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Polypyrrole-Functionalized Ruthenium Carbene Catalysts as Efficient Heterogeneous Systems for Olefin Epoxidation.

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CONTENTS.

Table S 1. Crystal data for the X-ray structures of complexes **2a** and **2b**.

	Complex **2a**	Complex **2b**
Chemical formula	$C_{21}H_{28}Cl_2N_4OSRu$	$C_{21}H_{28}Cl_2N_4OSRu$
Molecular weight	556.50	556.50
Crystal system	Monoclinic	Triclinic
Space group	P21/c	P-1
a[Å]	11.0431(5)	9.495(6)
b[Å]	12.1413(6)	15.469(10)
c[Å]	17.3390(8)	16.457(10)
α[º]	90.00	102.506(9)
β[º]	92.3280(10)	90.074(9)
γ[º]	90.00	94.764(10)
V [$Å^3$]	2322.85(19)	2351(3)
Z	4	4
Temperature, K	300(2)	300(2)
ρ_{calc}, [Mg/m^{-3}]	1.591	1.572
μ[mm^{-1}]	1.016	1.003
R_1[a] [I>2σ(I)]	R_1 = 0.0257	R_1 = 0.1806
wR_2[b] (all data)	R_1 = 0.0294 = 0.0694	R_1 = 0.2396 wR_2 = 0.4656

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$

[b] $wR_2 = [\sum\{w(F_o^2-F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{½}$, where $w = 1/[\sigma^2(Fo^2) + (0.0042P)^2]$ and $P=(F_o^2+2F_c^2)$.

Table S 2. Main bond lengths (Å) and angles (°) for the X-ray structure of complexes 2a and 2b.

Complex **2a**		Complex **2b**	
Ru(1)-N(1)	2,0685(15)	Ru(1)-N(3)	2,04(2)
Ru(1)-N(3)	2,0859(14)	Ru(1)-N(1)	2,097(16)
Ru(1)-N(2)	2,1656(14)	Ru(1)-N(2)	2,162(15)
Ru(1)-S(1)	2,2321(4)	Ru(1)-S(1)	2,227(6)
Ru(1)-Cl(2)	2,3957(5)	Ru(1)-Cl(1)	2,408(6)
Ru(1)-Cl(1)	2,4550(4)	Ru(1)-Cl(2)	2,439(6)
N(1)-Ru(1)-N(3)	160,82(5)	N(3)-Ru(1)-N(1)	82,9(7)
N(1)-Ru(1)-N(2)	81,16(5)	N(3)-Ru(1)-N(2)	82,6(7)
N(3)-Ru(1)-N(2)	79,78(5)	N(1)-Ru(1)-N(2)	82,1(6)
N(1)-Ru(1)-S(1)	96,22(4)	N(3)-Ru(1)-S(1)	91,3(6)
N(3)-Ru(1)-S(1)	102,95(4)	N(1)-Ru(1)-S(1)	173,9(4)
N(2)-Ru(1)-S(1)	174,82(4)	N(2)-Ru(1)-S(1)	99,0(4)
N(1)-Ru(1)-Cl(2)	90,81(4)	N(3)-Ru(1)-Cl(1)	172,6(6)
N(3)-Ru(1)-Cl(2)	88,16(4)	N(1)-Ru(1)-Cl(1)	91,9(4)
N(2)-Ru(1)-Cl(2)	93,20(4)	N(2)-Ru(1)-Cl(1)	91,6(4)
S(1)-Ru(1)-Cl(2)	91,295(16)	S(1)-Ru(1)-Cl(1)	94,1(2)
N(1)-Ru(1)-Cl(1)	90,81(4)	N(3)-Ru(1)-Cl(2)	96,2(6)
N(3)-Ru(1)-Cl(1)	91,17(4)	N(1)-Ru(1)-Cl(2)	90,8(4)
N(2)-Ru(1)-Cl(1)	89,66(4)	N(2)-Ru(1)-Cl(2)	172,9(4)
S(1)-Ru(1)-Cl(1)	85,903(16)	S(1)-Ru(1)-Cl(2)	88,0(2)
Cl(2)-Ru(1)-Cl(1)	176,900(16)	Cl(1)-Ru(1)-Cl(2)	89,1(2)
O(1)-S(1)-Ru(1)	117,59(6)	O(1)-S(1)-Ru(1)	119,4(8)

Figure S 1. Possible diastereoisomers for complex $[Ru^{II}Cl(CN\text{-}Me)(bpea\text{-}pyr)]^{+}$, **3**.

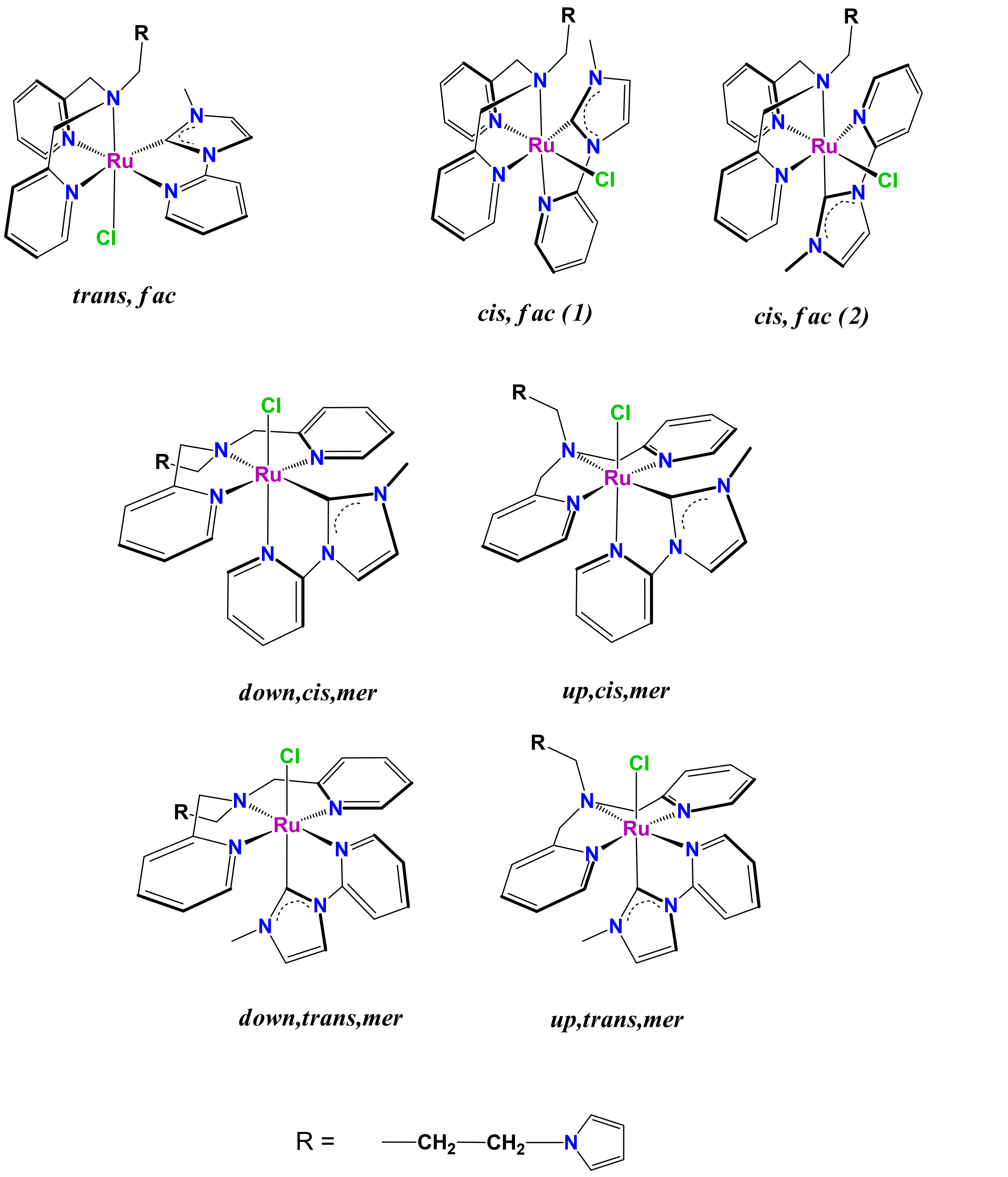
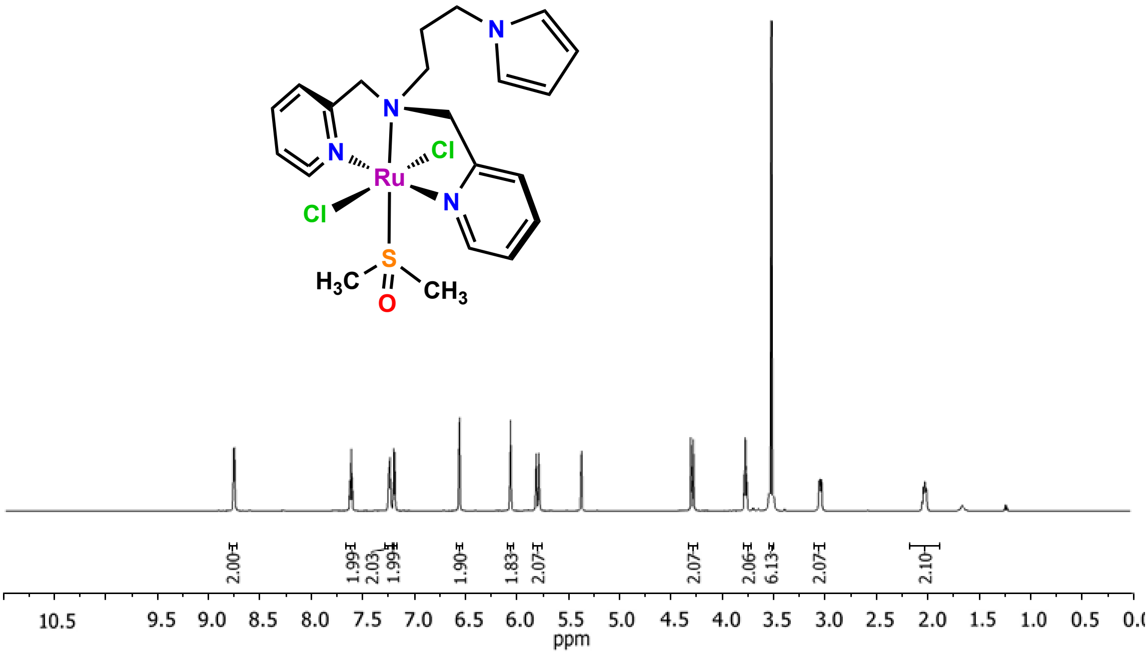


Figure S 2. NMR spectra (600 MHz, 298 K, d_6-acetone) of complex *trans,mer*- [$Ru^{II}Cl_2$(bpea-pyr)(dmso)], **2a**: (a) ^{1}H-NMR, (b) ^{13}C-NMR, (c) COSY, (d) NOESY, (e) HSQC, (f) HMBC.

