

Synthesis and characterization of a series of ruthenium tris(β -diketonato) complexes with UHV-STM investigation and numerical calculations

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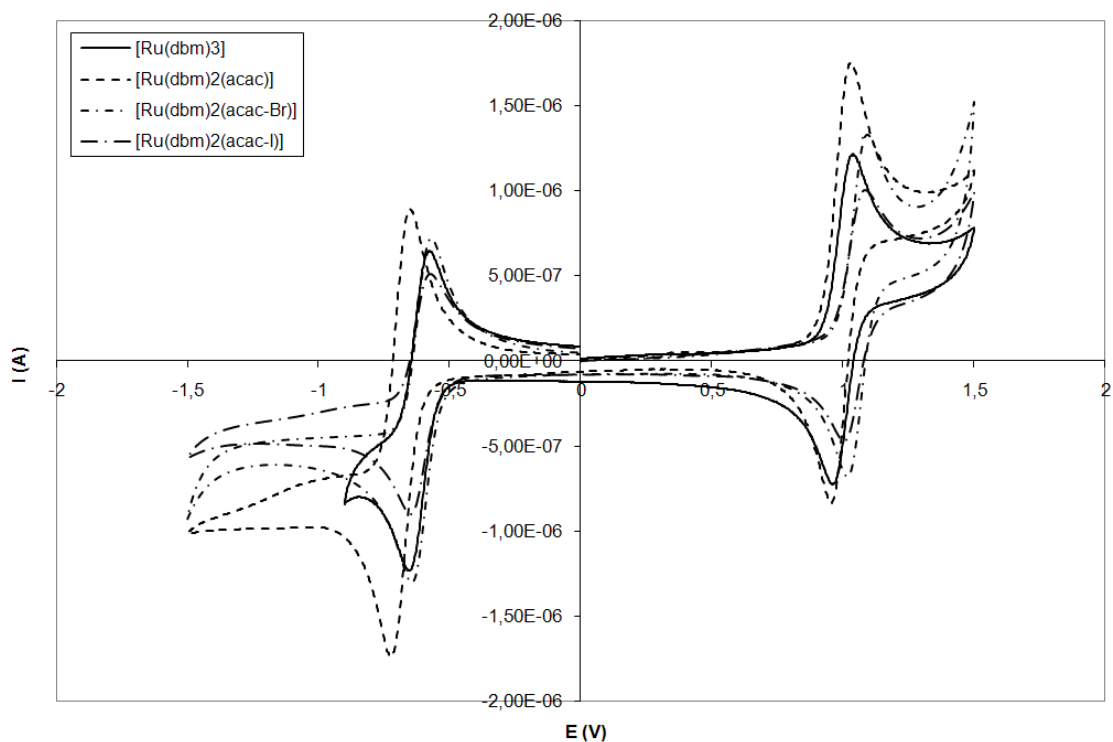


Figure S1. Cyclic Voltammetry of **1**, **2**, **5** and **6** (CH_2Cl_2 , 0.1 M TBAH, $0.1 \text{ V}\cdot\text{s}^{-1}$)

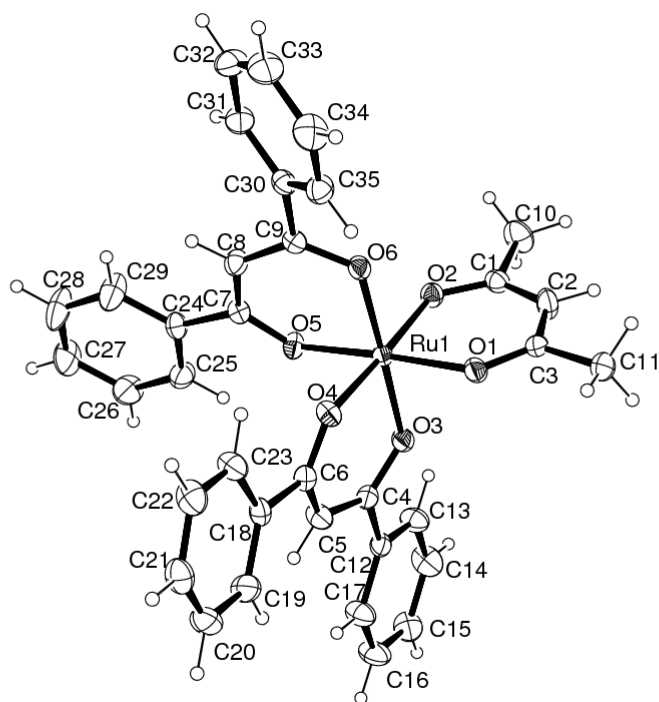


Figure S2. ORTEP drawing of $[\text{Ru}(\text{dbm})_2(\text{acac})]$ (**2**) (30% of probability thermal ellipsoids)

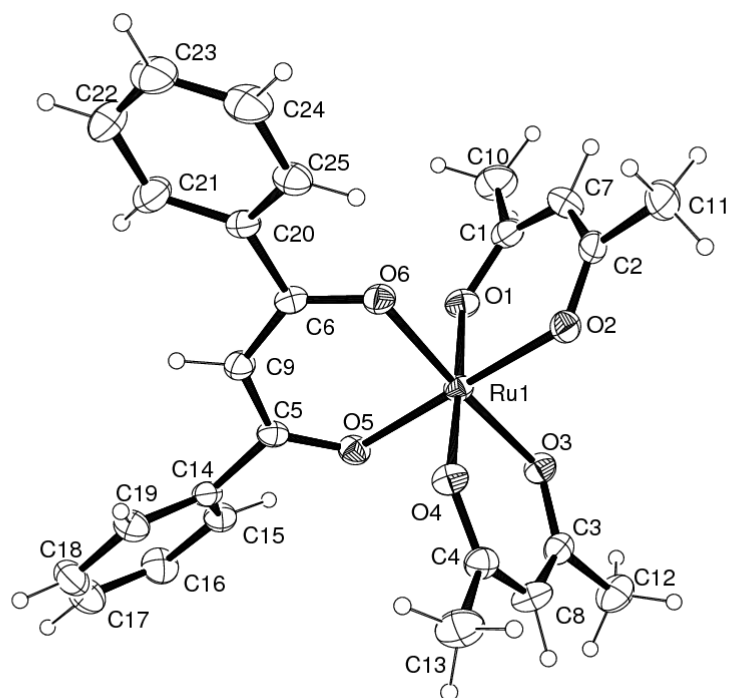


Figure S3. ORTEP drawing of $[\text{Ru}(\text{dbm})(\text{acac})_2]$ (**3**) (30% of probability thermal ellipsoids)

