Revised om-2012-0024ly

Supporting Informations

for

A Comparative Study on *ortho*-C-H *vs. ortho*-C-X (X = C, Cl, S) Bond Activation in *ortho*-$C_{aromatic}$-N bond fusion in Substituted Anilines Using Ruthenium(II) Mediators: Isolation and Characterization of Unusual Ru_2-Complexes

Sutanuva Mandal,[†] Subhas Samanta,[†] Tapan K. Mondal[‡] and Sreebrata Goswami[†,*]

[†] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India.

[‡]Department of Chemistry, Jadavpur University, Kolkata, 700032, India

E-mail: icsg@iacs.res.in

	TABLE OF CONTENTS	Page Number
	LIST OF TABLES	
Table S1	Optimization energies of the complexes **1** and **2** in different electronic configurations	4
Table S2	The bond distances (in Å) obtained at the B3LYP/SDD level optimized geometry of compounds **1**, [**1**]$^-$ and [**1**]$^+$	4
Table S3	The bond distances (in Å) obtained at the B3LYP/sdd level optimized geometry of compounds **2**, [**2**]$^-$ and [**2**]$^+$	5
Table S4	Some Selected Molecular Orbitals along with their energies and compositions of compound **1** in gas phase B3LYP/SDD level calculation	6
Table S5	Some Selected Molecular Orbitals along with their energies and compositions of compound **2** in gas phase B3LYP/SDD level calculation	7
Table S6	Selected list of vertical excitations computed at the TD-DFT/B3LYP/SDD level of theory for **1**	8
Table S7	Selected list of vertical excitations computed at the TD-DFT/B3LYP/SDD level of theory for **2**	8
Table S8	The bond distances (in Å) obtained at the B3LYP/SDD level optimized geometry of compound [**6**]$^{2+}$ in native state	9
Table S9	Some Selected Molecular Orbitals along with their energies and compositions of compound [**6**]$^{2+}$ in gas phase B3LYP/SDD level calculation	10
Table S10	Selected list of vertical excitations computed at the TD-DFT/B3LYP/SDD level of theory for [**6**]$^{2+}$	11
	LIST OF FIGURES	
Figures S1 - S6	ESI-MS spectra of the compounds, **1** - [**6**]Cl_2. Inset: simulated isotopic pattern	12 - 18
Figures S7 - S12	^{1}H NMR spectra of the compounds, **1** - [**6**]Cl_2.	19 - 24
Figure S13	ESI-MS spectrum of the compound [**7**]Cl. Inset: simulated isotopic pattern	25
Figure S14	^{1}H NMR spectrum of the compound [**7**]Cl.	26

Figure S15	ORTEP and atom numbering scheme of the compound **8**.	27
Figure S16	ESI-MS spectrum of the compound [**9**]Cl_2. Inset: simulated isotopic pattern	28
Figure S17	^{1}H NMR spectrum of the compound [**9**]Cl_2.	29
Figure S18	Cyclic voltammogram of complex [**6**]Cl_2 in CH_3CN/0.1 M NEt_4ClO_4.	30

Table S1. Optimization energies (a.u.) of the complexes **1** and **2** in different electronic configurations

Configuration	Complex **1**	Complex **2**
E (Singlet)	-1321.22015744	-2990.63077632
E(Triplet)	-1321.19661497	-2990.60661859
E (BS, singlet)	-1321.21940001	**-**

Table S2. The bond distances (Å) obtained at the B3LYP/SDD level optimized geometry of compounds [**1**], [**1**]$^-$ and [**1**]$^+$