(a)



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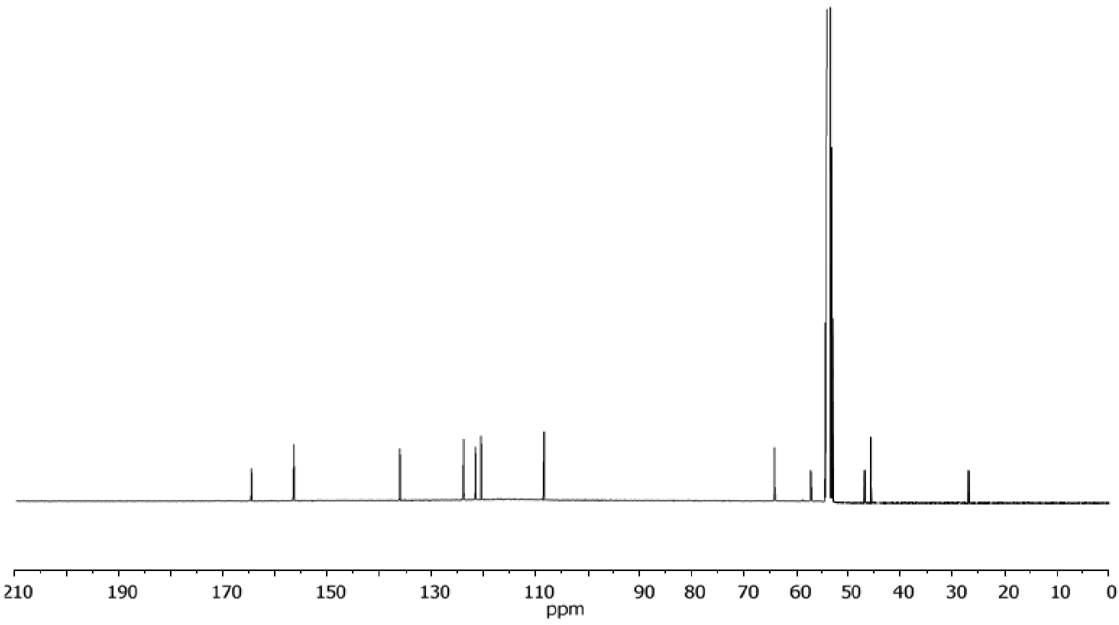

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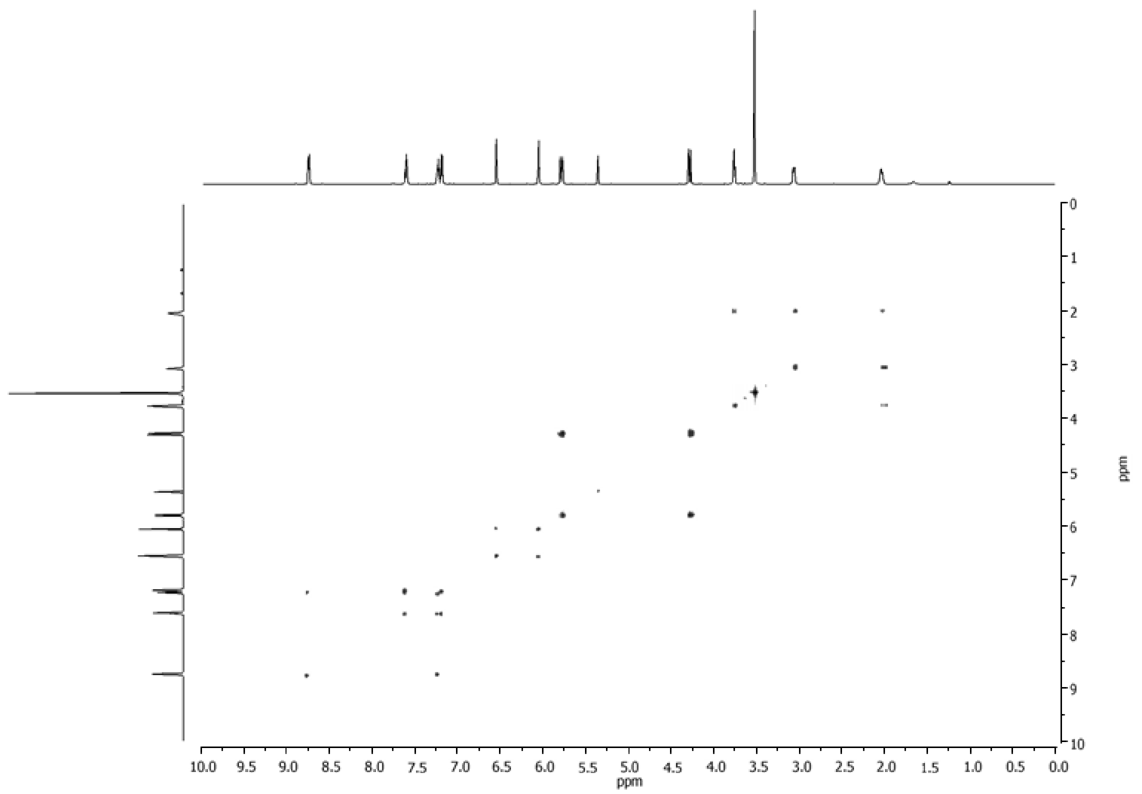
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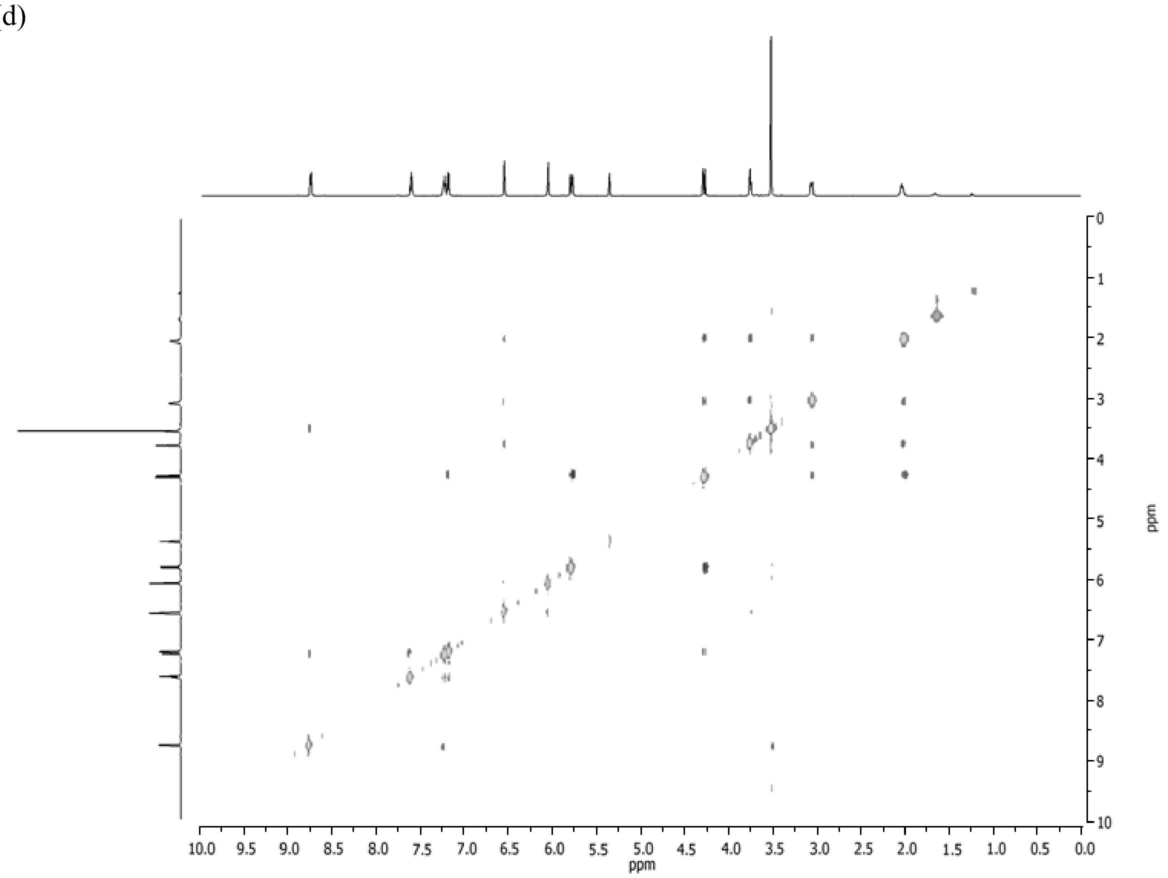
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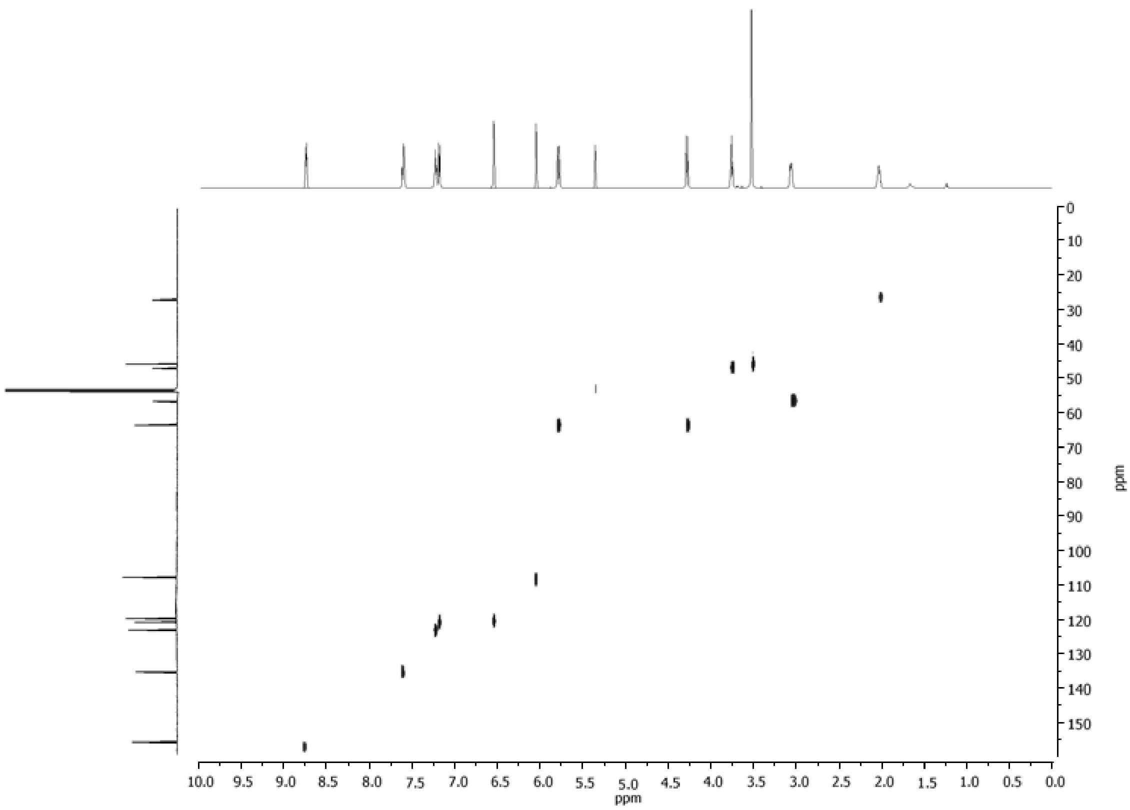
(e)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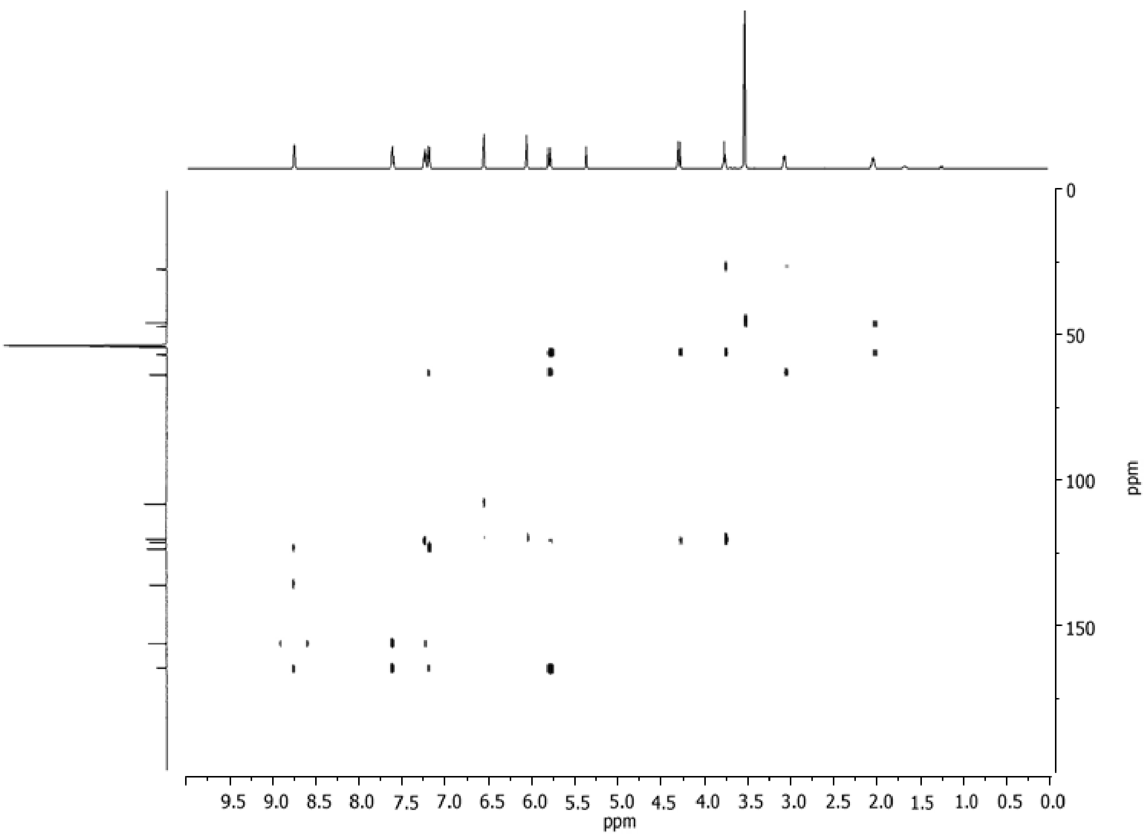
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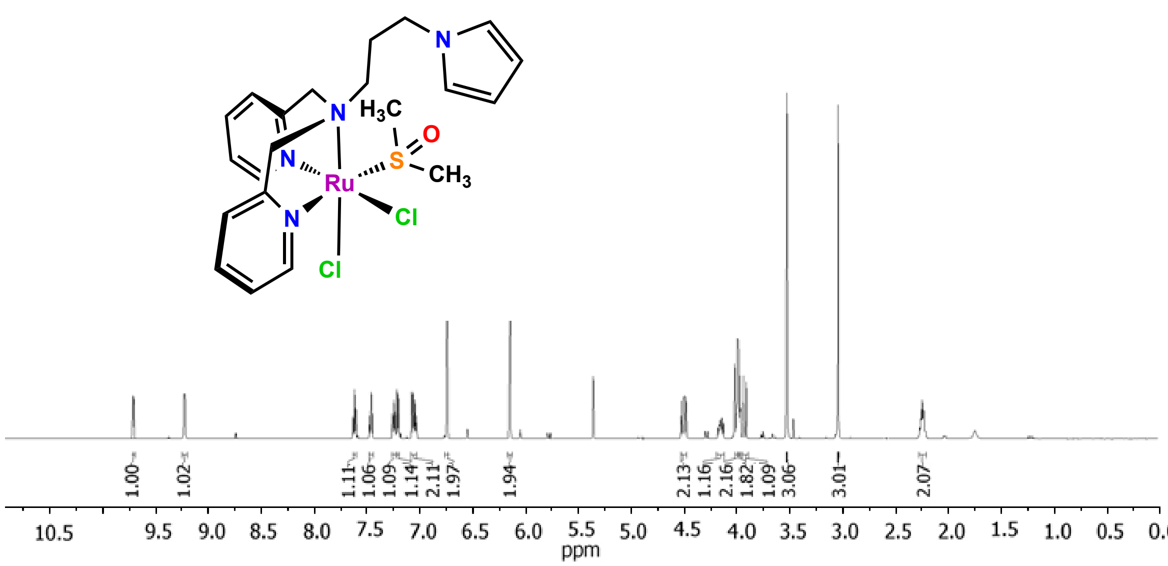
Figure S 3. NMR spectra (600 MHz, 298 K, d_6-acetone) of complex *cis,fac*-[$Ru^{II}Cl_2$(bpea- pyr)(dmso)], **2b**: (a) ^{1}H-NMR, (b) ^{13}C-NMR, (c) COSY, (d) NOESY, (e) HSQC, (f) HMBC.