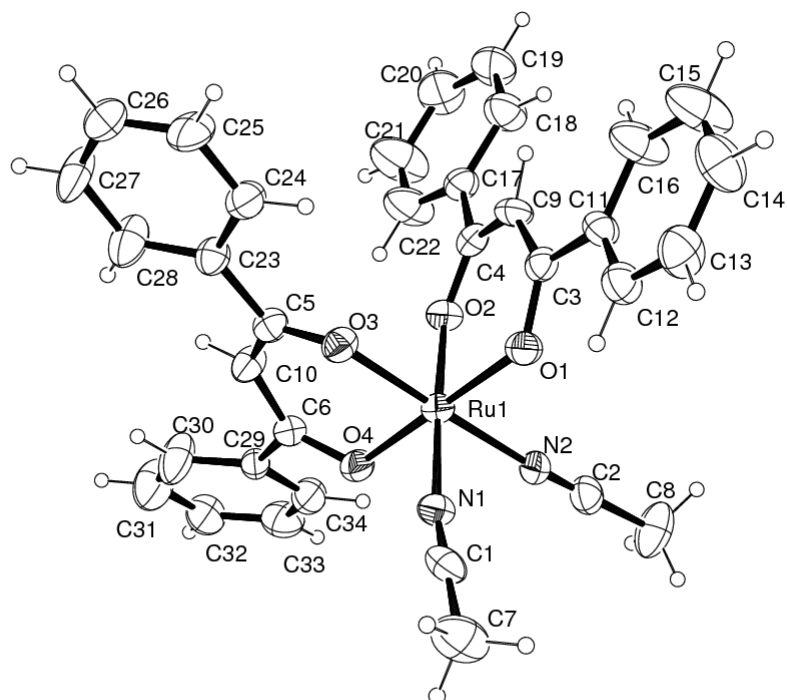


Figure S4. ORTEP drawing of the $[\text{Ru}(\text{dbm})_2(\text{CH}_3\text{CN})_2]\text{CF}_3\text{SO}_3$ (**4**) (the counter anion has been omitted for the sake of clarity, 30% of probability thermal ellipsoids).

Table S1

Crystallographic data for **1-4, 6**

	1	2	3	4	6
Empirical Formula	C ₄₅ H ₃₃ O ₆ Ru	C ₃₅ H ₂₉ O ₆ Ru	C ₂₅ H ₂₅ O ₆ Ru	C ₃₅ H ₂₈ F ₃ N ₂ RuS	C ₃₅ H ₂₈ O ₆ BrRu
Formula Weight	770.78	646.65	522.52	778.72	725.55
Wavelength (Å)	0.71073				
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P21/c$	$P21/c$	$P21/n$
<i>a</i> (Å)	10.40340(10)	10.2725(2)	14.438(0)	17.3990(0)	9.9050(0)
<i>b</i> (Å)	11.6813(11)	11.0561(10)	8.379(0)	13.1420(0)	18.0420(0)
<i>c</i> (Å)	16.3554(13)	14.3319(12)	20.3080(0)	16.2060(0)	17.2670(0)
α (°)	108.794(7)	94.261(7)	90.000(0)	90.000(0)	90.000(0)
β (°)	96.491(3)	91.932(4)	108.095(0)	110.154(0)	95.577(0)
γ (°)	101.502(4)	112.794(4)	90.000(0)	90.000(0)	90.000(0)
Volume (Å ³)	1809.8(2)	1493.00(30)	2335.28(0)	3478.7(0)	3071.11(0)
<i>Z</i>	2	2	4	4	4
<i>D</i> _{calc} (Mg/m ³)	1.414	1.438	1.486	1.487	1.569
μ (MoK α) (mm ⁻¹)	0.483	0.570	0.709	0.576	1.857
<i>F</i> (000)	790	661.9	1067.9	1579.8	1459.8
Crystal size (mm)	0.778 × 0.224 × 0.094	0.364 × 0.228 × 0.186	0.541 × 0.187 × 0.210	0.384 × 0.235 × 0.305	0.159 × 0.283 × 0.134
θ Range for data collection (°)	5.57-31.98	5.52-32	5.54-30	5.52-28.46	5.57-27.49
Limiting indices	-13 ≤ <i>h</i> ≤ 13	-15 ≤ <i>h</i> ≤ 15	-20 ≤ <i>h</i> ≤ 19	-19 ≤ <i>h</i> ≤ 20	-11 ≤ <i>h</i> ≤ 12
	-17 ≤ <i>k</i> ≤ 15	-16 ≤ <i>k</i> ≤ 16	-11 ≤ <i>k</i> ≤ 11	-16 ≤ <i>k</i> ≤ 13	-22 ≤ <i>k</i> ≤ 22
	-23 ≤ <i>l</i> ≤ 24	-21 ≤ <i>l</i> ≤ 21	-28 ≤ <i>l</i> ≤ 28	-18 ≤ <i>l</i> ≤ 17	-22 ≤ <i>l</i> ≤ 20
Reflections (observed/unique)	59103/13868	53319/11750	52853/9262	59094/17478	69553/10537
Refinement method	Full-matrix least-squares on F ²				
Data/parameters	8170/469	9713/405	6398/314	4155/480	6288/444
Goodness of fit on F ²	1.228	1.183	1.197	1.159	1.196
Final R indices	R ₁ =0.0522, wR ₂ =0.0872	R ₁ =0.0409, wR ₂ =0.0886	R ₁ =0.0379, wR ₂ =0.0874	R ₁ =0.0467, wR ₂ =0.109	R ₁ =0.0680, wR ₂ =0.1152
	[<i>I</i> > 2σ(<i>I</i>)]	[<i>I</i> > 2σ(<i>I</i>)]	[<i>I</i> > 2σ(<i>I</i>)]	[<i>I</i> > 2σ(<i>I</i>)]	[<i>I</i> > 2σ(<i>I</i>)]
Largest difference in peak and hole (e Å ⁻³)	0.883 and -0.513	0.80 and -0.59	0.649 and -1.059	0.672 and -0.407	1.03 and -0.7

Table S2. Selected bond lengths (Å) with estimated standard deviations in parentheses

1

Ru(1) - O(1)	1.995(3)
Ru(1) - O(2)	2.005(2)
Ru(1) - O(3)	2.019(3)
Ru(1) - O(4)	2.029(3)
Ru(1) - O(5)	2.010(2)
Ru(1) - O(6)	2.008(3)

2

Ru(1)- O(1)	2.027(2)
Ru(1) - O(2)	2.032(2)
Ru(1)- O(3)	2.005(2)
Ru(1)- O(4)	2.001(2)
Ru(1) - O(5)	2.000(2)
Ru(1) - O(6)	2.011(2)

