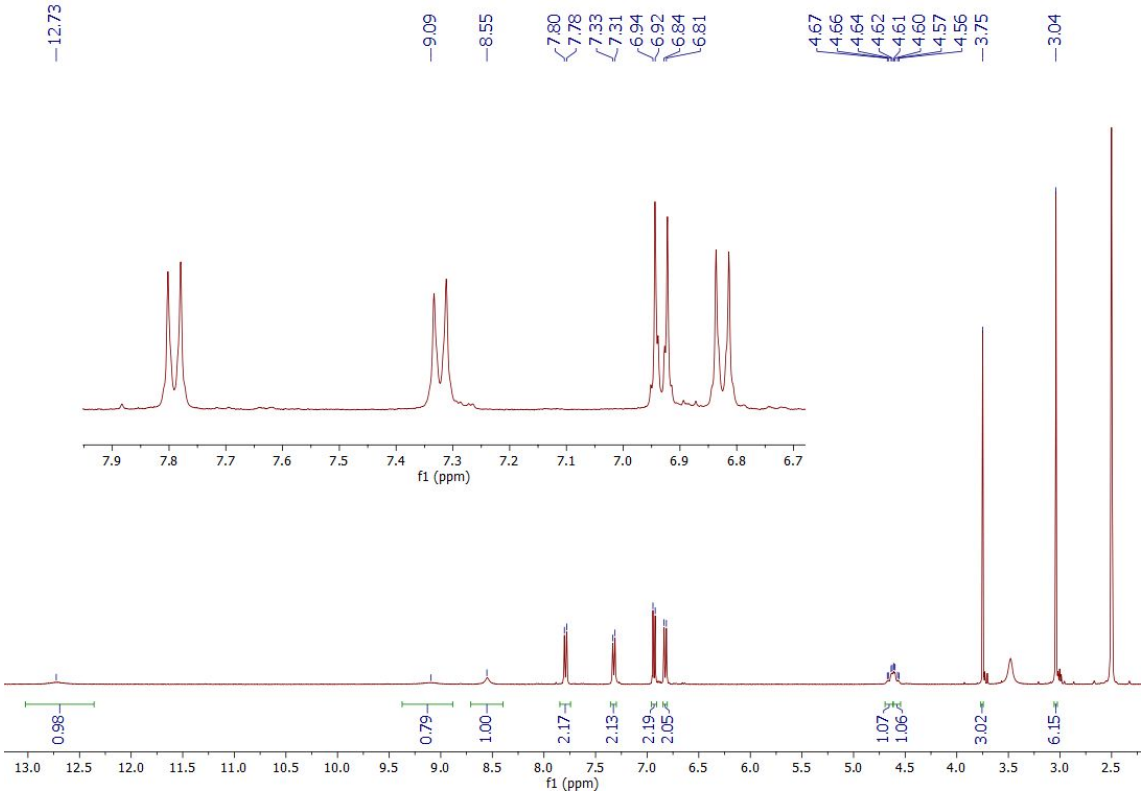
Spectroscopic characterization of **[ReBr(κ²*S*,*N*3-HL^{B})(CO)$_3$]**