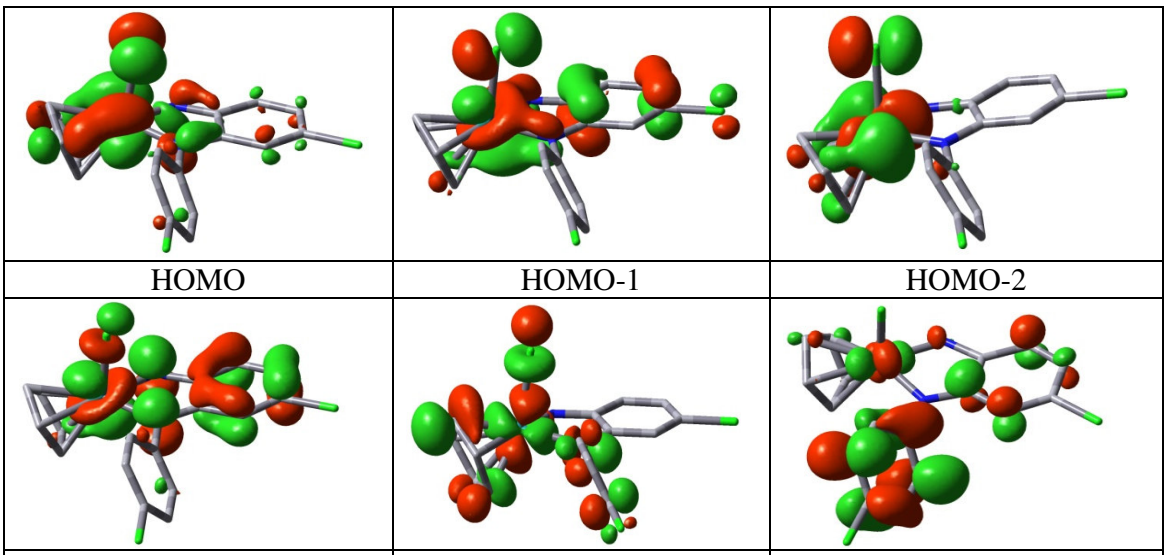
Bond Parameters	[**1**]		[**1**]$^-$ Calculated	[**1**]$^+$ Calculated
	Experimental	Calculated		
Ru1-N11	1.987(4)	2.011	2.040	1.987
Ru1-N18	2.029(4)	2.038	2.109	2.031
C12-C13	1.418(5)	1.420	1.415	1.420
C12-C17	1.443(6)	1.442	1.424	1.443
C13-C14	1.373(6)	1.373	1.390	1.372
C14-C15	1.488(6)	1.422	1.405	1.424
C15-C16	1.323(6)	1.374	1.393	1.374
C16-C17	1.376(6)	1.424	1.413	1.421
C12-N11	1.328(6)	1.334	1.353	1.334
C17-N18	1.418(6)	1.349	1.369	1.347
C19-N18	1.391(6)	1.422	1.396	1.417
N11-Ru1-N18	77.54(17)	76.29	75.59	76.91

Table S3. The bond distances (Å) obtained at the B3LYP/SDD level optimized geometry of compounds [**2**], [**2**]$^+$ and [**2**]$^-$

Bond parameters	[**2**]		[**2**]$^+$ Calculated	[**2**]$^-$ Calculated
	Experimental	Calculated		
Ru1-Ru2	2.683(8)	2.689	2.673	2.942
Ru1-N1	2.067(4)	2.093	2.097	2.158
Ru1-N2	2.063(5)	2.091	2.091	2.153
Ru1-Cl3	2.397(17)	2.419	2.355	2.477
Ru2-N1	2.068(4)	2.098	2.092	2.149
Ru2-N2	2.051(4)	2.091	2.098	2.161
Ru2-Cl4	2.399(19)	2.419	2.354	2.475
N1-C1	1.430(9)	1.417	1.420	1.397
N2-C7	1.419(8)	1.418	1.420	1.396
Ru1-N1-Ru2	80.91(17)	79.86	79.29	86.18
Ru1-N2-Ru2	81.41(14)	80.05	79.29	86.02
N1-Ru1-N2	81.99(19)	81.77	81.44	80.72
N1-Ru1-Cl3	84.52(13)	83.94	83.97	83.73
N1-Ru2-N2	82.25(18)	81.87	81.39	80.72
N1-Ru2-Cl4	83.52(15)	84.47	85.22	84.38

Table S4. Some Selected Molecular Orbitals along with their energies and compositions of compound [**1**] in gas phase B3LYP/SDD level calculation

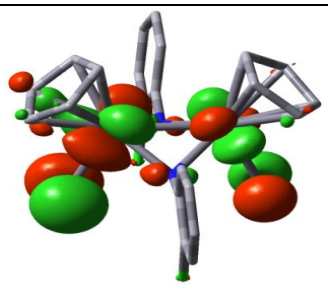
MO	Energy, eV	% of composition			
		Ru	L^{2a}	Cp	Cl
LUMO+5	-0.18	27	65	08	0
LUMO+4	-0.30	79	19	02	0
LUMO+3	-0.65	12	82	05	01
LUMO+2	-0.72	12	81	06	01
LUMO+1	-1.09	43	22	26	09
LUMO	-3.10	28	62	04	06
HOMO	-5.28	53	16	14	17
HOMO-1	-5.92	38	41	05	16
HOMO-2	-6.23	72	05	09	14
HOMO-3	-5.52	02	73	02	23
HOMO-4	-6.86	05	61	12	22
HOMO-5	-7.14	17	37	12	34
HOMO-6	-7.46	04	76	03	17
HOMO-7	-7.62	11	41	12	36
HOMO-8	-7.97	21	33	45	01
HOMO-9	-8.29	15	27	31	27
HOMO-10	-8.63	22	40	03	35

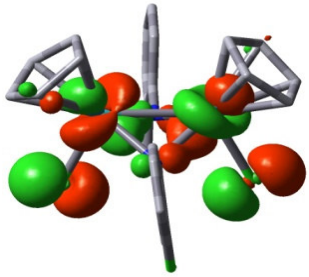


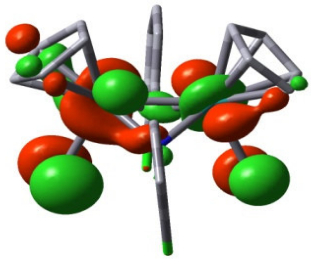
Contour plots of some selected MOs of [**1**] in native state