(a)



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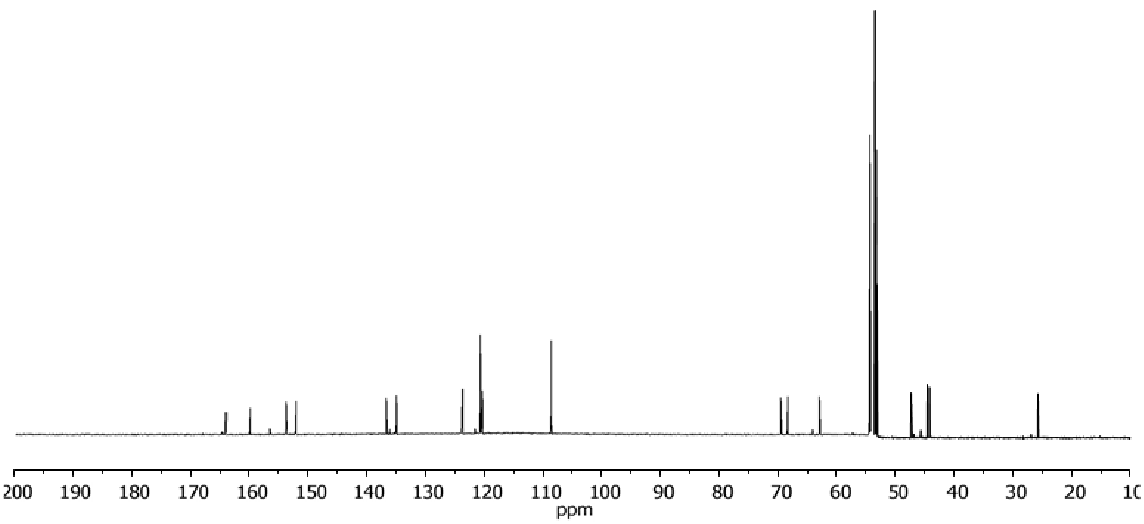