3

Ru(1) - O(1)	2.007(3)
Ru(1) - O(2)	2.019(2)
Ru(1) - O(3)	2.019(2)
Ru(1) - O(4)	2.013(2)
Ru(1) - O(5)	2.017(2)
Ru(1) - O(6)	2.009(2)

4

Ru(1) - O(1)	1.992(4)
Ru(1) - O(2)	1.980(4)
Ru(1) - O(3)	1.982(4)
Ru(1) - O(4)	1.994(5)
Ru(1) - N(1)	2.050(6)
Ru(1) - N(2)	2.031(6)

6

Ru(1) - O(1)	2.010(4)
Ru(1) - O(2)	2.017(4)
Ru(1) - O(3)	2.008(4)
Ru(1) - O(4)	1.986(4)
Ru(1) - O(5)	1.984(4)
Ru(1) - O(6)	2.006(4)

Table S3. Selected bond angles (°) with estimated deviations in parentheses

1

O(1)-Ru(1)-O(3)	89.0(1)	O(1)-Ru(1)-O(4)	177.7(1)
O(1)-Ru(1)-O(5)	86.6(1)	O(1)-Ru(1)-O(6)	88.9(1)
O(2)-Ru(1)-O(3)	91.1(1)	O(2)-Ru(1)-O(4)	89.3(1)
O(2)-Ru(1)-O(5)	177.8(1)	O(2)-Ru(1)-O(6)	90.1(1)
O(3)-Ru(1)-O(4)	91.5(1)	O(3)-Ru(1)-O(5)	86.7(1)
O(3)-Ru(1)-O(6)	177.5(1)	O(4)-Ru(1)-O(5)	91.2(1)
O(4)-Ru(1)-O(6)	90.6(1)	O(5)-Ru(1)-O(6)	92.0(1)
O(1)-Ru(1)-O(2)	92.9(1)		

2

O(1)-Ru(1)-O(3)	90.8(1)	O(1)-Ru(1)-O(4)	89.2(1)
O(1)-Ru(1)-O(5)	177.3(1)	O(1)-Ru(1)-O(6)	89.8(1)
O(2)-Ru(1)-O(3)	89.8(1)	O(2)-Ru(1)-O(4)	177.6(1)
O(2)-Ru(1)-O(5)	89.8(1)	O(2)-Ru(1)-O(6)	91.5(1)
O(3)-Ru(1)-O(4)	92.3(1)	O(3)-Ru(1)-O(5)	87.3(1)
O(3)-Ru(1)-O(6)	178.6(1)	O(4)-Ru(1)-O(5)	89.0(1)
O(4)-Ru(1)-O(6)	86.4(1)	O(5)-Ru(1)-O(6)	92.1(1)
O(1)-Ru(1)-O(2)	92.0(1)		

3

O(1)-Ru(1)-O(3)	88.7(1)	O(1)-Ru(1)-O(4)	178.2(1)
O(1)-Ru(1)-O(5)	90.1(1)	O(1)-Ru(1)-O(6)	89.6(1)
O(2)-Ru(1)-O(3)	92.2(1)	O(2)-Ru(1)-O(4)	88.5(1)

O(2)-Ru(1)-O(5)	176.8(1)	O(2)-Ru(1)-O(6)	85.0(1)
O(3)-Ru(1)-O(4)	92.4(1)	O(3)-Ru(1)-O(5)	89.1(1)
O(3)-Ru(1)-O(6)	176.7(1)	O(4)-Ru(1)-O(5)	88.5(1)
O(4)-Ru(1)-O(6)	89.4(1)	O(5)-Ru(1)-O(6)	93.8(1)
O(1)-Ru(1)-O(2)	92.9(1)		

4

O(1)-Ru(1)-O(3)	89.8(2)	O(1)-Ru(1)-O(4)	179.4(2)
O(1)-Ru(1)-N(1)	86.3(2)	O(1)-Ru(1)-N(2)	90.0(2)
O(2)-Ru(1)-O(3)	88.5(2)	O(2)-Ru(1)-O(4)	88.2(2)
O(2)-Ru(1)-N(1)	177.5(2)	O(2)-Ru(1)-N(2)	89.7(2)
O(3)-Ru(1)-O(4)	90.8(2)	O(3)-Ru(1)-N(1)	92.9(2)
O(3)-Ru(1)-N(2)	178.2(2)	O(4)-Ru(1)-N(1)	93.8(2)
O(4)-Ru(1)-N(2)	89.4(2)	N(1)-Ru(1)-N(2)	88.8(3)
O(1)-Ru(1)-O(2)	91.7(2)		

6

O(1)-Ru(1)-O(3)	87.9(2)	O(1)-Ru(1)-O(4)	178.6(2)
O(1)-Ru(1)-O(5)	91.1(2)	O(1)-Ru(1)-O(6)	90.5(2)
O(2)-Ru(1)-O(3)	92.5(2)	O(2)-Ru(1)-O(4)	91.0(2)
O(2)-Ru(1)-O(5)	178.4(2)	O(2)-Ru(1)-O(6)	87.2(2)
O(3)-Ru(1)-O(4)	92.4(2)	O(3)-Ru(1)-O(5)	88.0(2)
O(3)-Ru(1)-O(6)	178.3(2)	O(4)-Ru(1)-O(5)	87.5(2)
O(4)-Ru(1)-O(6)	89.3(2)	O(5)-Ru(1)-O(6)	92.3(2)
O(1)-Ru(1)-O(2)	90.4(2)		