IR spectrum

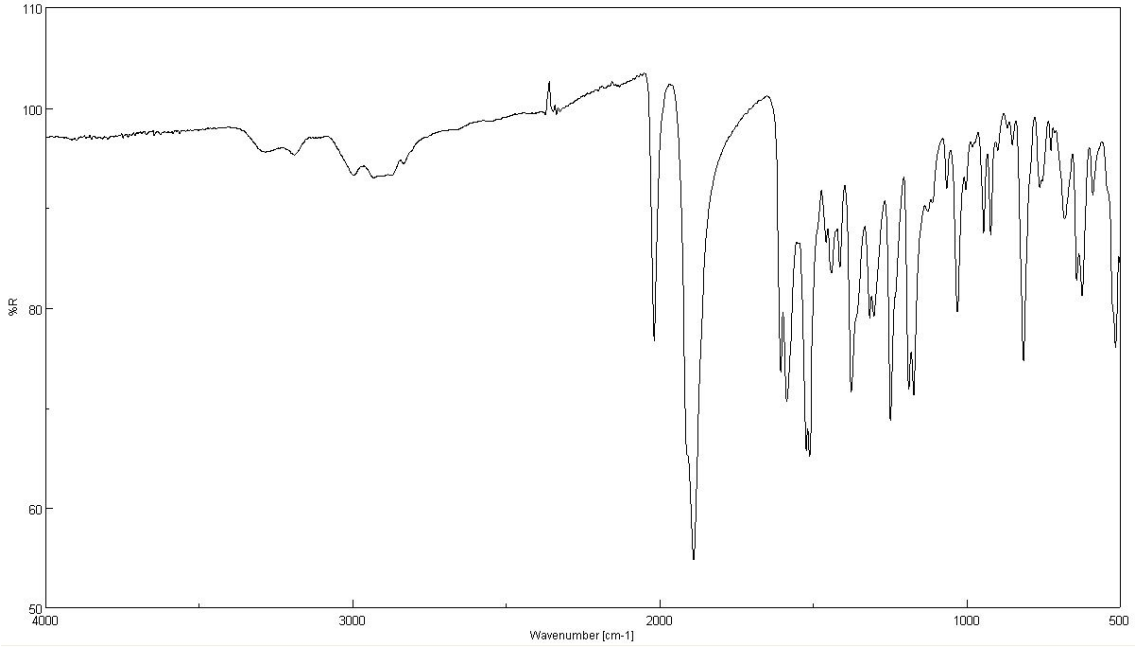


^{1}H-NMR spectrum in acetone-d$_6$

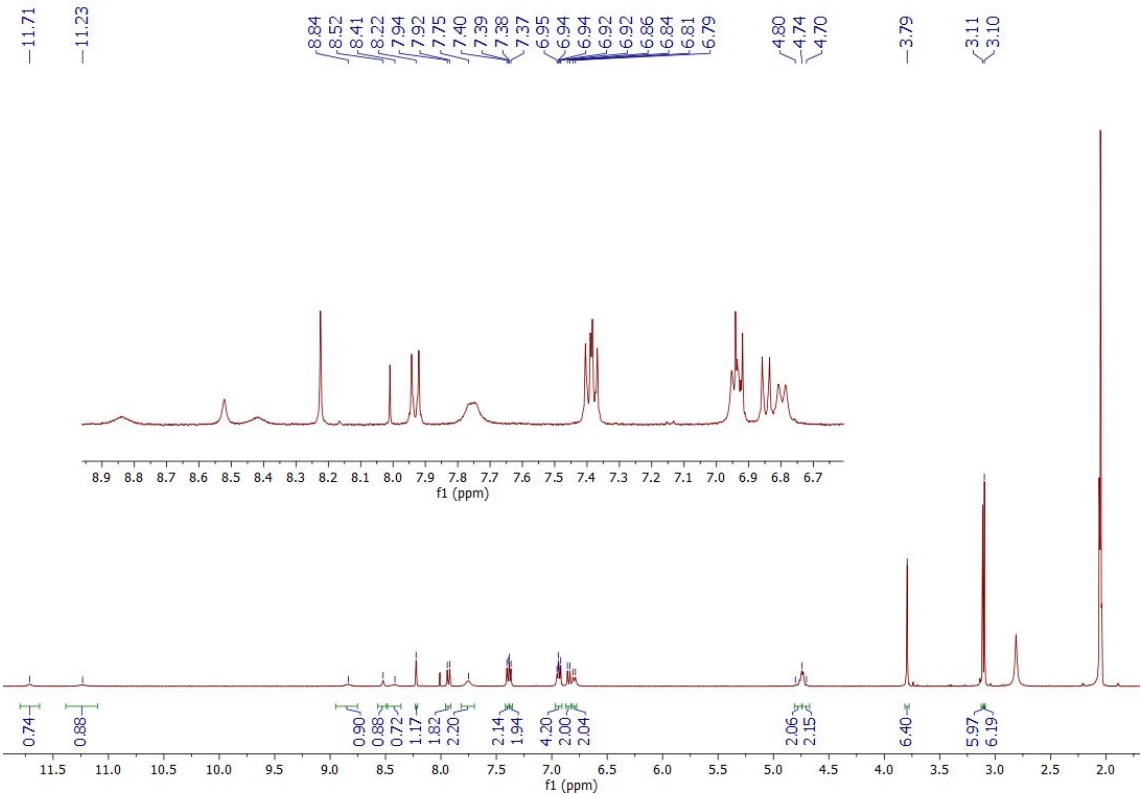


^{1}H-NMR spectrum in DMSO-d_6

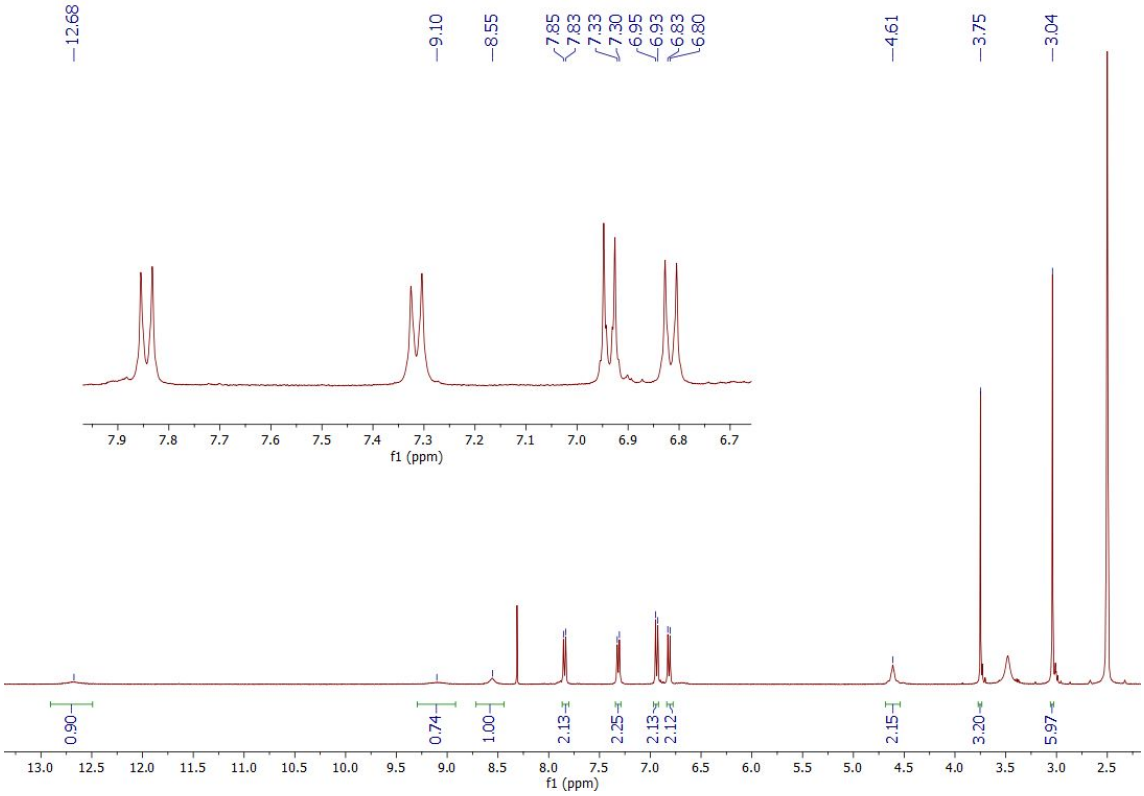
Spectroscopic characterization of **[ReCl(κ²*S*,*N*3-HL^{B})(CO)$_3$]**