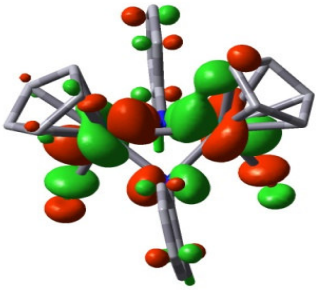
Table S5. Some Selected Molecular Orbitals along with their energies and compositions of compound [**2**] in gas phase B3LYP/SDD level calculation

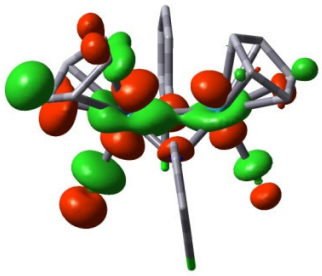
MO	Energy, eV	% of composition			
		Ru	Cp	$(L^{1a})^-$	Cl
LUMO+5	-0.49	11	03	86	0
LUMO+4	-0.55	54	24	22	0
LUMO+3	-1.41	38	18	44	0
LUMO+2	-1.50	58	28	02	12
LUMO+1	-1.70	51	28	06	15
LUMO	-2.72	54	11	27	08
HOMO	-5.75	45	08	11	26
HOMO-1	-5.88	54	06	10	30
HOMO-2	-5.92	50	10	07	33
HOMO-3	-6.13	24	14	62	0
HOMO-4	-6.40	28	02	68	02
HOMO-5	-6.49	50	07	03	40
HOMO-6	-6.62	72	16	04	08
HOMO-7	-6.88	02	03	94	01
HOMO-8	-6.91	05	03	81	11
HOMO-9	-7.07	27	12	07	54
HOMO-10	-7.18	17	16	28	39

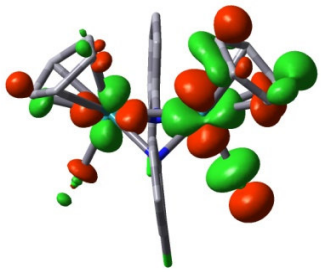

HOMO


HOMO-1


HOMO-2


LUMO


LUMO+1


LUMO+2

Contour plots of some selected MOs of [**2**] in native state

Table S6. Selected list of vertical excitations computed at the TD-DFT/B3LYP/SDD level of theory for [**1**]

$E_{excitation}$ (eV)	$\lambda_{excitationc}$ (nm)	Osc. Strength (f)	Key Transition	Character
2.6582	466.4	0.1398	(39%)HOMO-1→LUMO+1 (28%)HOMO-2→LUMO	Ru(dπ)/ L^{2a}(π)→ L^{2a}(π^*)/Ru(dπ) Ru(dπ)→ L^{2a}(π^*)
2.7380	452.8	0.1114	(37%)HOMO-1→LUMO+1 (26%)HOMO-2→LUMO	Ru(dπ)/ L^{2a}(π)→ L^{2a}(π^*)/Ru(dπ) Ru(dπ)→ L^{2a}(π^*)
3.4230	362.2	0.0568	(78%)HOMO-3→LUMO	L^{2a}(π)→ L^{2a}(π^*)/Ru(dπ)
3.5907	345.3	0.1116	(75%)HOMO-4→LUMO	L^{2a}(π)→ L^{2a}(π^*)/Ru(dπ)
4.5684	271.4	0.0469	(65%)HOMO-3→LUMO+2	L^{2a}(π)→ L^{2a}(π^*)
5.0144	247.2	0.1703	(66%)HOMO-4→LUMO+3	L^{2a}(π)→ L^{2a}(π^*)

Table S7. Selected list of vertical excitations computed at the TD-DFT/B3LYP/SDD level of theory for [**2**]

$E_{excitation}$ (eV)	$\lambda_{excitation}$ (nm)	Osc. Strength (f)	Key Transition	Character
2.6453	468.7	0.1174	(42%)HOMO-1→LUMO+1 (36%)HOMO-2→LUMO+1	Ru(dπ)/Cl(pπ)→Ru(dπ)/Cp
3.2542	381.0	0.0293	(83%)HOMO-7→LUMO+1	$(L^{1a})^-$π→ Ru(dπ)/Cp
3.3922	365.5	0.0915	(49%)HOMO-3→LUMO+2 (43%)HOMO-8→LUMO+1	$(L^{1a})^-$π→ Ru(dπ)/Cp

Table S8. The bond distances (in Å) obtained at the B3LYP/SDD level optimized geometry of the complex [**6**]$^{2+}$ in native state.