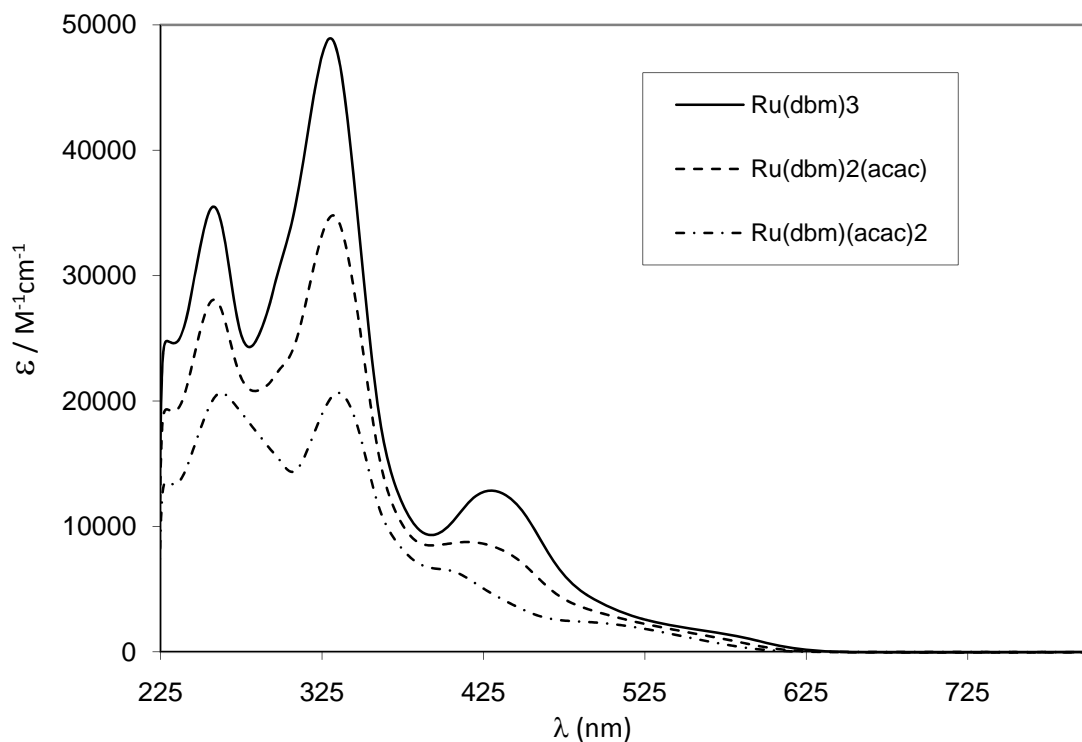


Figure S5. UV-Vis spectra of complexes **1-3** in CH_2Cl_2 .

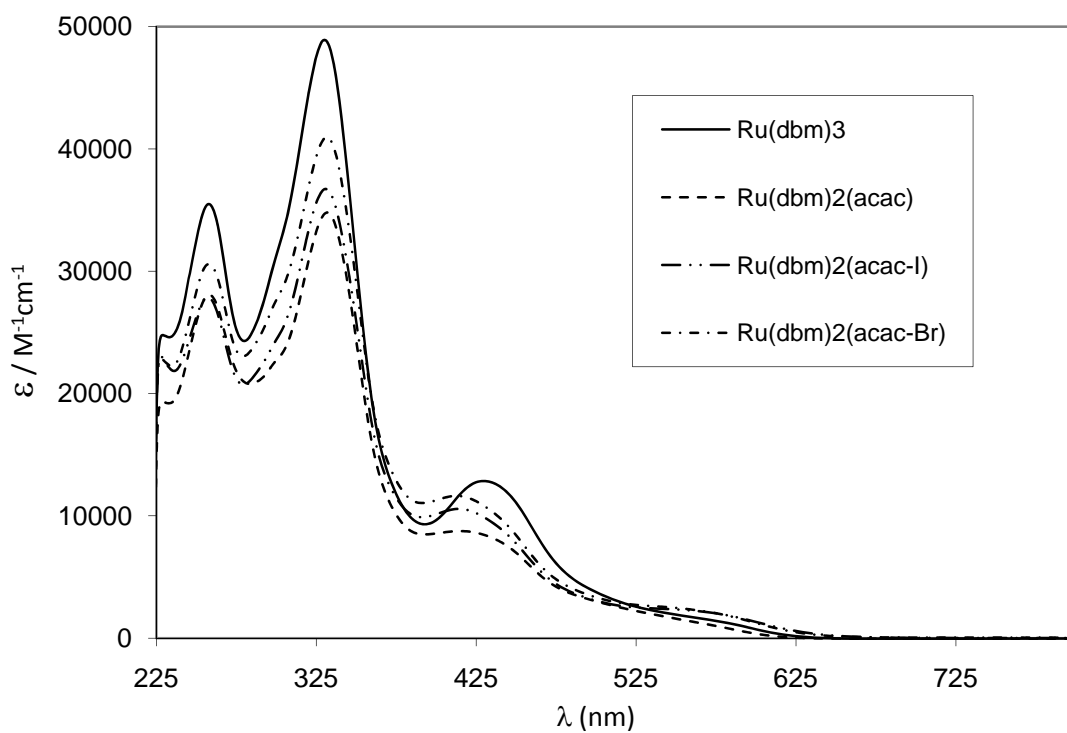


Figure S6. UV-Vis spectra of complexes **1,2,5,6** in CH_2Cl_2 .