IR spectrum

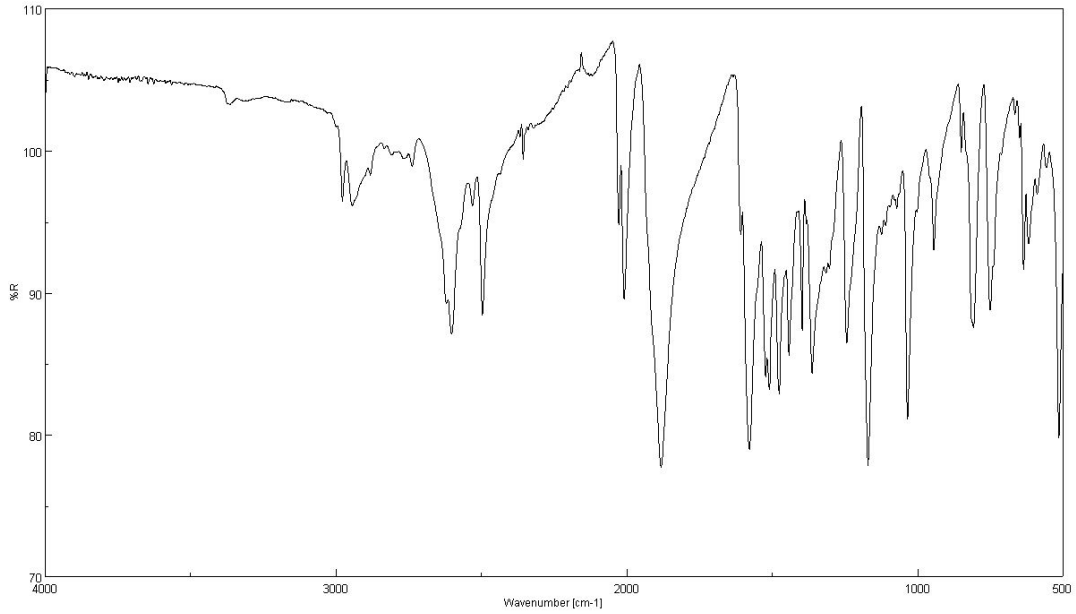


^{1}H-NMR spectrum in acetone-d$_6$

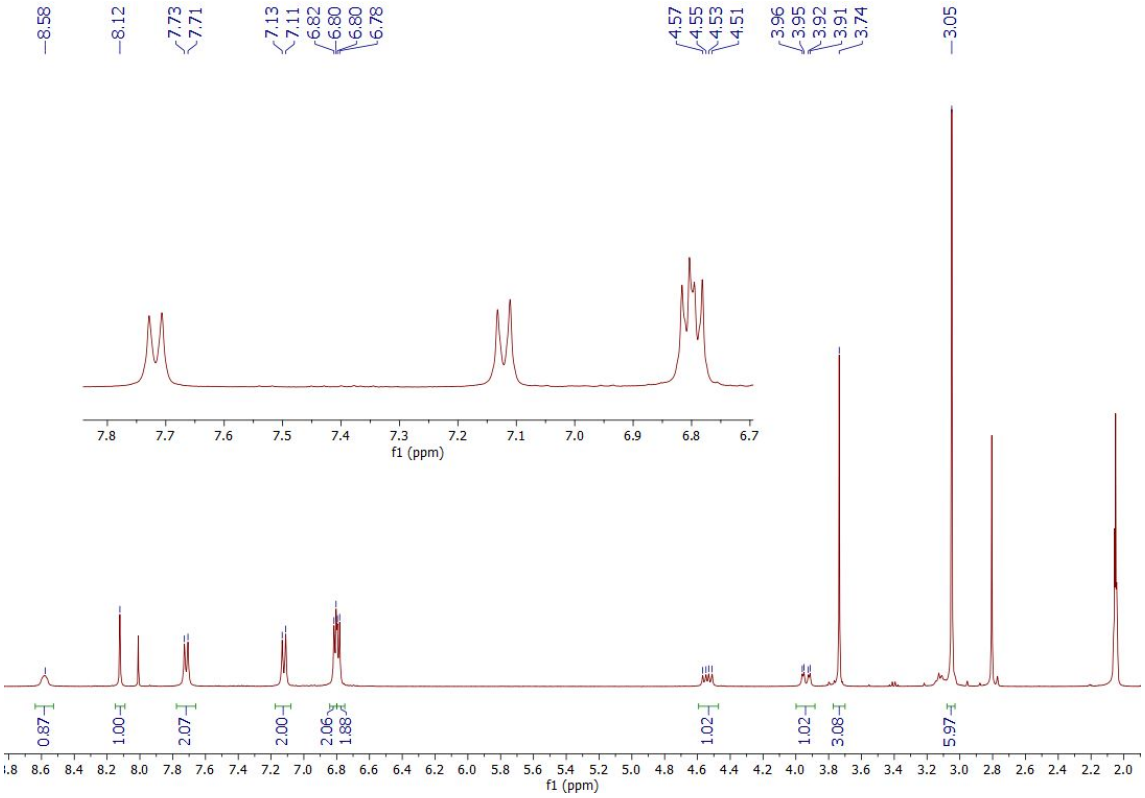


^{1}H-NMR spectrum in DMSO-d_6

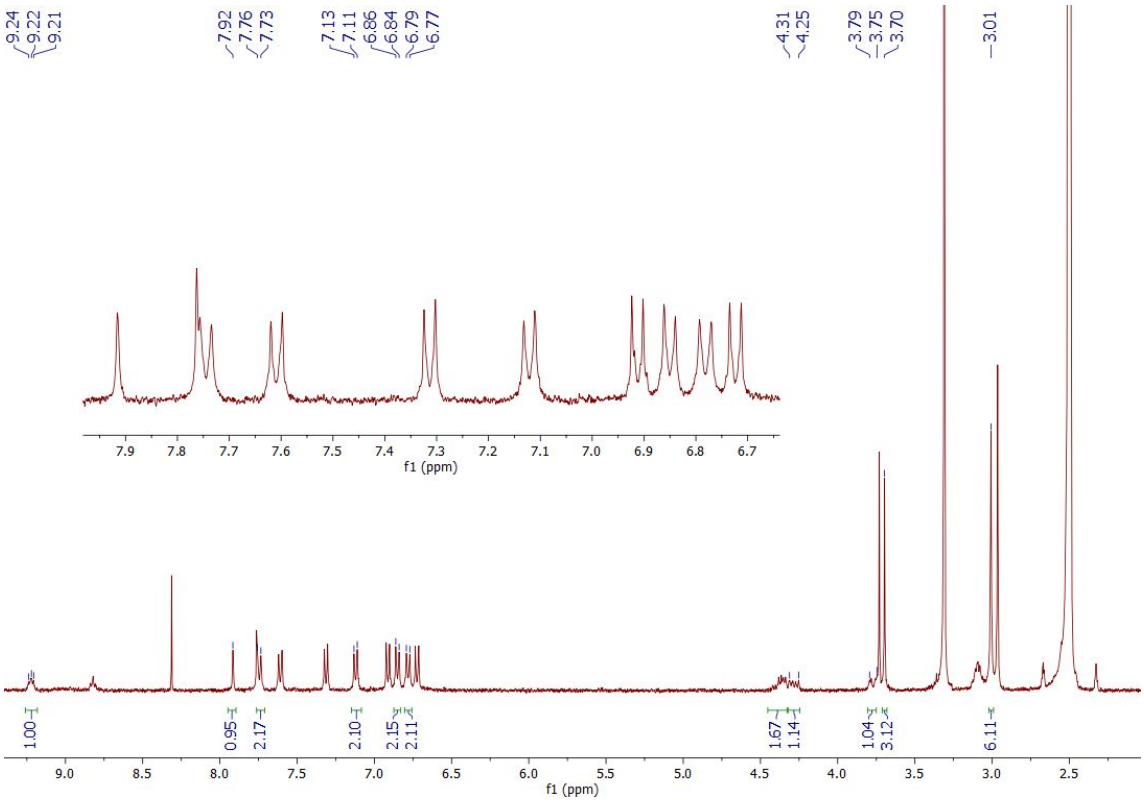
Spectroscopic characterization of **[Re_2(μ-κ^2*S,N2*:κ*S*-L^B)$_2$(CO)$_6$]**
(Structure 1B)