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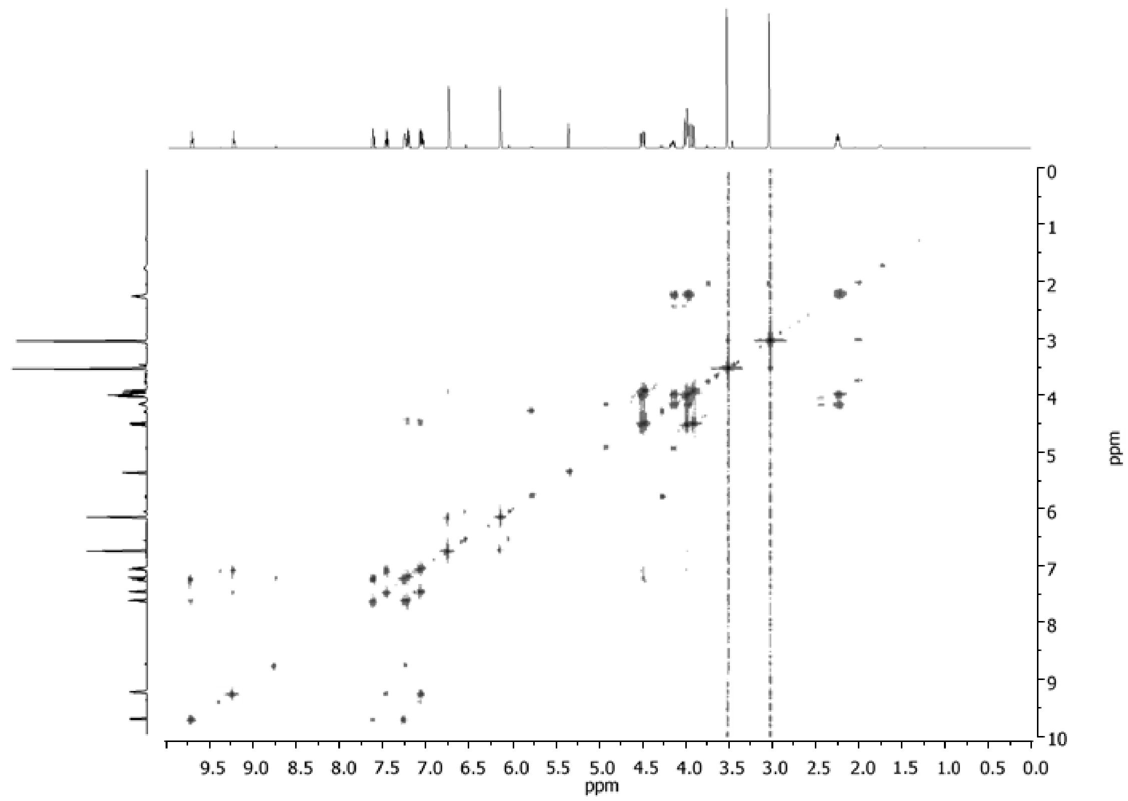
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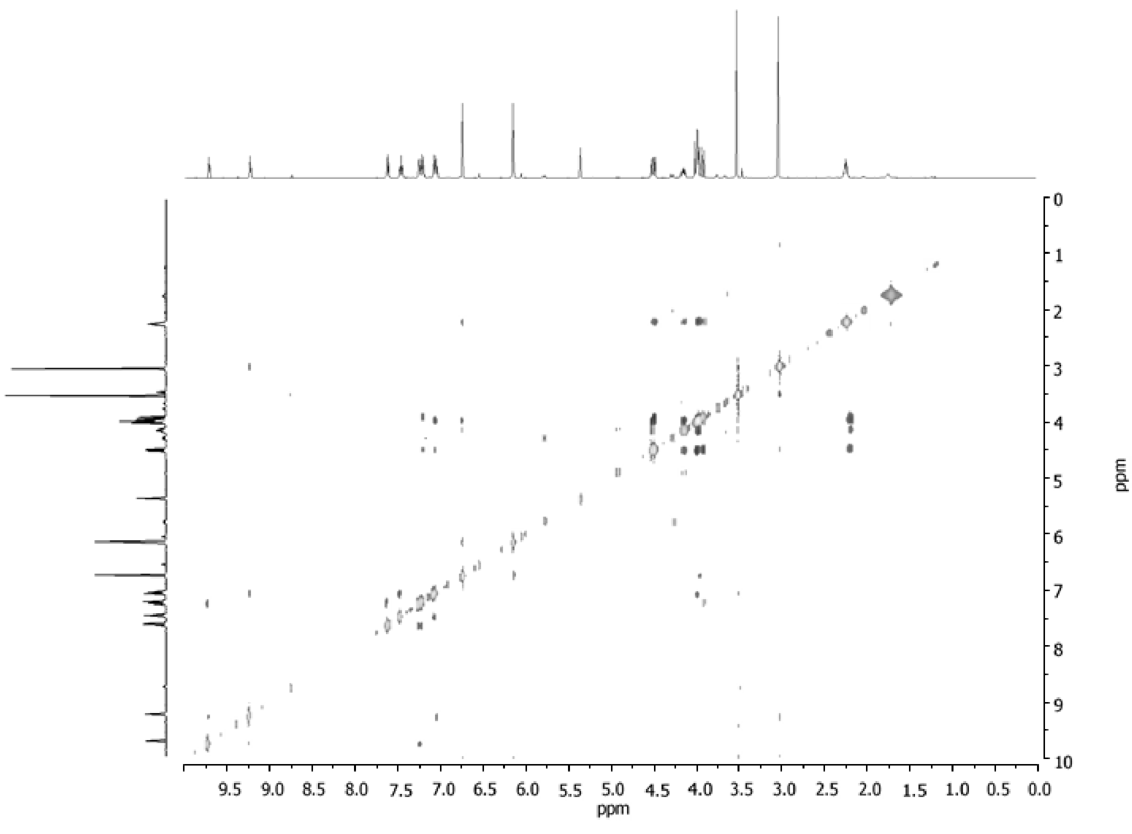
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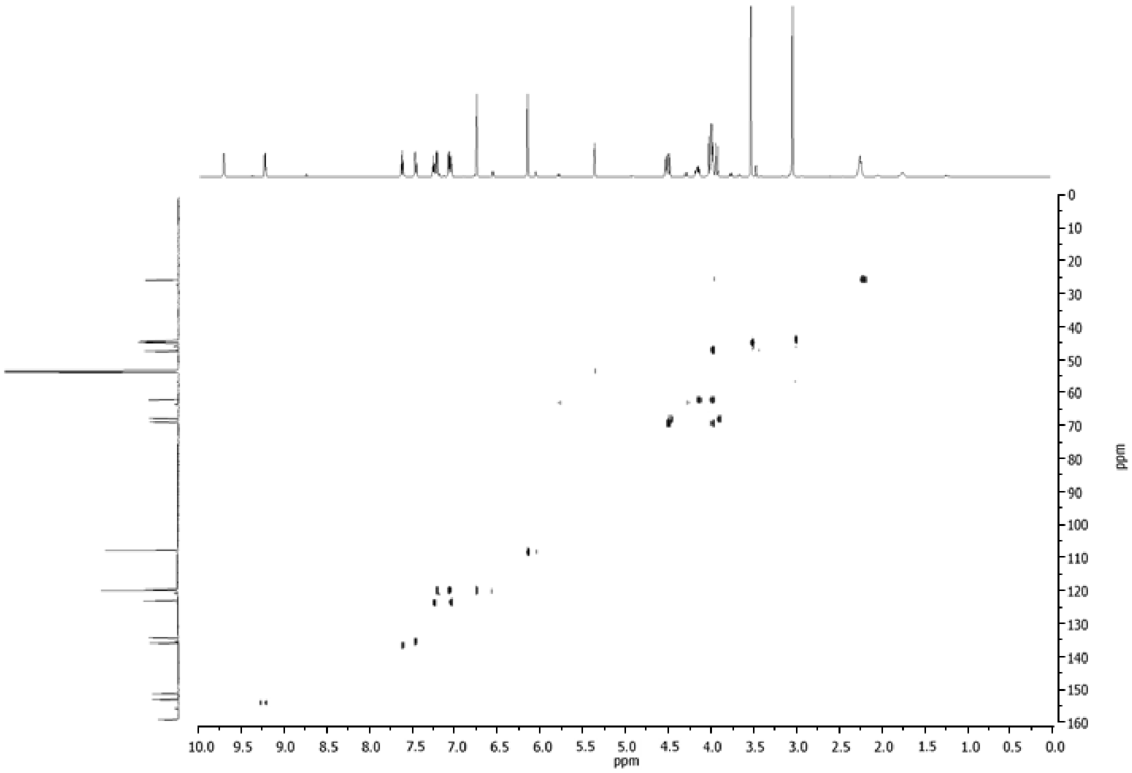
(e)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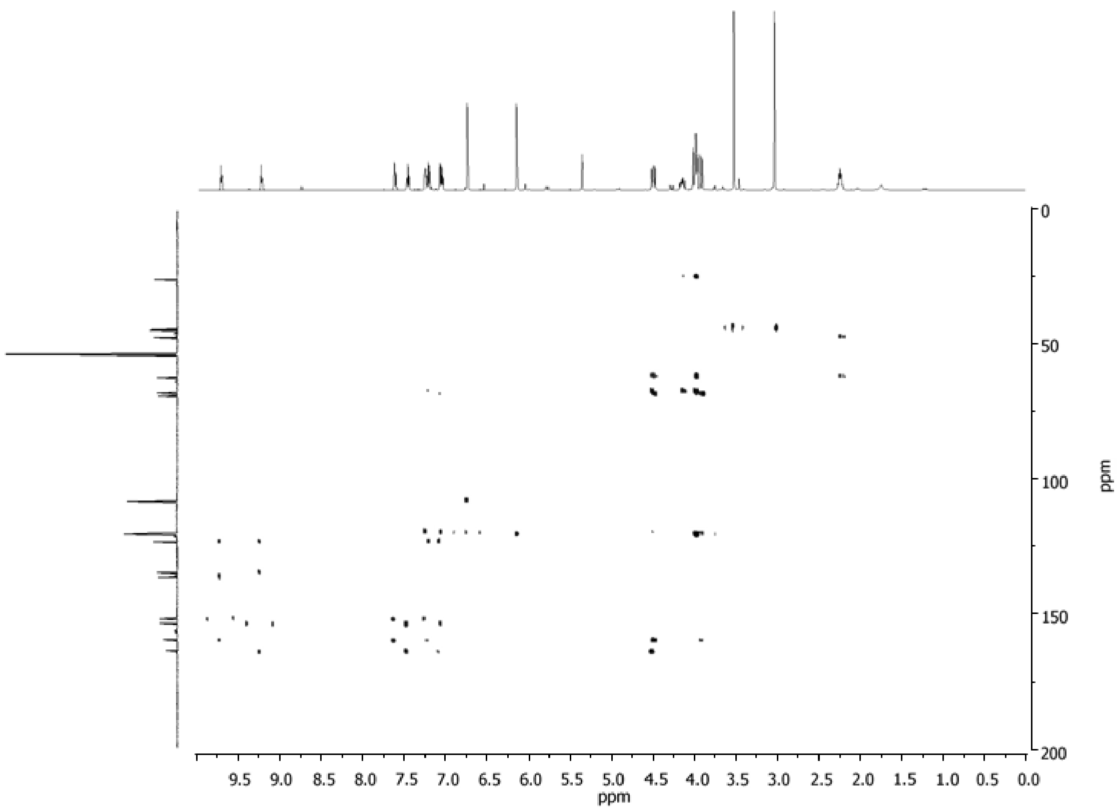
(f)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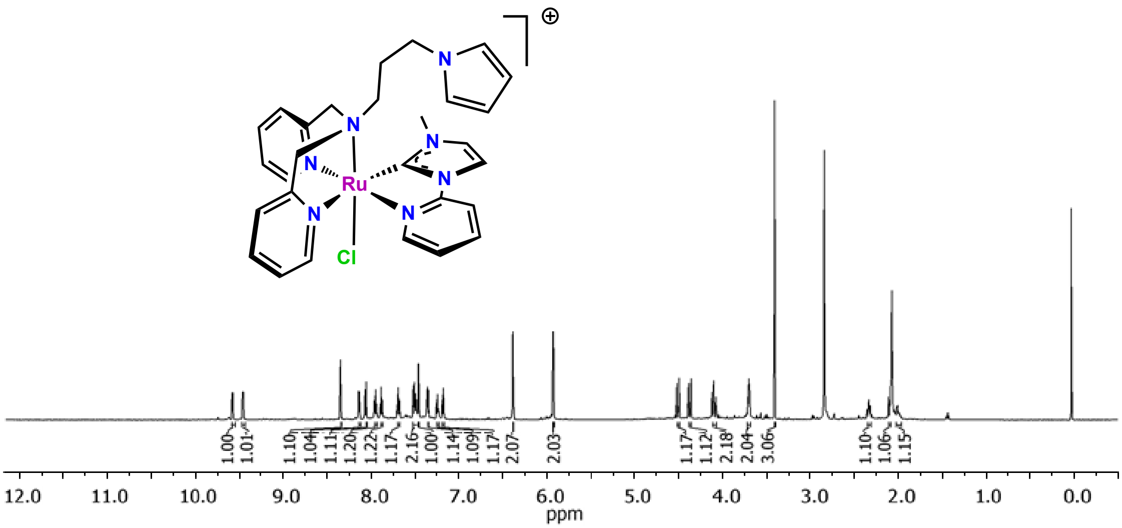
ppm

Figure S 4. NMR spectra (600 MHz, 298 K, d_6-acetone) *trans,fac*-[Ru^{II}Cl(CN-Me)(bpea-pyr)]$^+$, **3**: (a) ^{1}H-NMR, (b) ^{13}C-NMR, (c) COSY, (d) NOESY, (e) HSQC, (f) HMBC.