Bond Parameters	Experimental	Calculated
Ru1-Ru2	2.626(7)	2.684
Ru1-N1	2.042(7)	2.131
Ru1-N2	2.096(7)	2.067
Ru1-S1	2.363(13)	2.415
Ru2-N1	2.101(4)	2.069
Ru2-N2	2.047(4)	2.129
Ru2-S2	2.358(13)	2.406
N1-Ru1-N2	93.93(15)	93.82
N1-Ru1-S1	82.85(11)	88.88
N1-Ru2-N2	93.64(15)	93.81
N1-Ru2-S2	88.87(12)	82.10
N2-Ru1-S1	89.97(12)	81.87
N2-Ru2-S2	82.36(13)	88.95
Ru1-N1-Ru2	79.38(13)	79.40
Ru1-N2-Ru2	79.38(15)	79.48

Table S9. Some Selected Molecular Orbitals along with their energies and compositions of compound [**6**]$^{2+}$ in gas phase B3LYP/SDD level calculation

MO	Energy, eV	% of composition		
		Ru	$(L^{1b})^{-}$	Cp
LUMO+5	-6.62	09	89	02
LUMO+4	-6.96	54	20	26
LUMO+3	-7.46	49	24	27
LUMO+2	-7.48	55	17	28
LUMO+1	-7.71	51	22	27
LUMO	-8.93	55	35	10
HOMO	-11.94	48	40	12
HOMO-1	-12.18	07	87	06
HOMO-2	-12.35	35	58	07
HOMO-3	-12.59	63	27	10
HOMO-4	-12.70	13	85	02
HOMO-5	-12.79	33	62	05
HOMO-6	-12.84	73	16	11
HOMO-7	-13.00	42	45	13
HOMO-8	-13.39	67	21	12
HOMO-9	-13.80	19	35	46
HOMO-10	-14.05	30	09	61

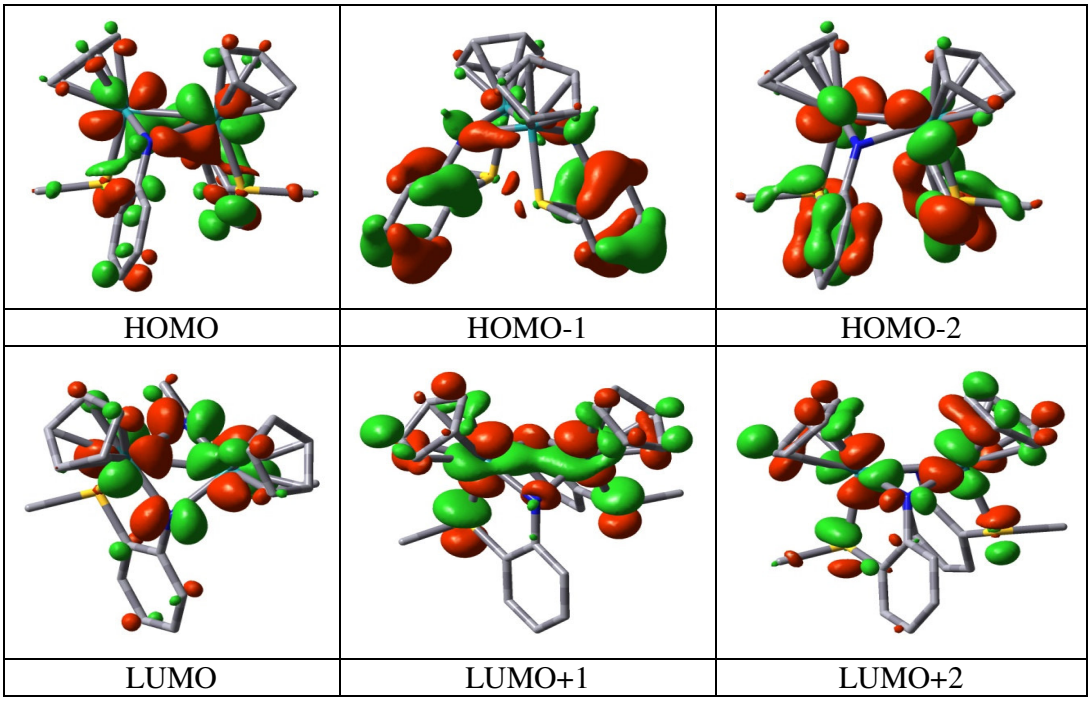


Table S10. Selected list of vertical excitations computed at the TD-DFT/B3LYP/SDD level of theory for [**6**]$^{2+}$