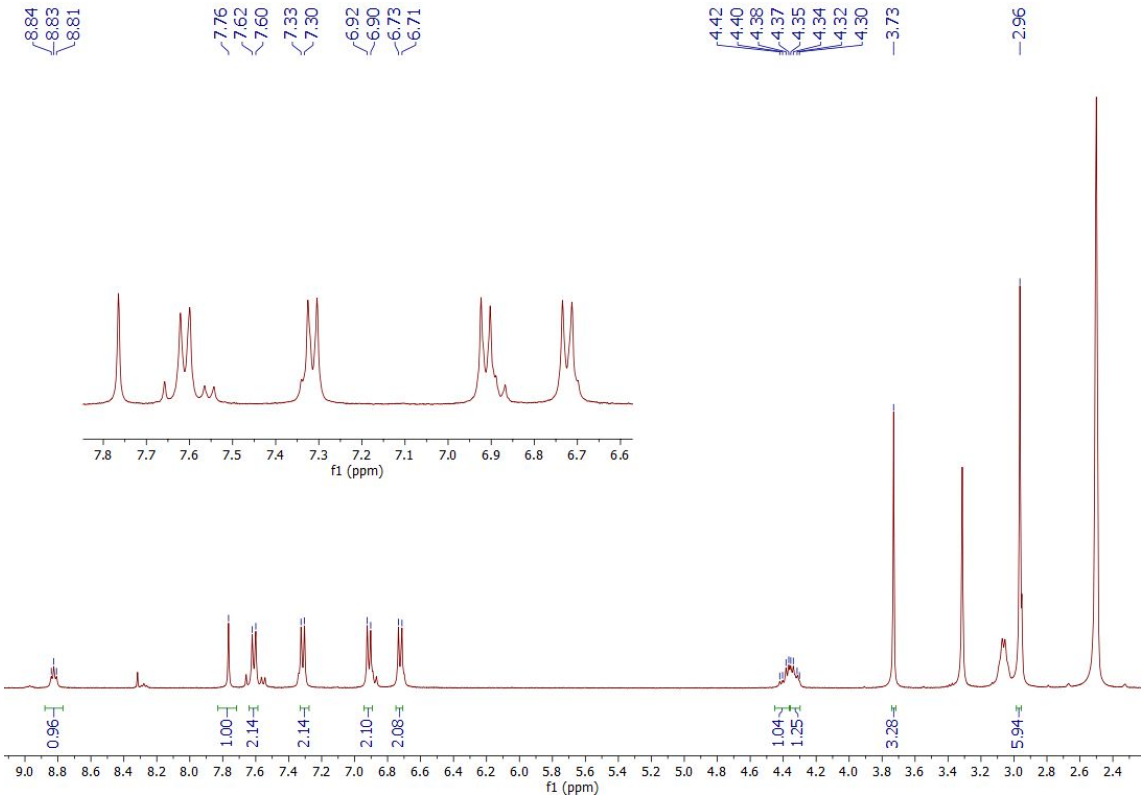
IR spectrum



^{1}H-NMR spectrum in acetone-d_6

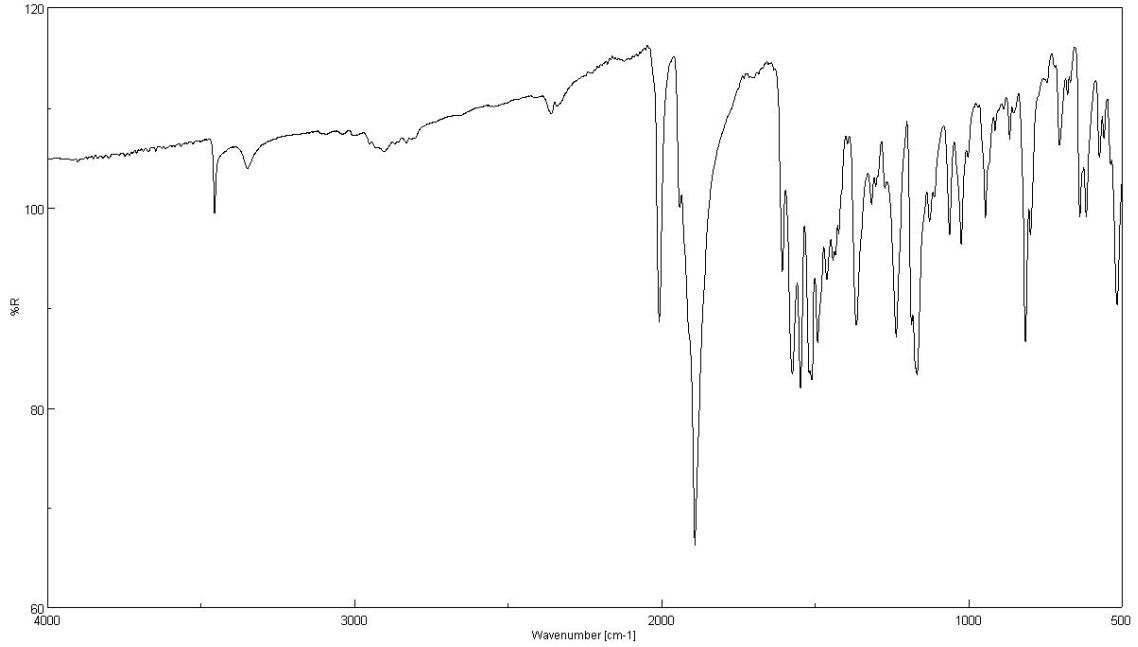


^{1}H-NMR spectrum in DMSO-d_6 (freshly prepared solution).