(a)



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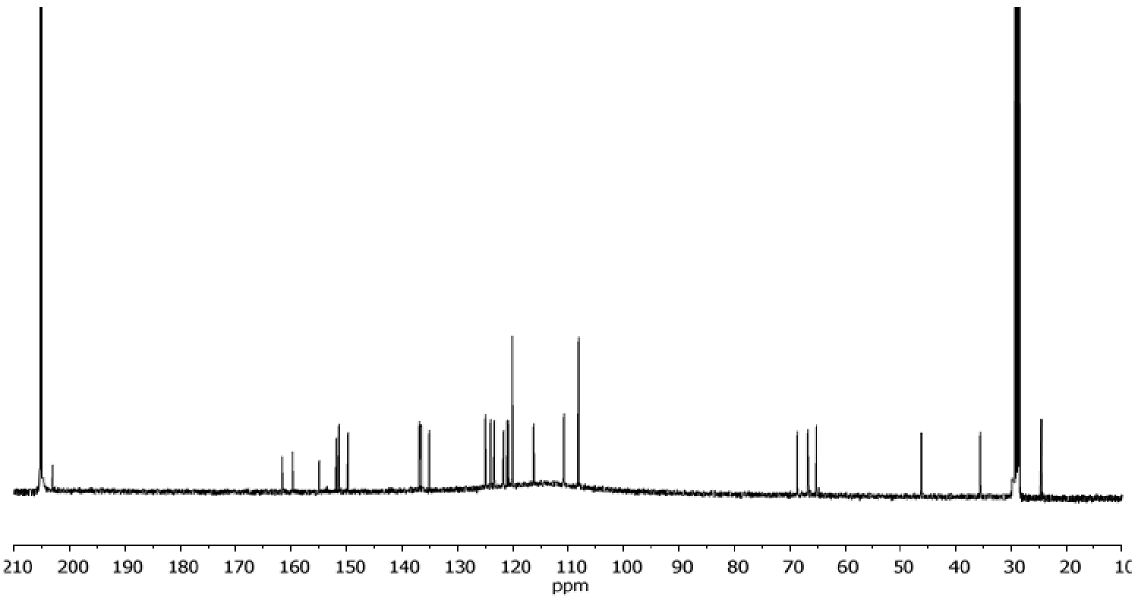

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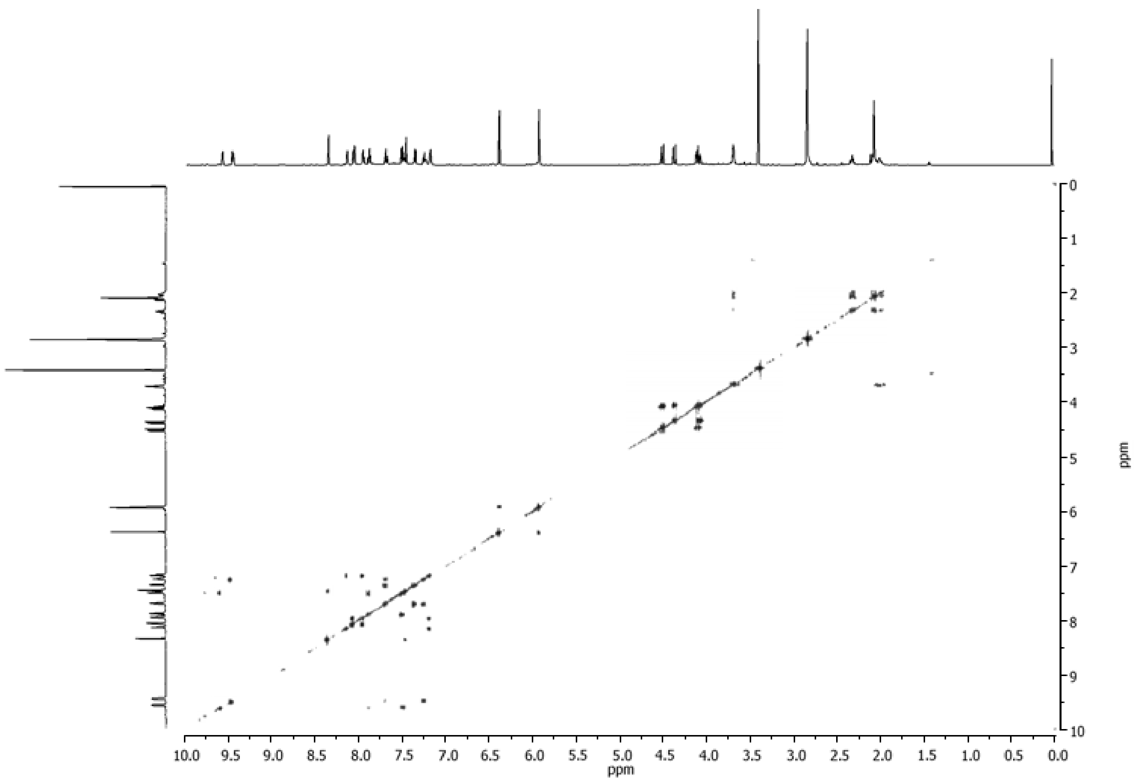
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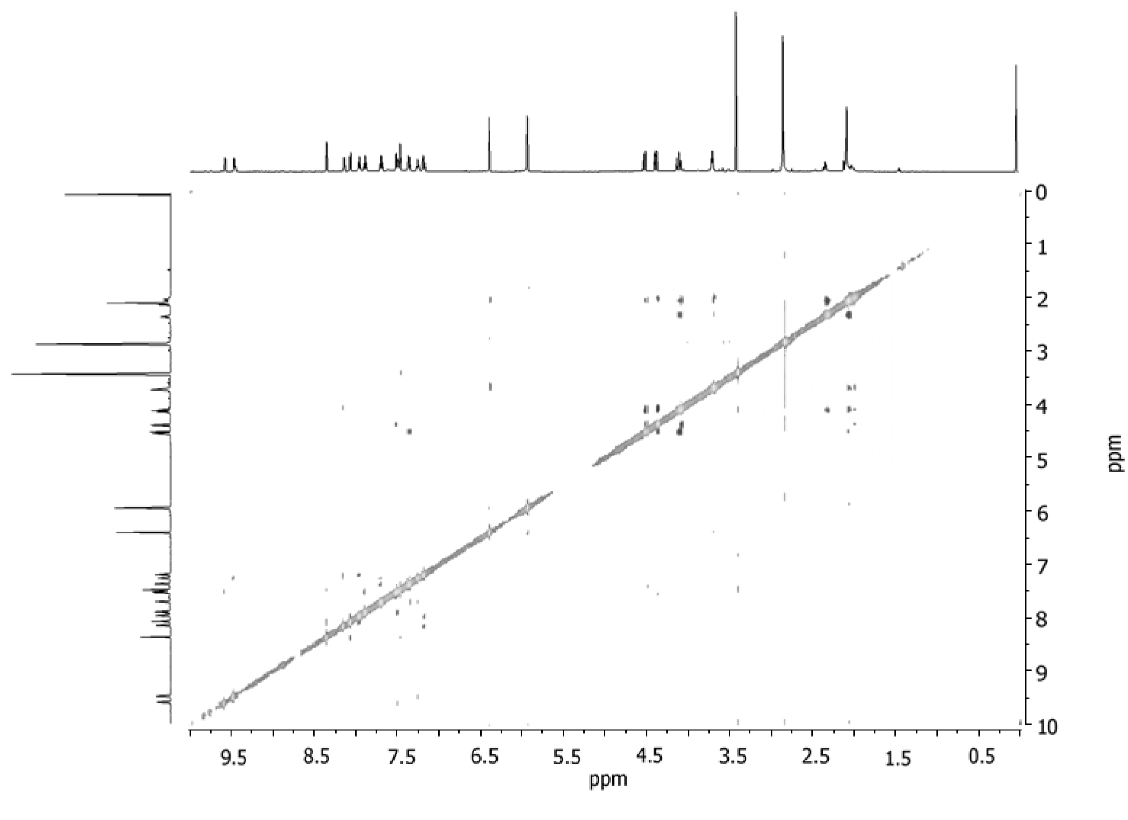
(d)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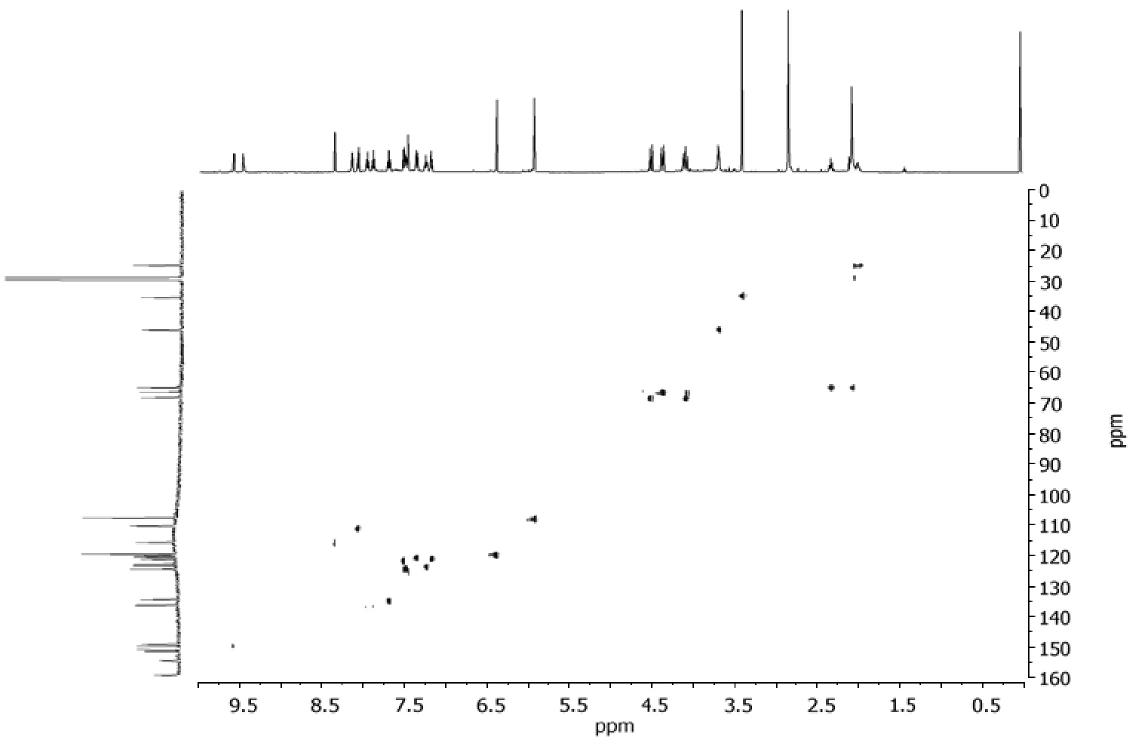
(e)



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(f)