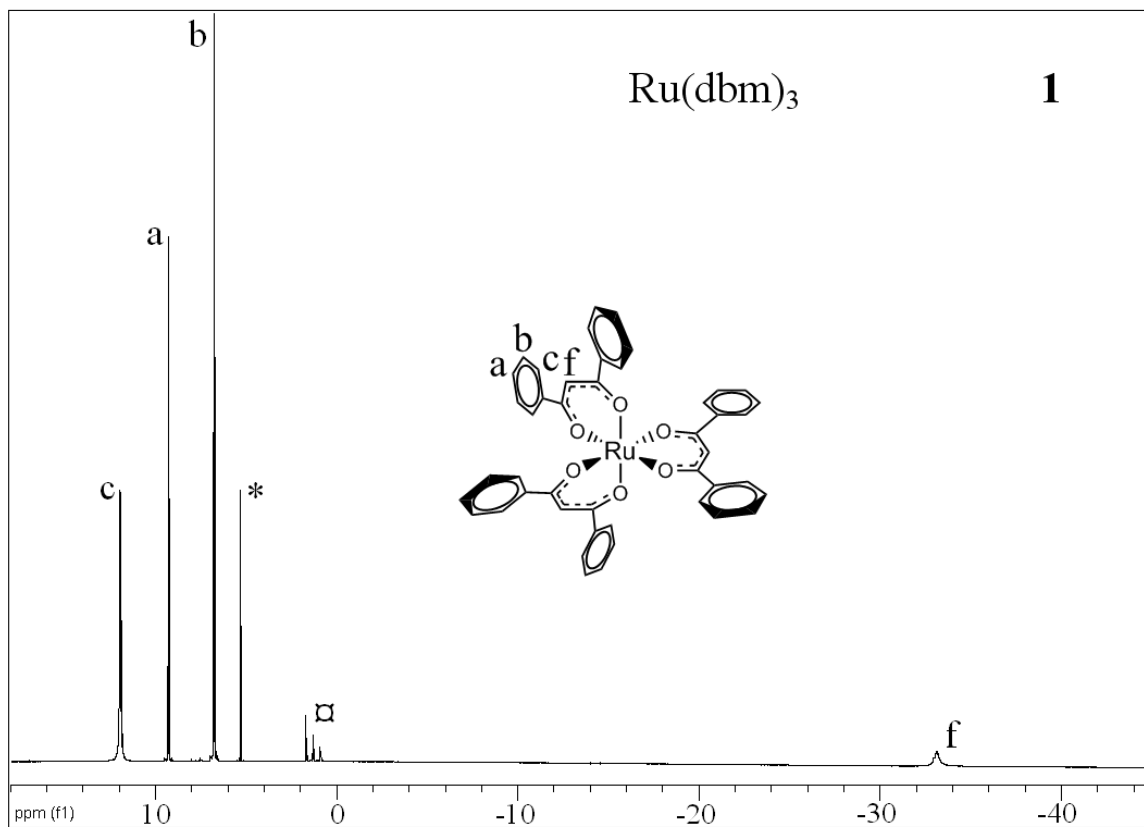


Figure S7. ^1H NMR spectrum of complex **1** in CD_2Cl_2

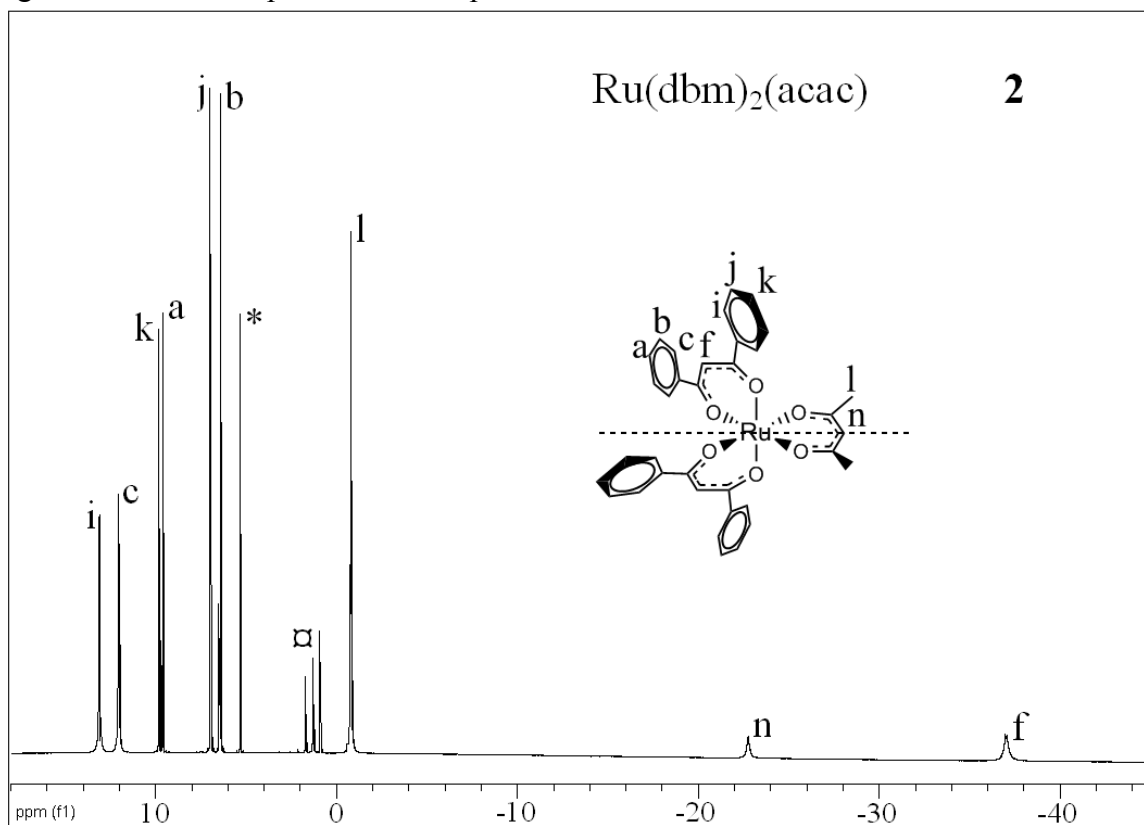


Figure S8. ^1H NMR spectrum of complex **2** in CD_2Cl_2

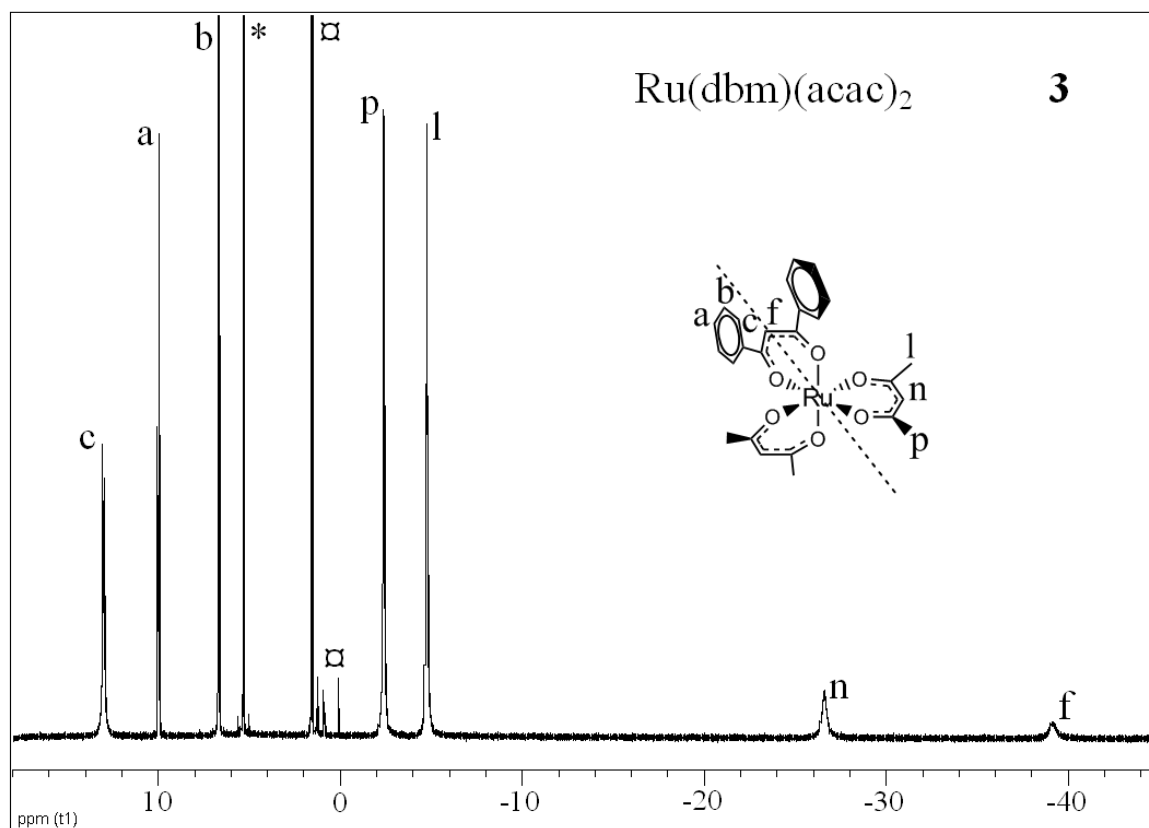