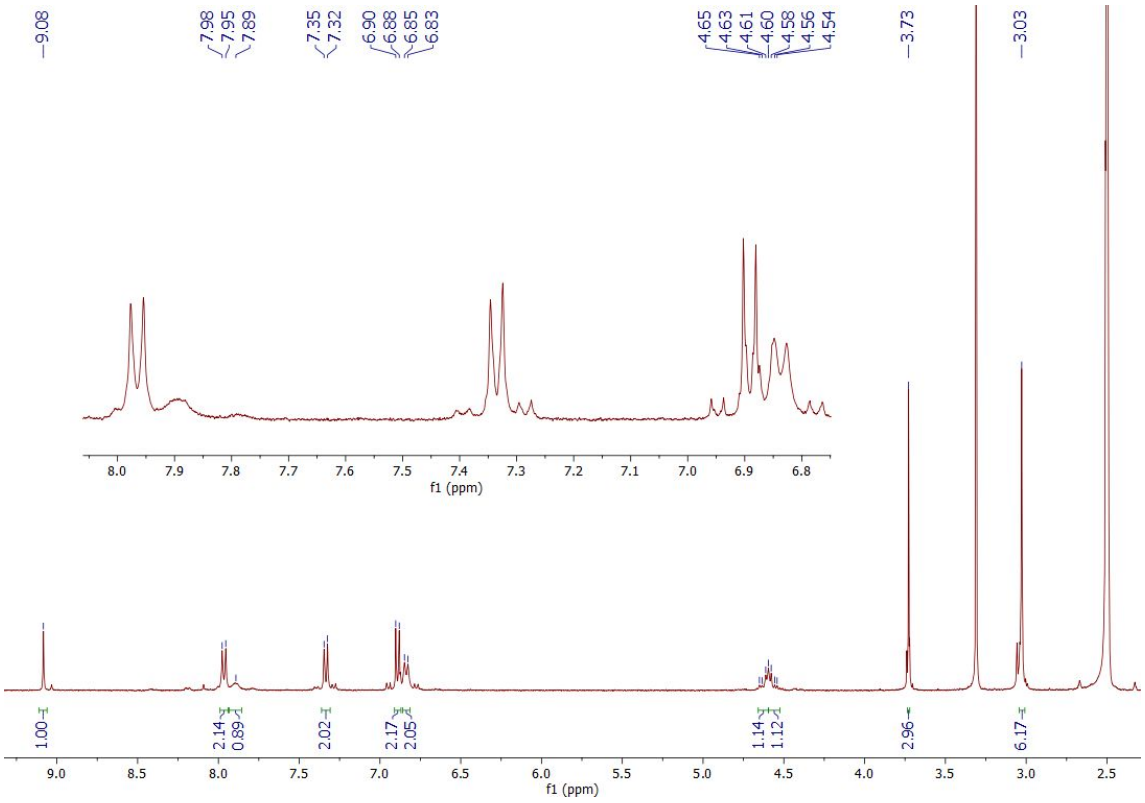


^{1}H-NMR spectrum in DMSO-d_6 (after 5 h).

Spectroscopic characterization of **[Re_2(μ-κ^2*S*,*N3*:κ*S*-L^B)$_2$(CO)$_6$]**
(E configuration in C2-N3 bond - Structures 2.2B')