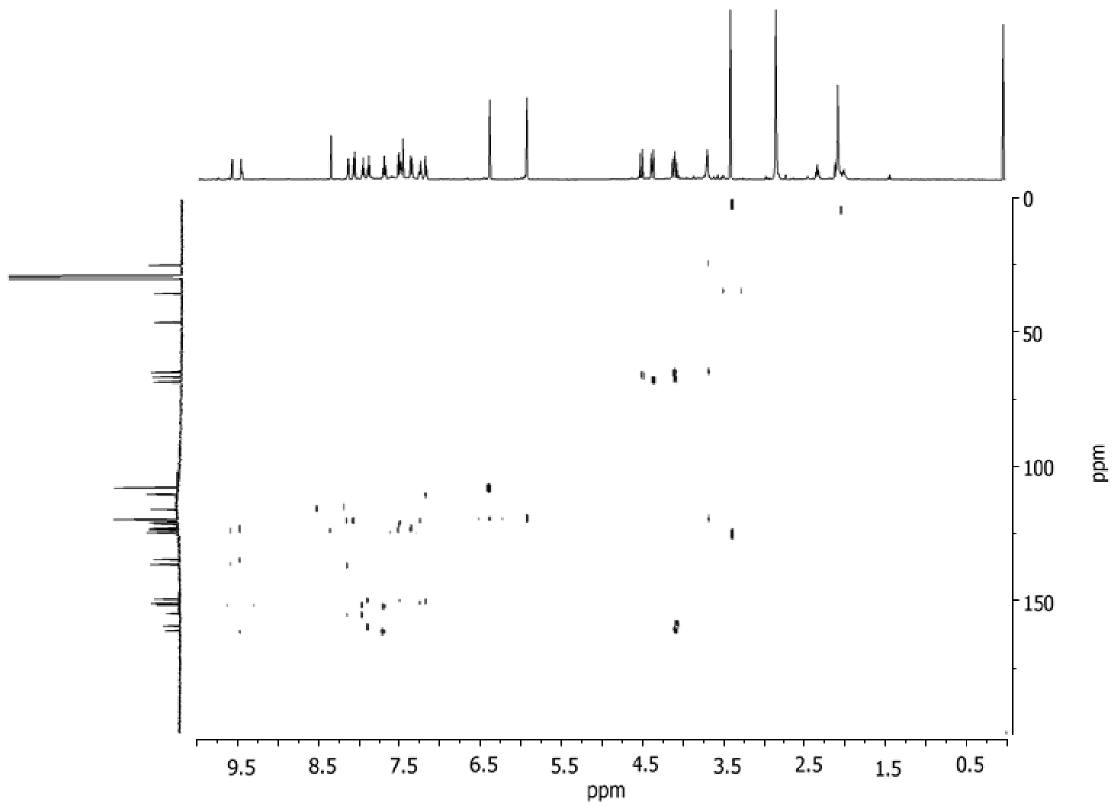

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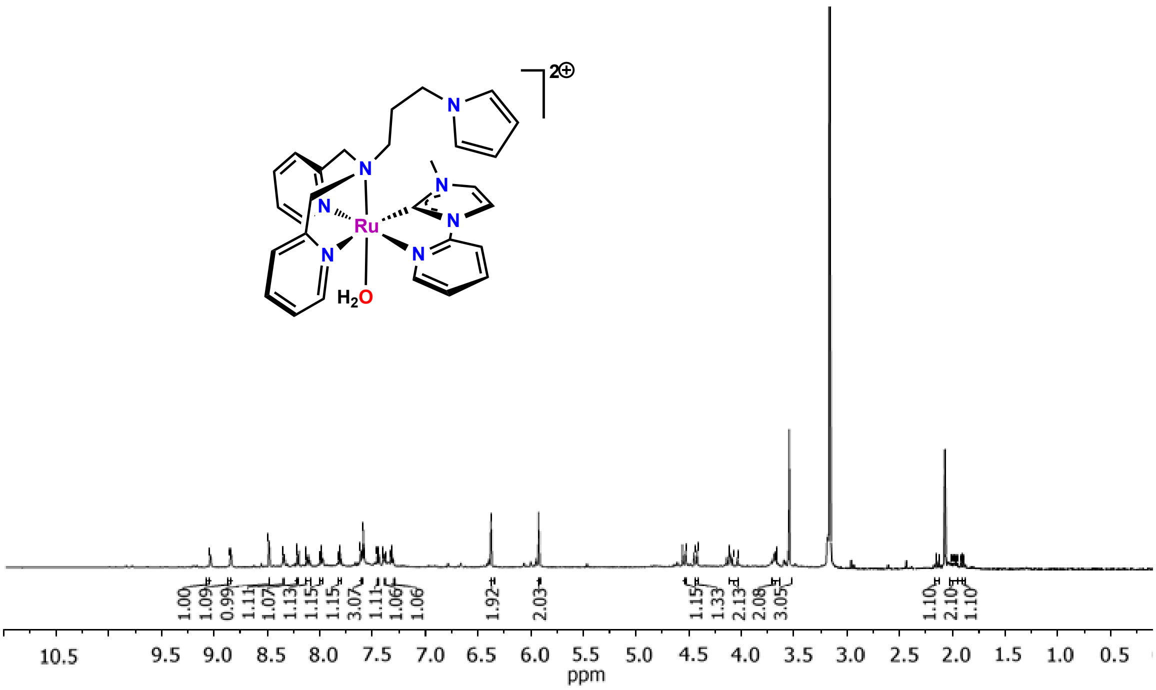
Figure S 5. NMR spectra (600 MHz, 298 K, d_6-acetone) *trans,fac*-$[Ru^{II}(CN\text{-}Me)(bpea\text{-}pyr)(H_2O)]^{2+}$, **4**: (a) ^{1}H-NMR, (b) ^{13}C-NMR, (c) COSY, (d) NOESY, (e) HSQC, (f) HMBC.

(a)



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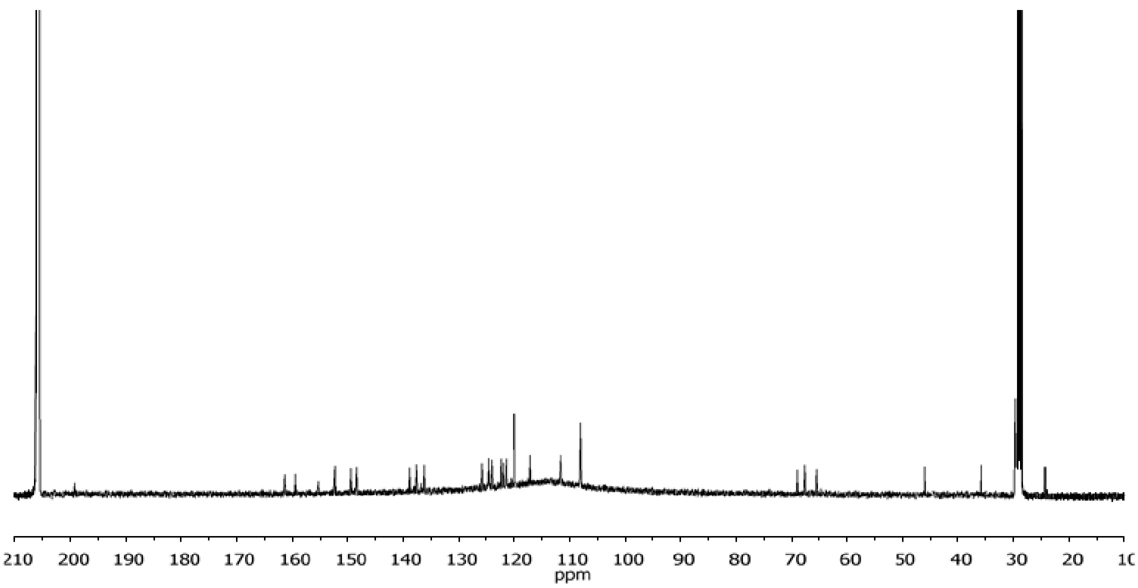

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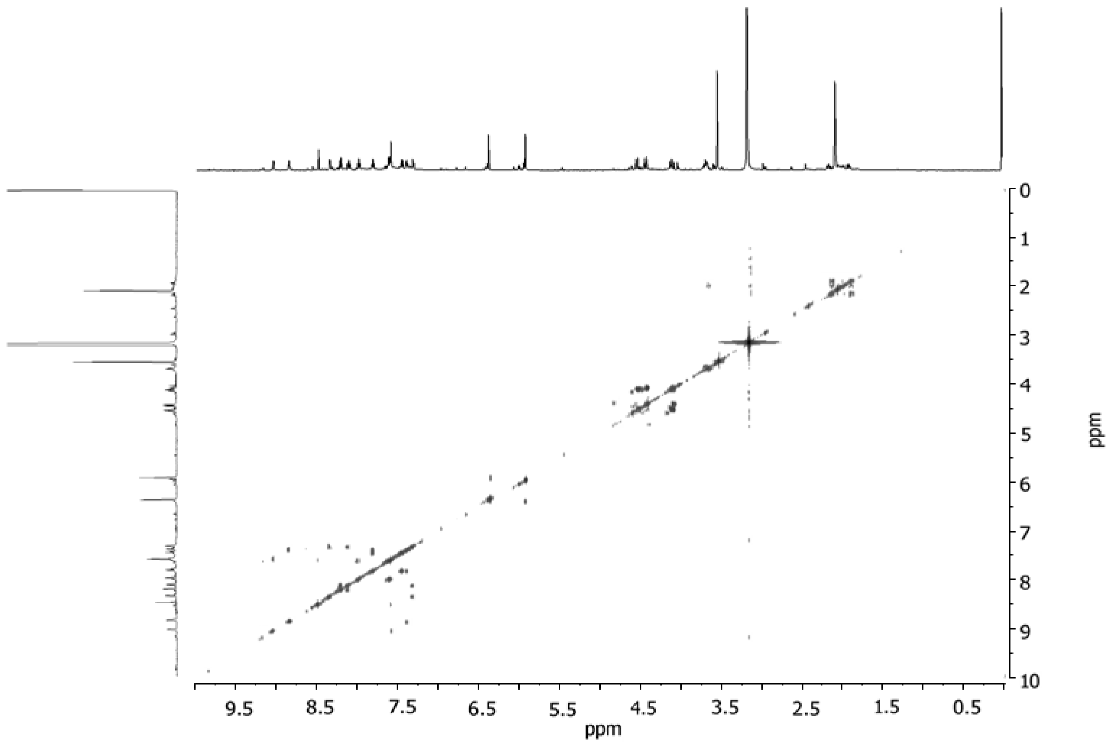