$E_{excitation}$ (eV)	$\lambda_{excitation}$ (nm)	Osc. Strength (f)	Key Transition	Character
1.4455	857.7	0.1136	(85%)HOMO→LUMO	Ru(dπ)/$(L^{1b})^{-}$→Ru(dπ)
1.8445	672.2	0.0136	(64%)HOMO-2→LUMO	Ru(dπ)/$(L^{1b})^{-}$→Ru(dπ)
2.6748	463.5	0.0378	(80%)HOMO-1→LUMO	$(L^{1b})^{-}$→Ru(dπ)
3.1874	389.0	0.0467	(41%)HOMO-4→LUMO (22%)HOMO-5→LUMO	$(L^{1b})^{-}$→Ru(dπ)
3.6534	339.4	0.0275	(58%)HOMO-4→LUMO+1	$(L^{1b})^{-}$→Ru(dπ)/Cp
4.0254	308.0	0.0431	(55%)HOMO-4→LUMO+2	$(L^{1b})^{-}$→Ru(dπ)/Cp
4.1615	297.9	0.0453	(72%)HOMO-1→LUMO+3	$(L^{1b})^{-}$→Ru(dπ)/Cp
4.2351	292.7	0.0711	(64%)HOMO-4→LUMO+3	$(L^{1b})^{-}$→Ru(dπ)/Cp

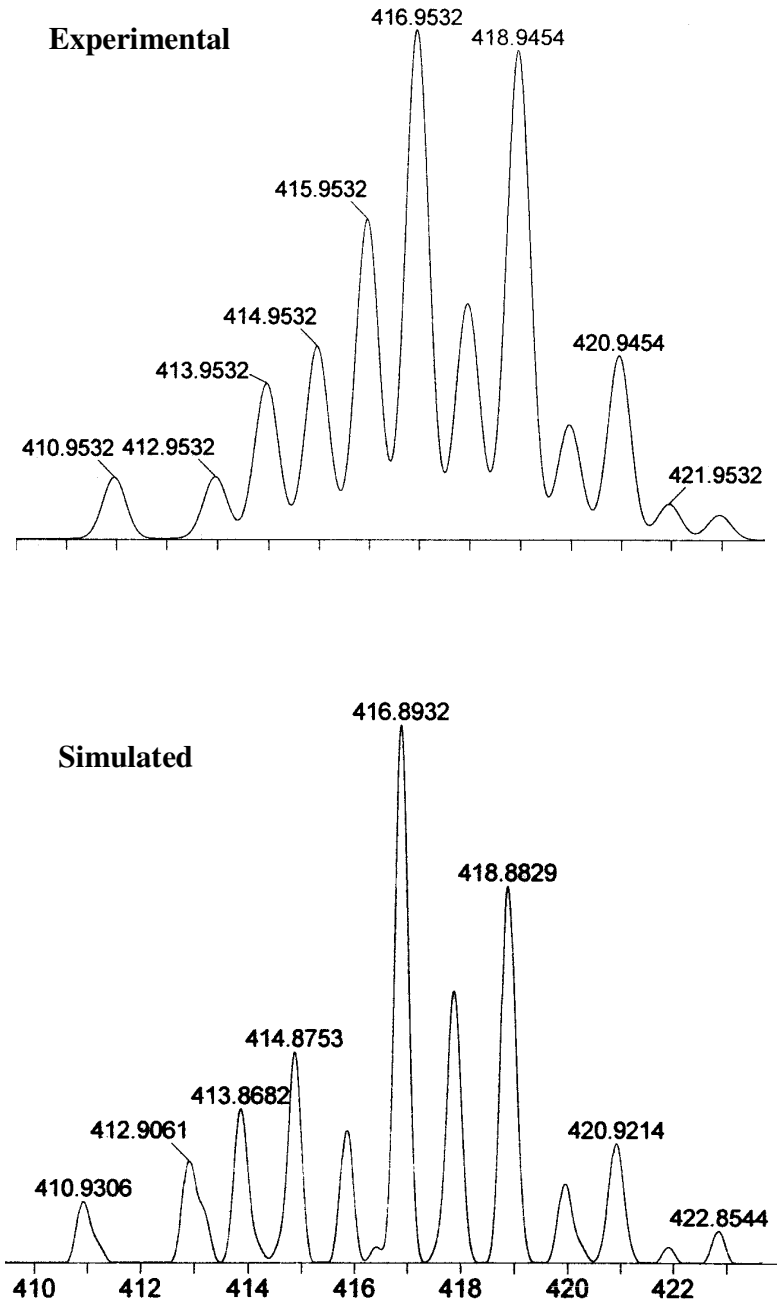


Figure S1. Experimental and simulated ESI-MS spectra of the compound **1**.