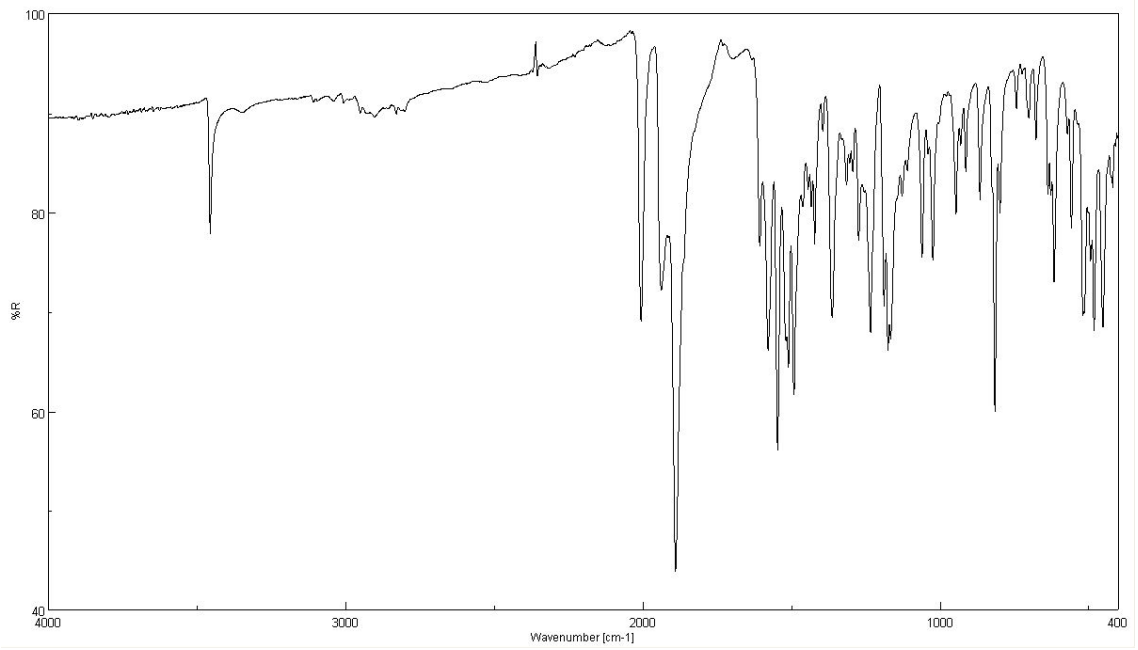


IR spectrum

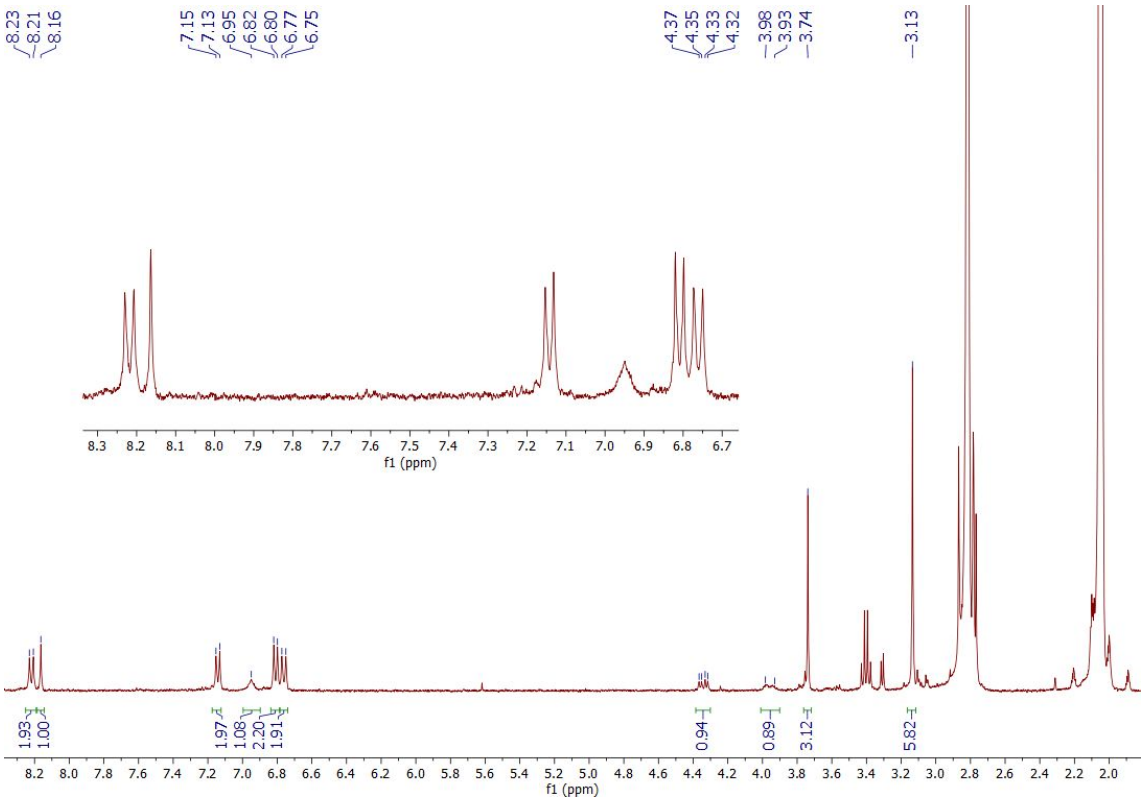


^{1}H-NMR spectrum in DMSO-d_6.

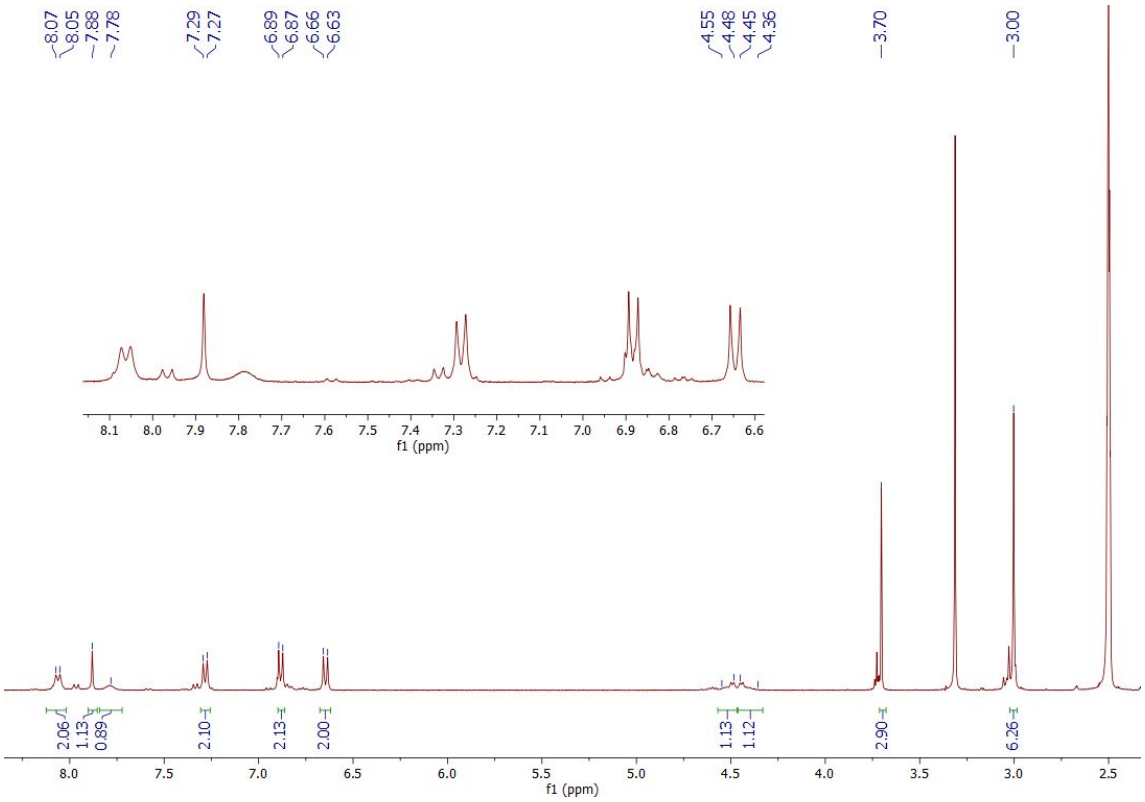
Spectroscopic characterization of **[Re_2(μ-κ^2*S*,*N3*:κ*S*-L^B)$_2$(CO)$_6$]**
(Z configuration in C2-N3 bond - Structures 2.3B and 2.3B')