Figure S9. ¹H NMR spectrum of complex **3** in CD₂Cl₂

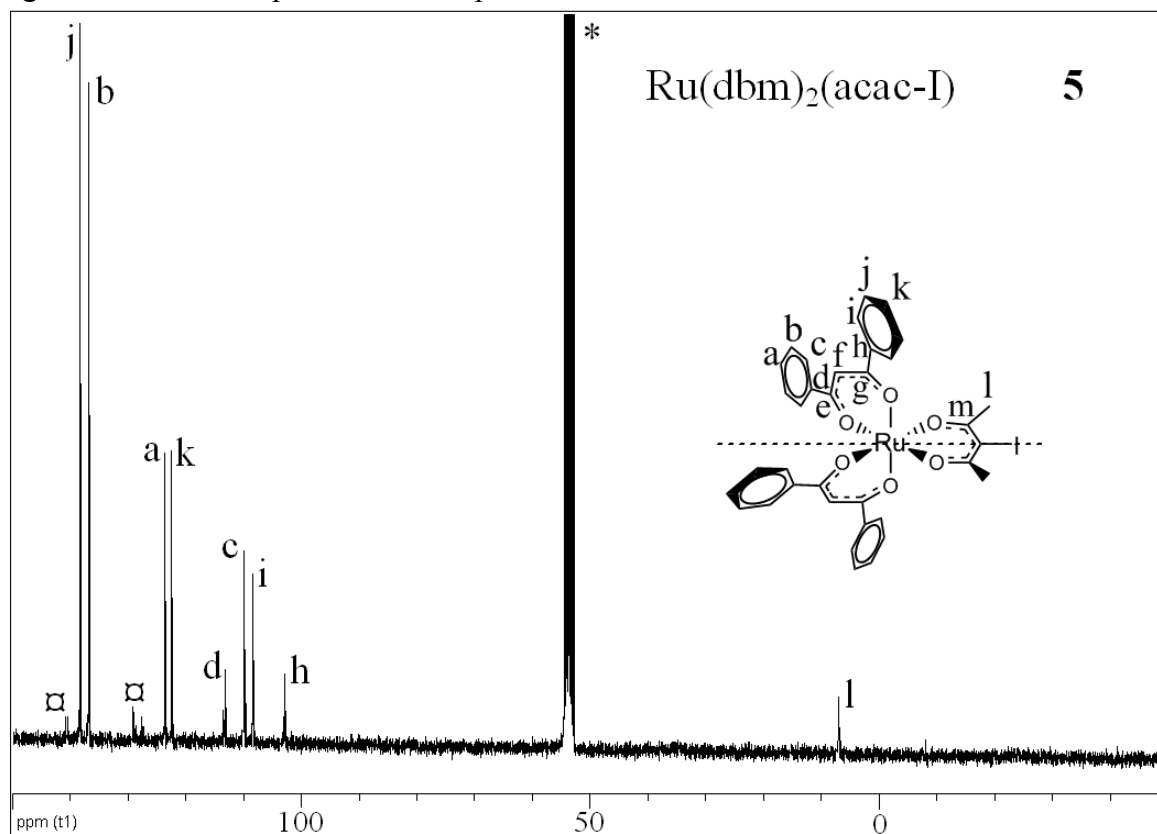


Figure S10. ¹H NMR spectrum of complex **5** in CD₂Cl₂

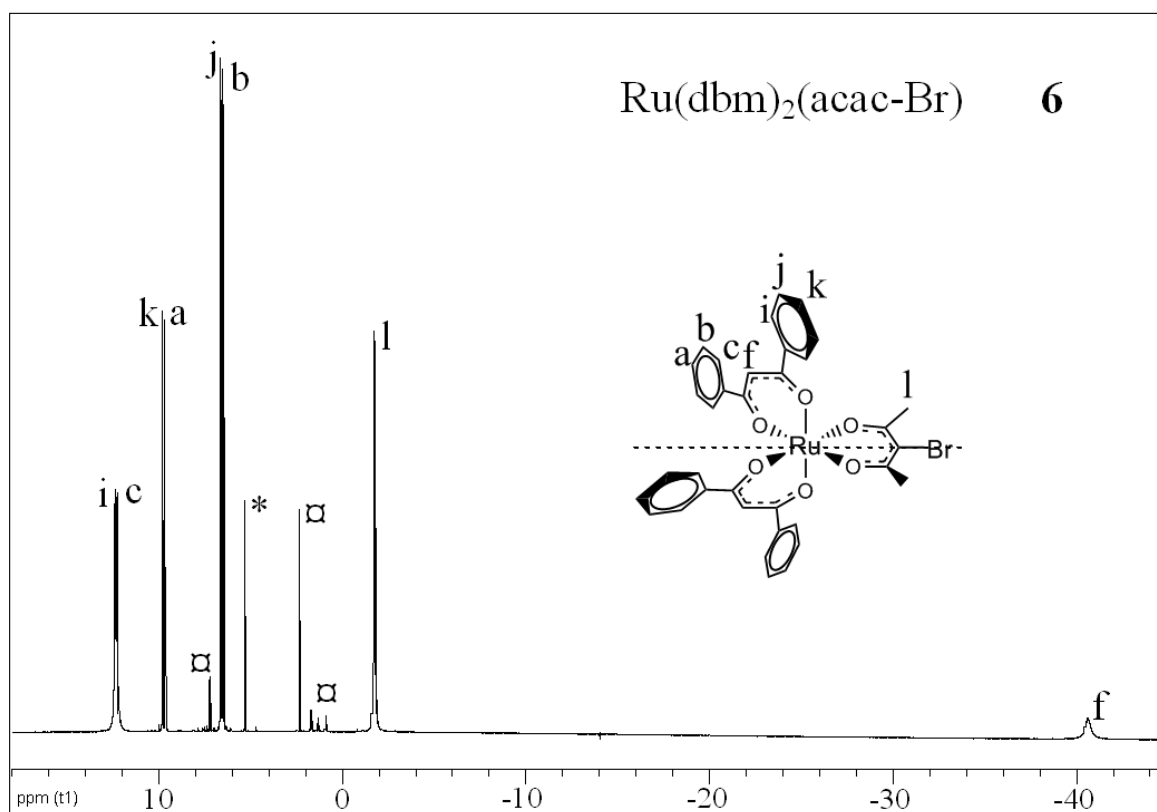