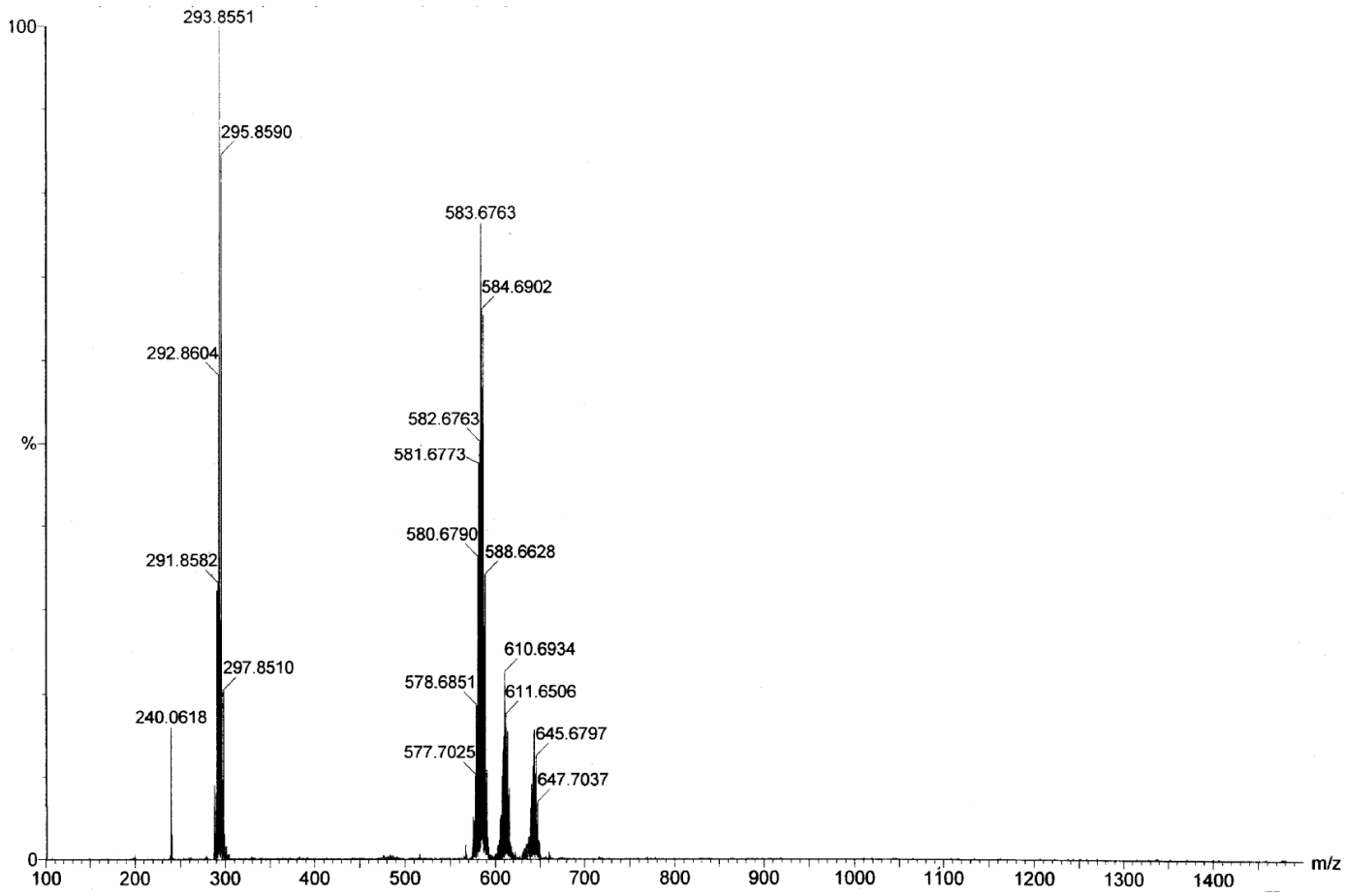


Figure S2.a. Experimental ESI-MS spectrum of the compound **2**