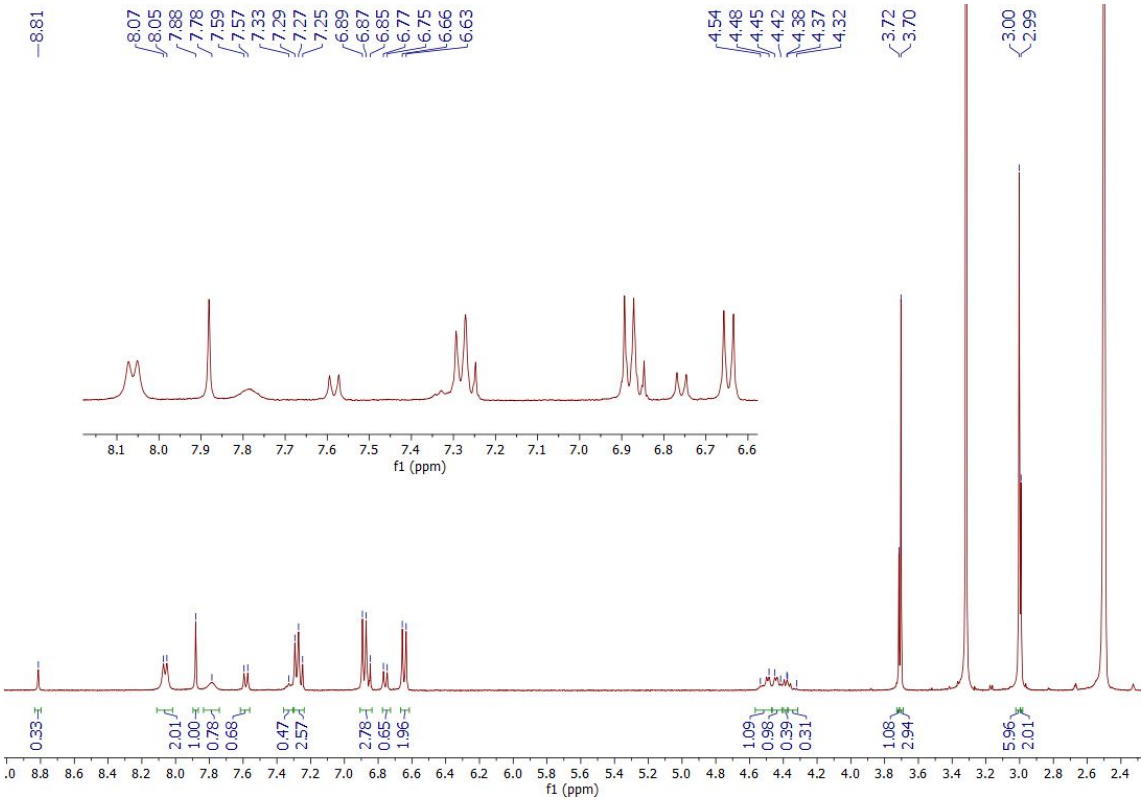
IR spectrum



^{1}H-NMR spectrum in acetone-d_6

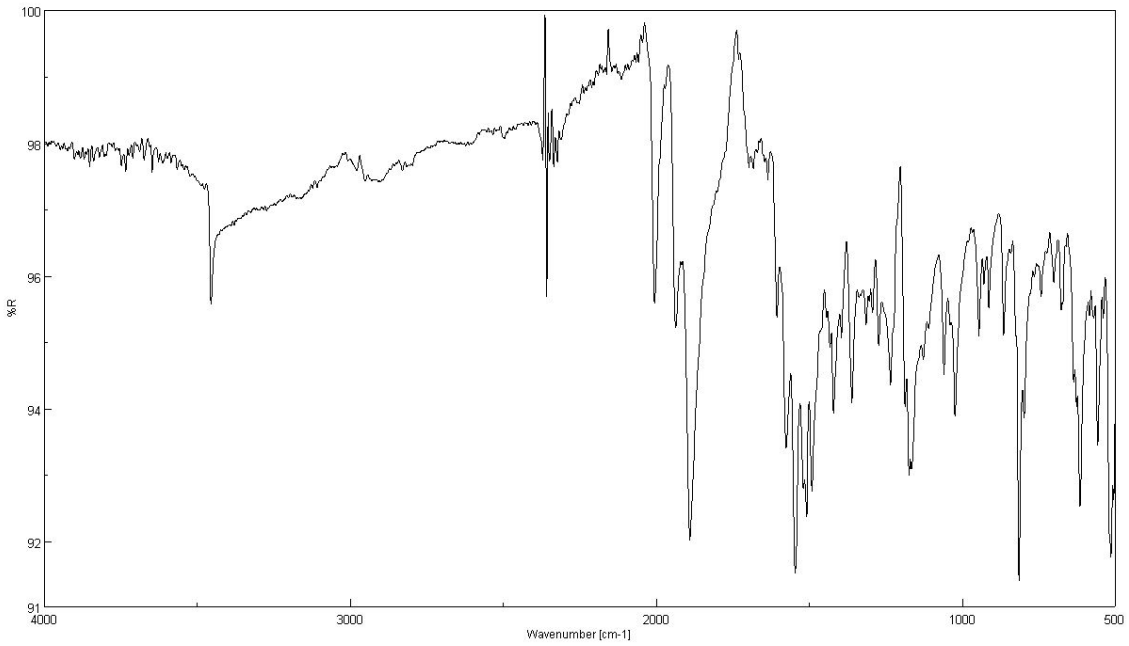


^{1}H-NMR spectrum in DMSO-d_6 (freshly prepared solution).



^{1}H-NMR spectrum in DMSO-d_6 (after 5 h).

Spectroscopic characterization of **[Re_2(μ-κ^2*S,N2*:κ*N3*-L^B)$_2$(CO)$_6$]**
(Structure 4B')



IR spectrum