Figure S11. ¹H NMR spectrum of complex **6** in CD₂Cl₂

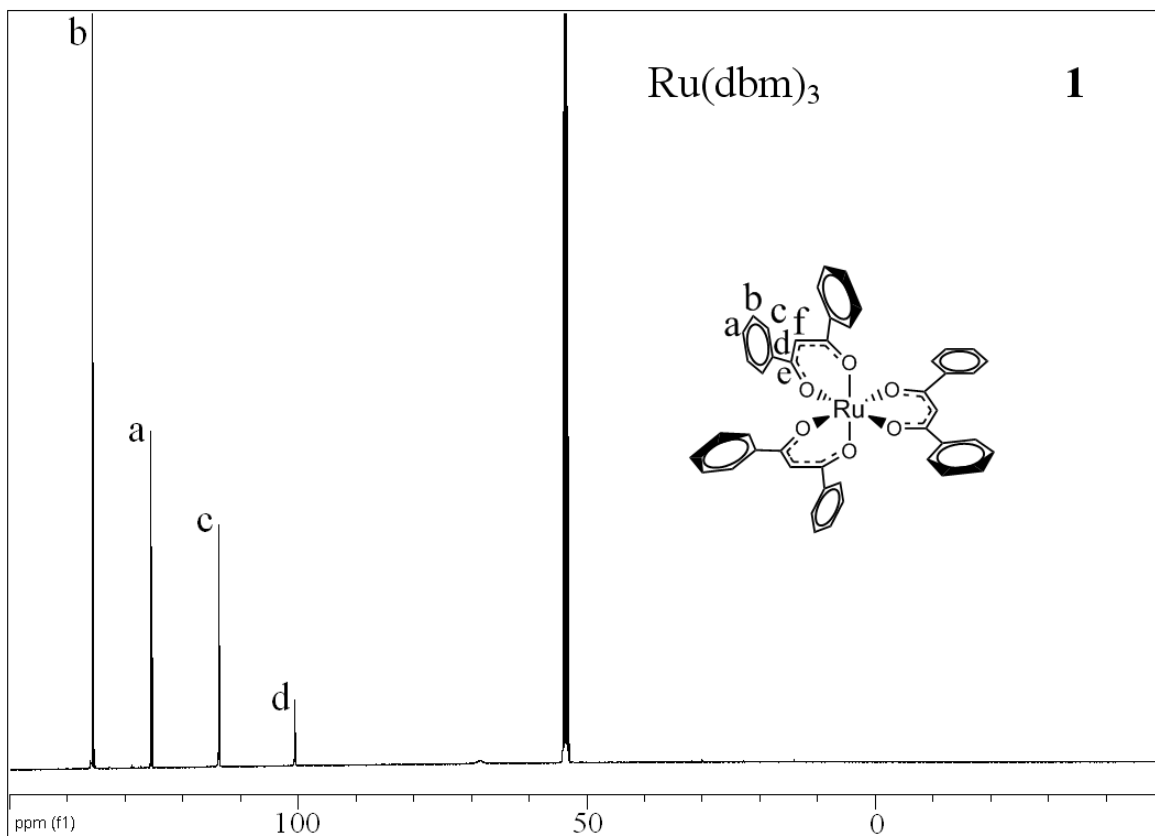


Figure S12. ^{13}C NMR spectrum of complex **1** in CD_2Cl_2

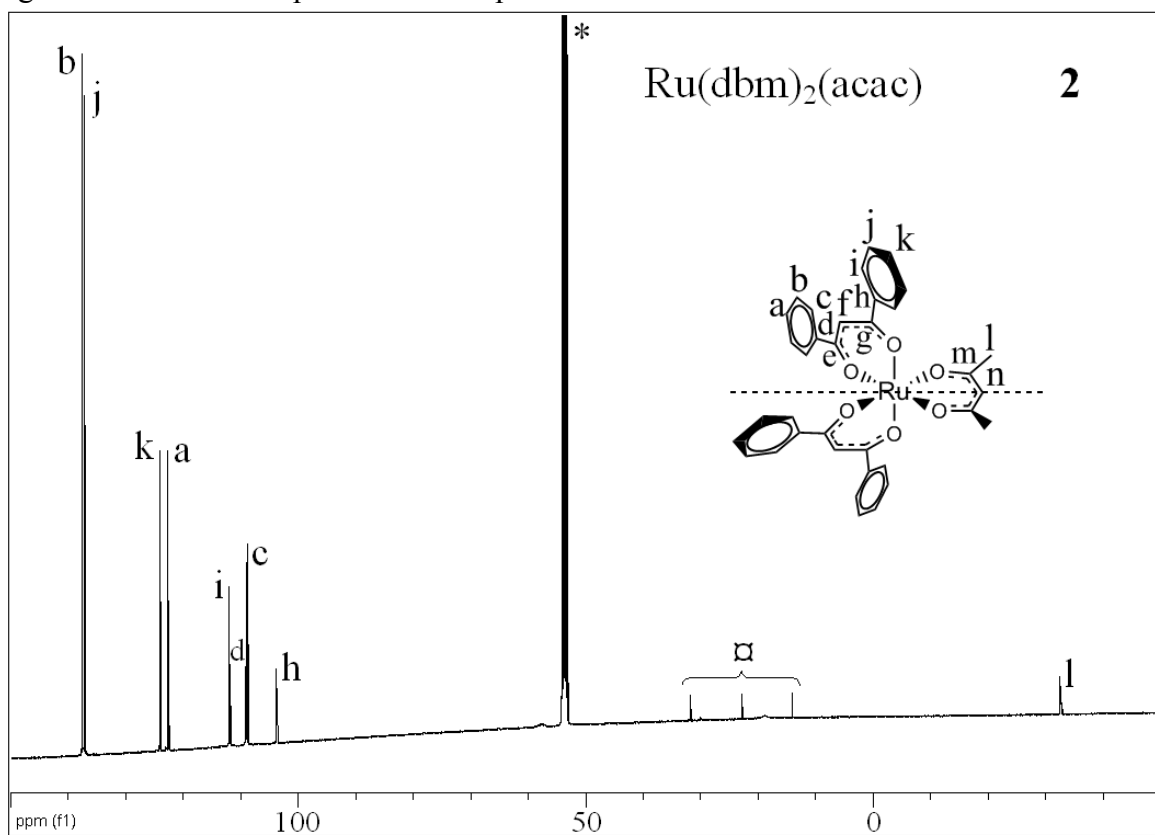


Figure S13. ^{13}C NMR spectrum of complex **2** in CD_2Cl_2