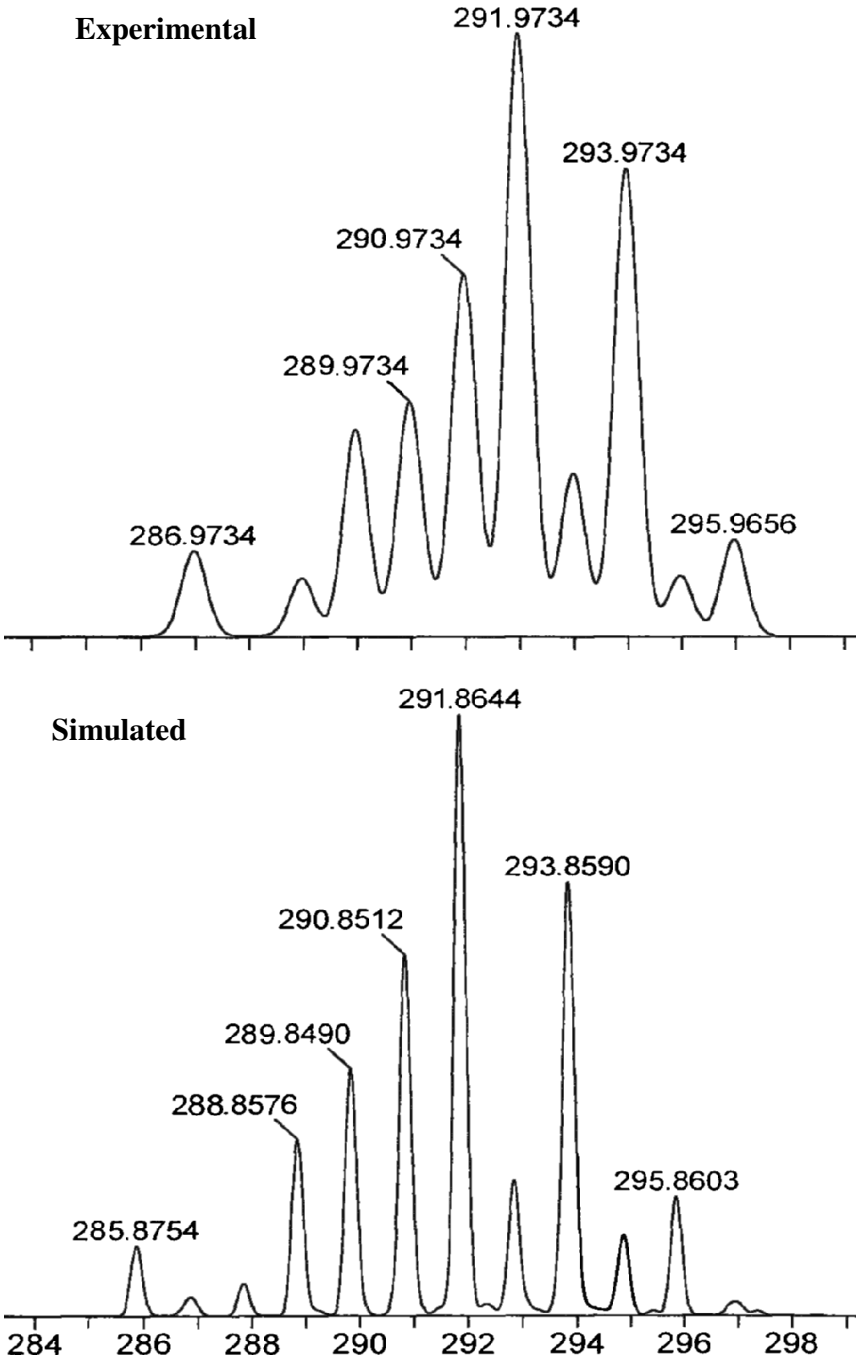


Figure S2.b. Experimental and simulated ESI-MS spectra of the compound **2** at $[M/2\text{-}Cl]^+$.