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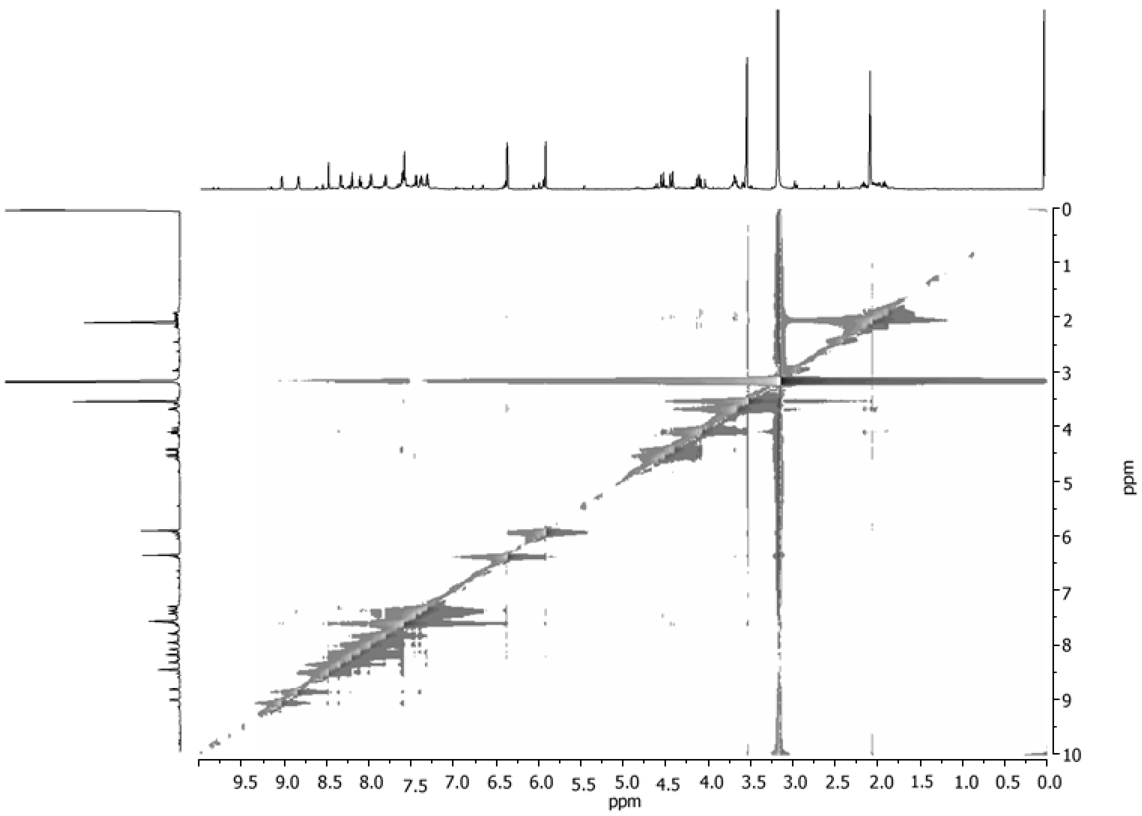

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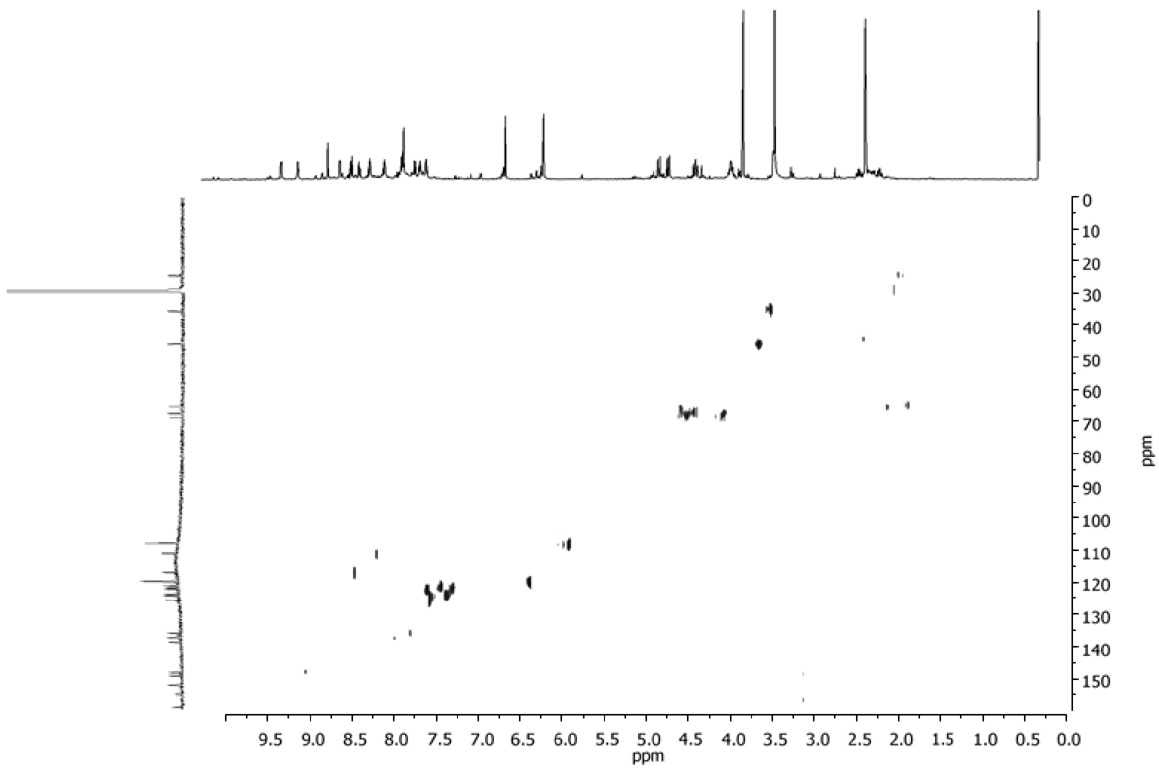
(e)



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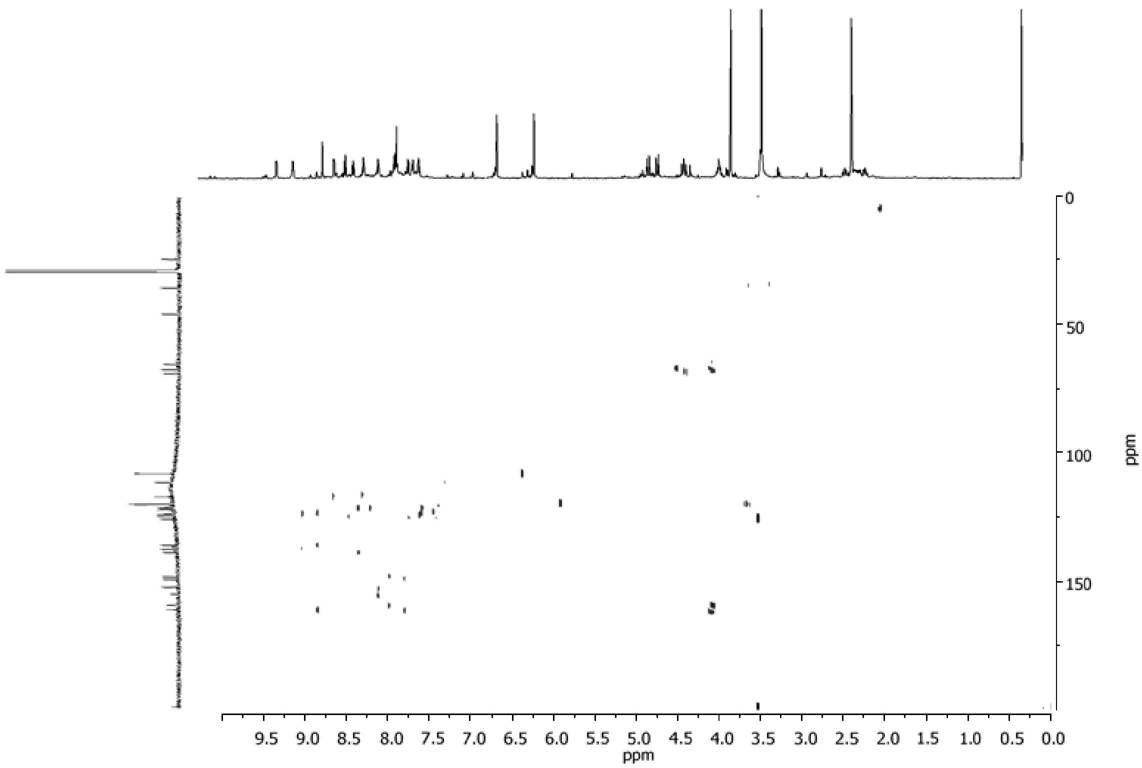
(f)



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ppm

Figure S 6. Cyclic voltammogram of complex **3** (1 mM) registered in CH_2Cl_2 + 0.1 M TBAH at a glassy carbon disk electrode (scan rate = 100 mV s^{-1}).

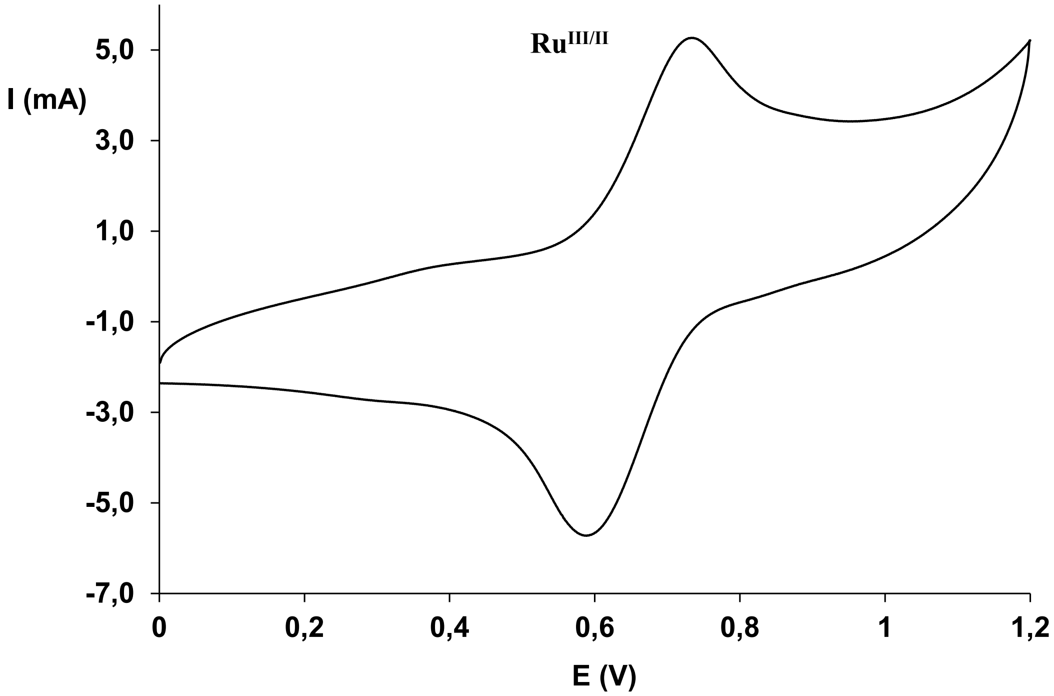


Figure S 7. Cyclic voltammogram of complex **4** (1 mM) in CH_2Cl_2 + 0.1 M TBAH at a glassy carbon disk electrode (scan rate = 100 mV s^{-1}).