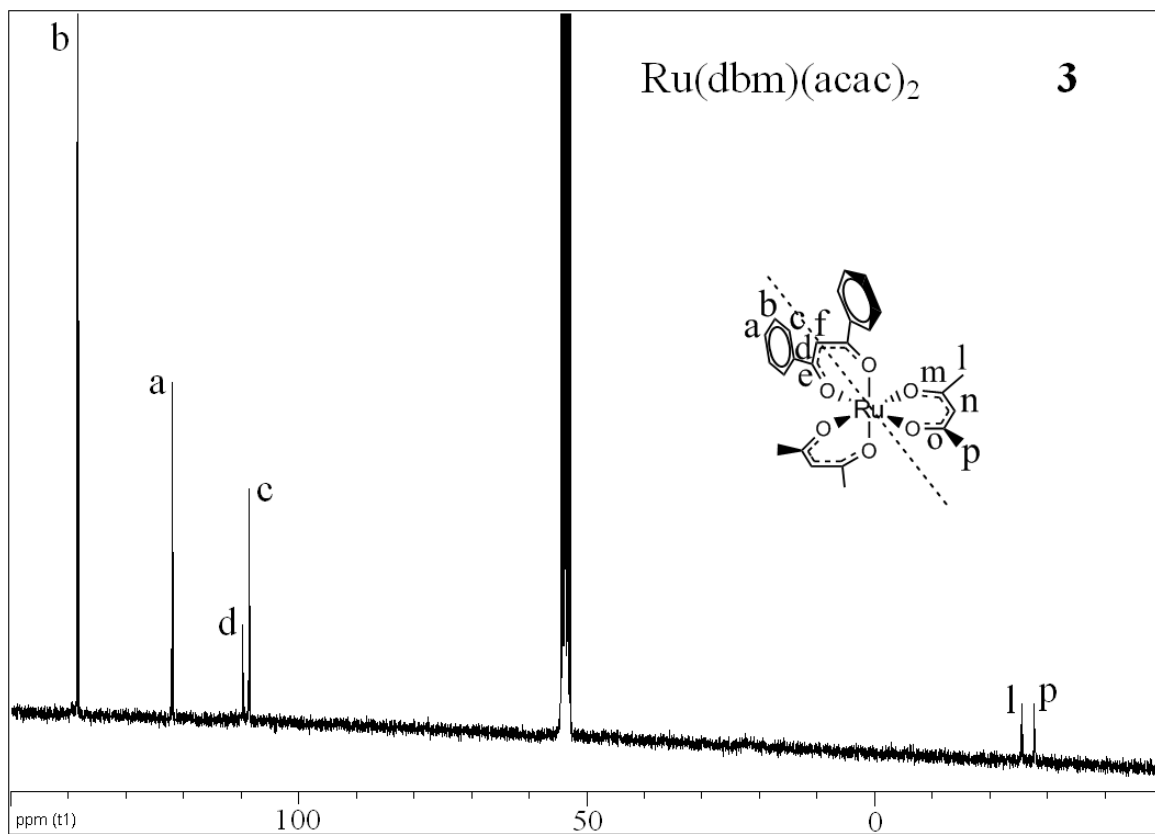


Figure S14. ¹³C NMR spectrum of complex **3** in CD₂Cl₂

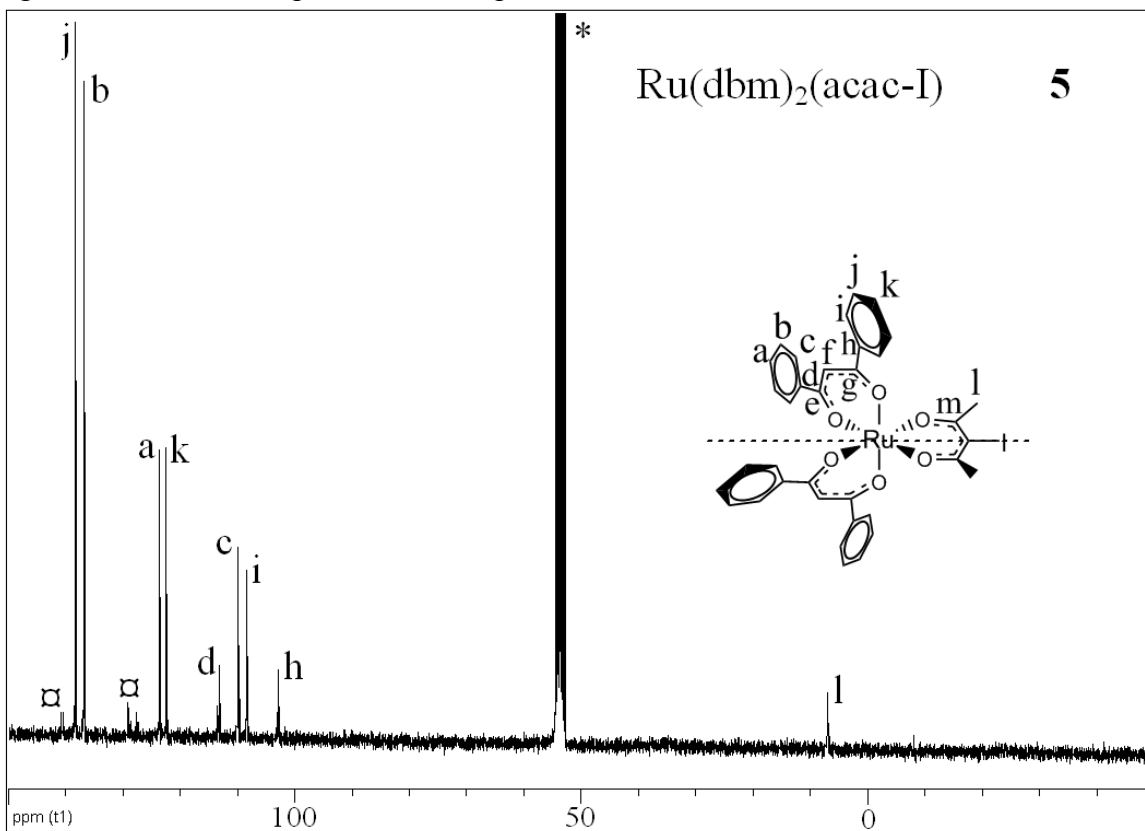


Figure S15. ¹³C NMR spectrum of complex **5** in CD₂Cl₂