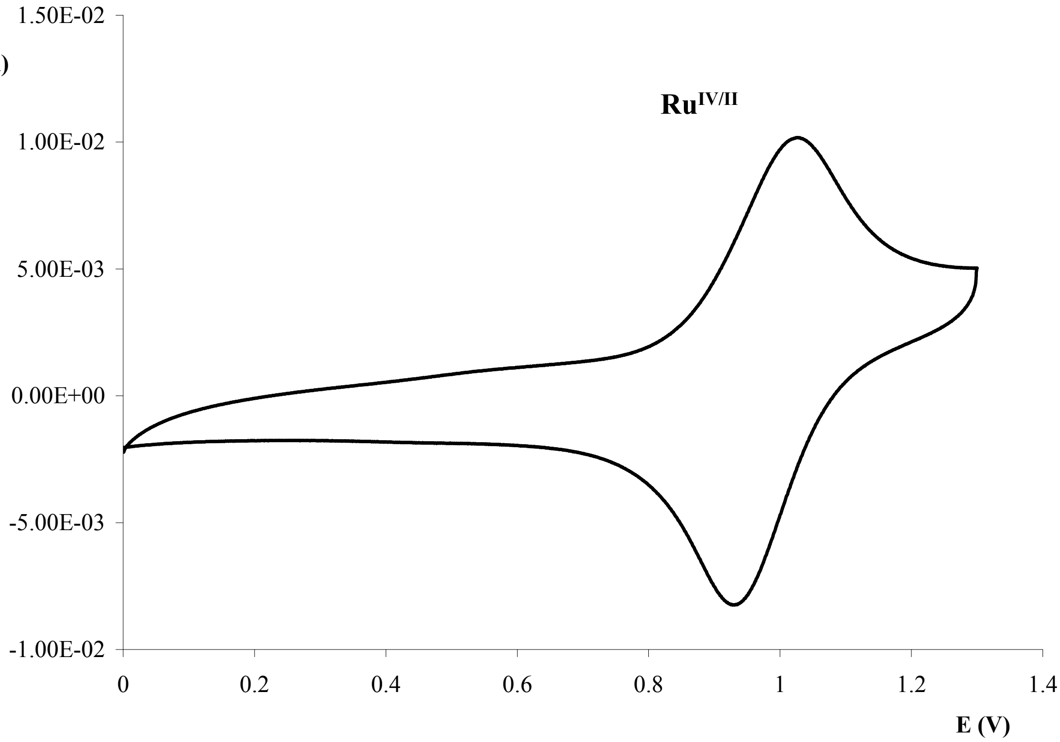
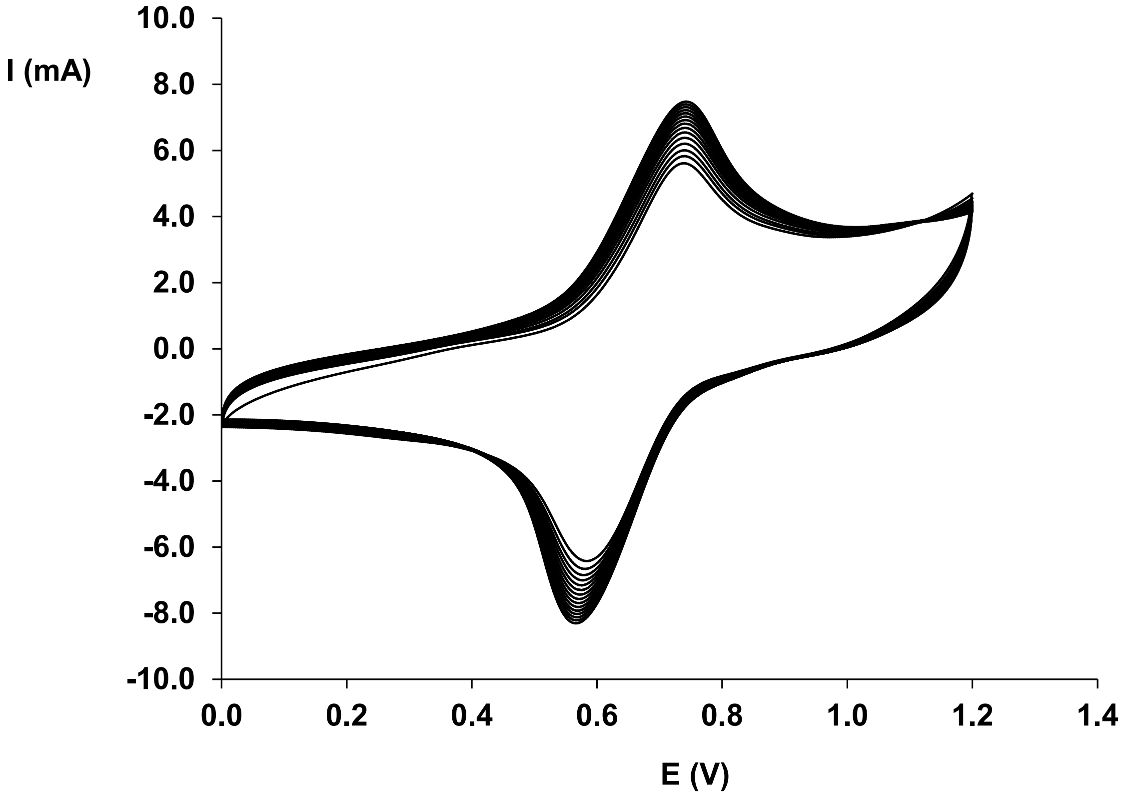


Figure S 8. (a) Growing of a **C/poly-3** film in CH_2Cl_2 + 0.1 M TBAH at a glassy carbon disk electrode (diameter = 3 mm) by scanning the potential between 0 and 1.3 V throughout 30 cycles (scan rate = 100 mV s^{-1}). (b) Cyclic voltammograms registered after transferring the **C/poly-3** modified electrode into a blank electrolyte solution (5 cycles were registered; final amount of anchored complex = $4.36 \cdot 10^{-10}$ mols·cm^{-2}).

(a)



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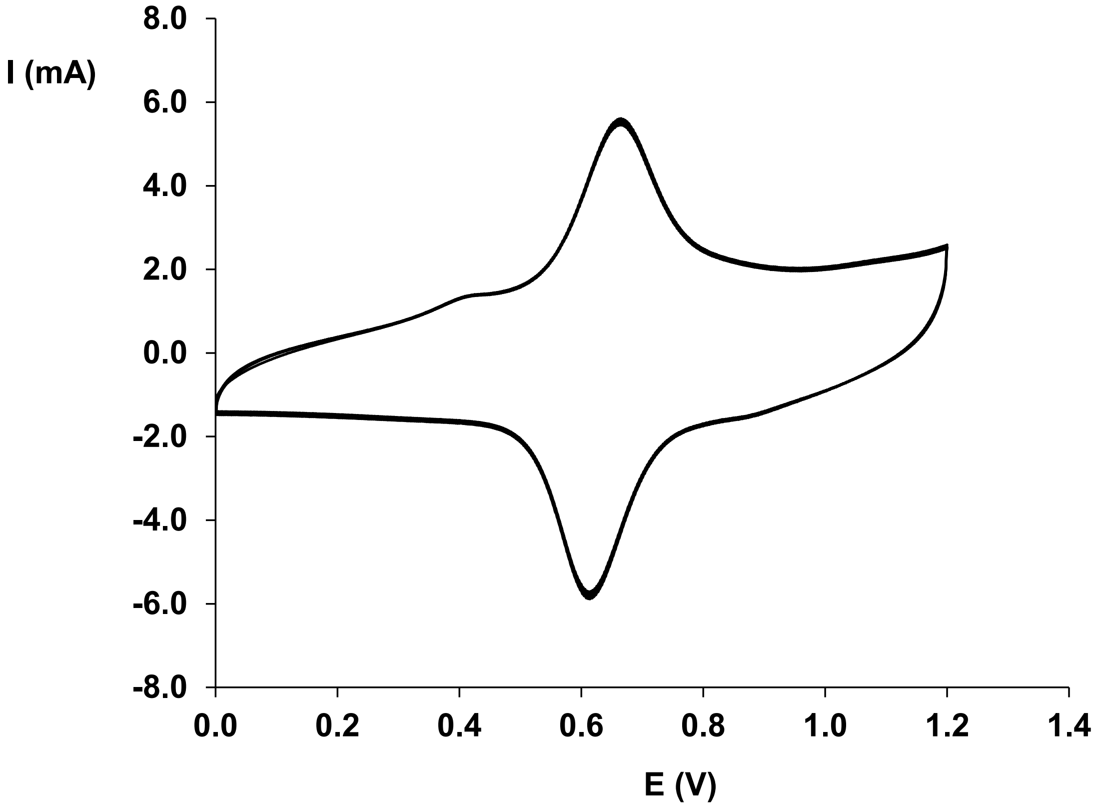
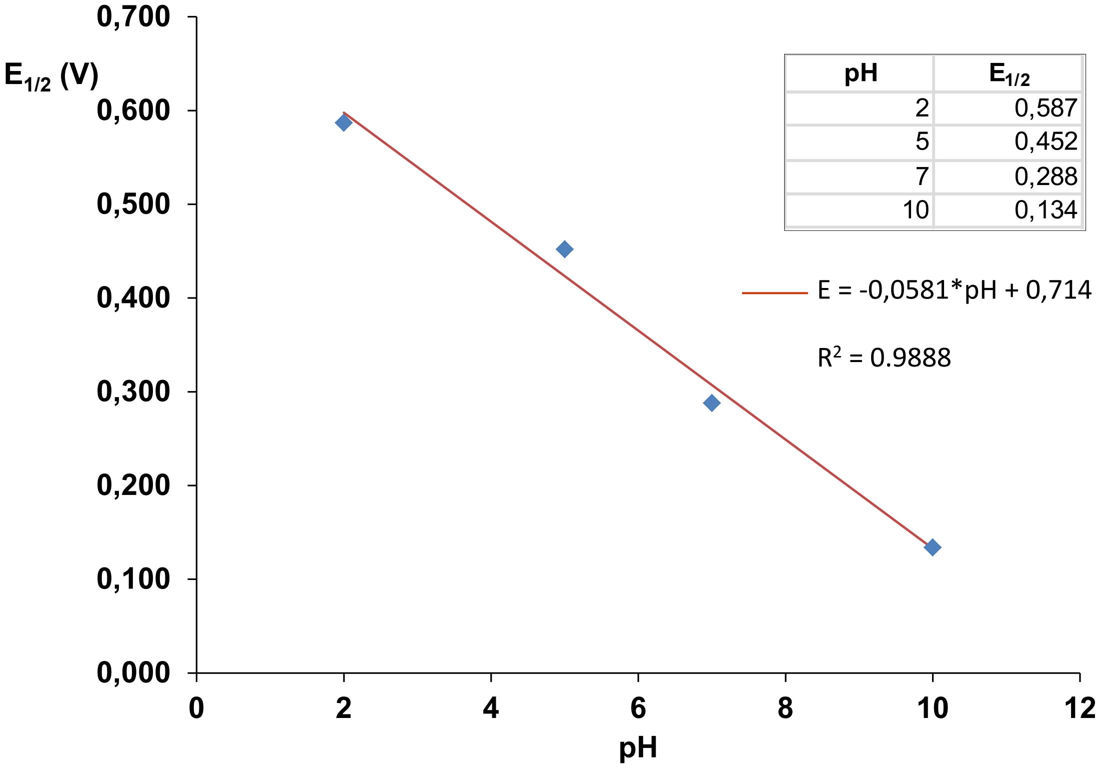


Figure S 9. Linear regression of $E_{1/2}$ values vs. pH for the cyclic voltammograms of complex **4** registered in aqueous media.



pH	$E_{1/2}$
2	0,587
5	0,452
7	0,288
10	0,134