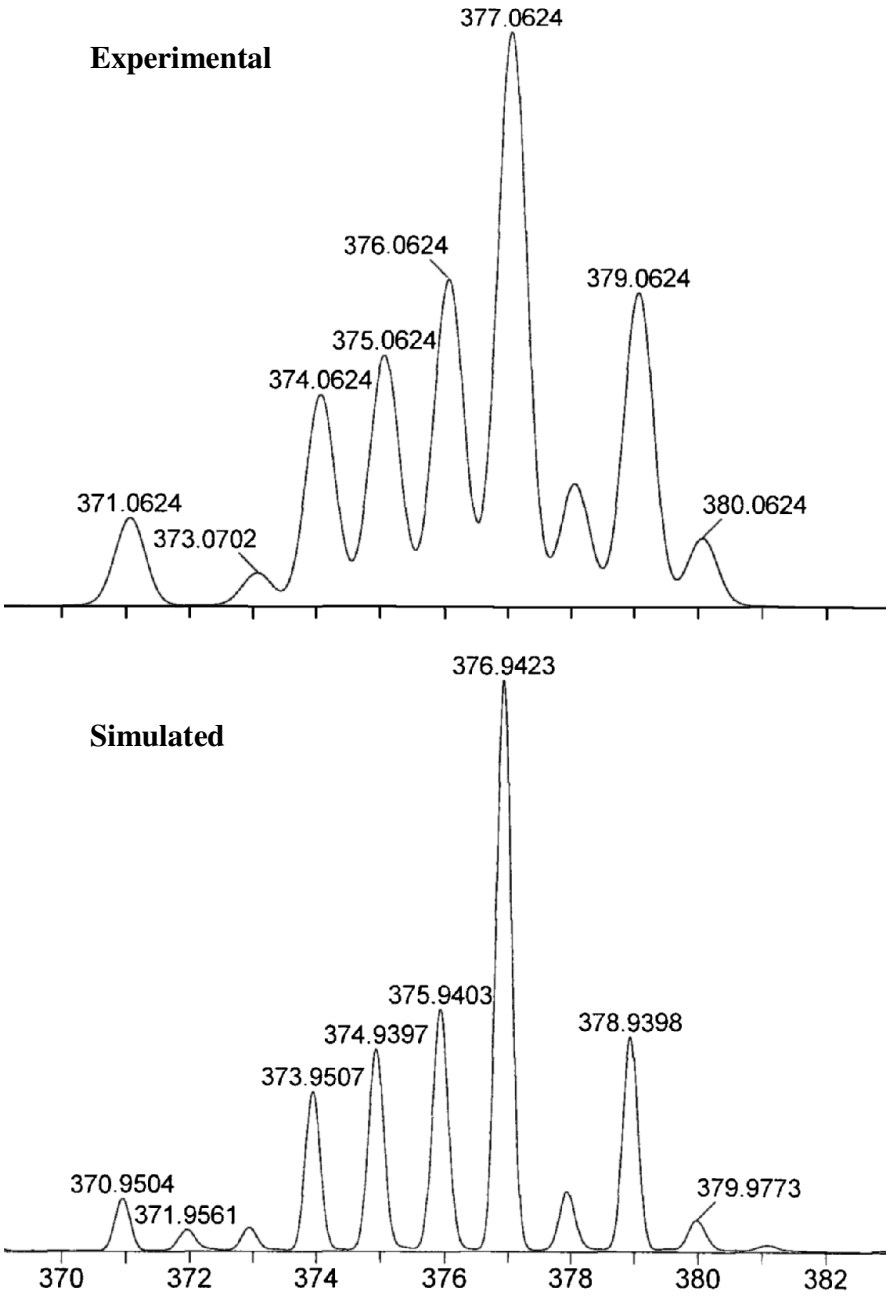


Figure S3. Experimental and simulated ESI-MS spectra of the compound, **3**.

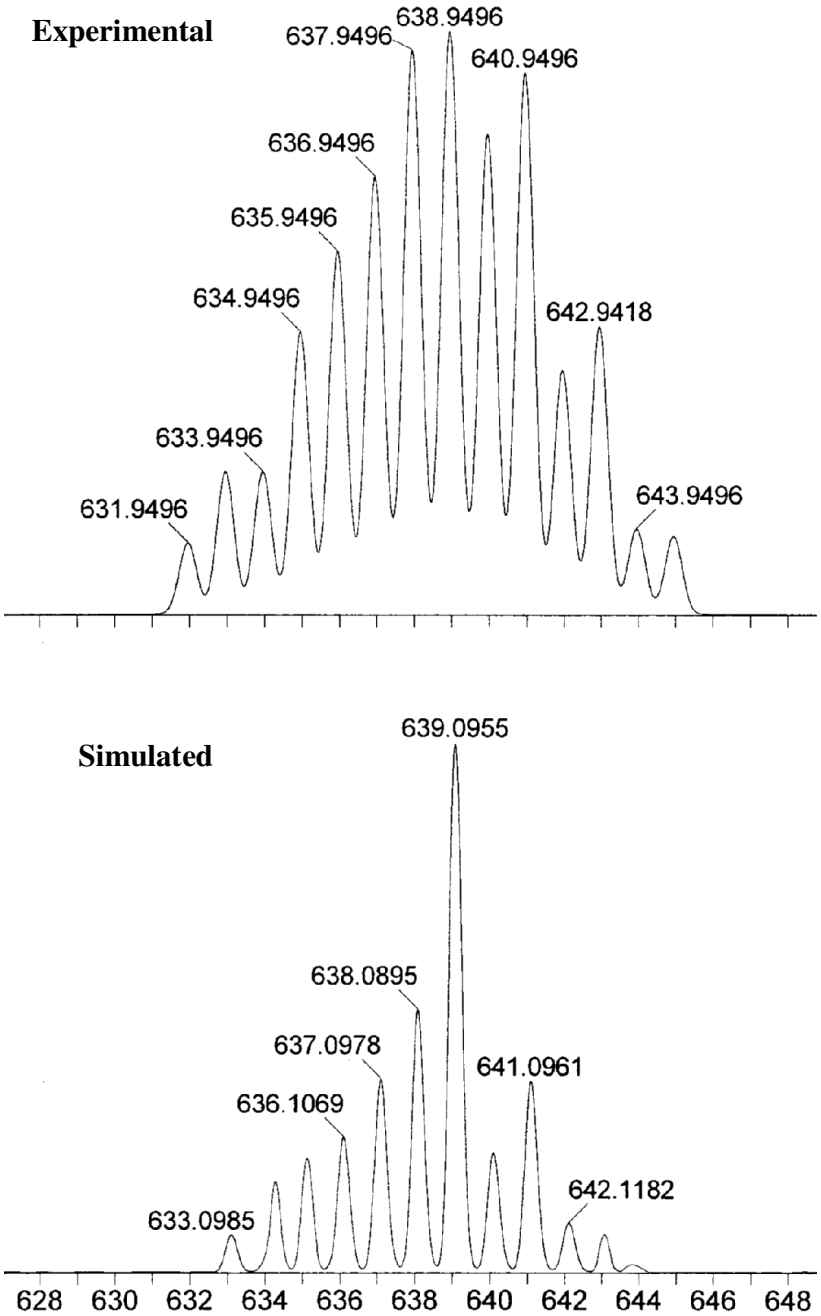


Figure S4. Experimental and simulated ESI-MS spectra of the compound, **4**.

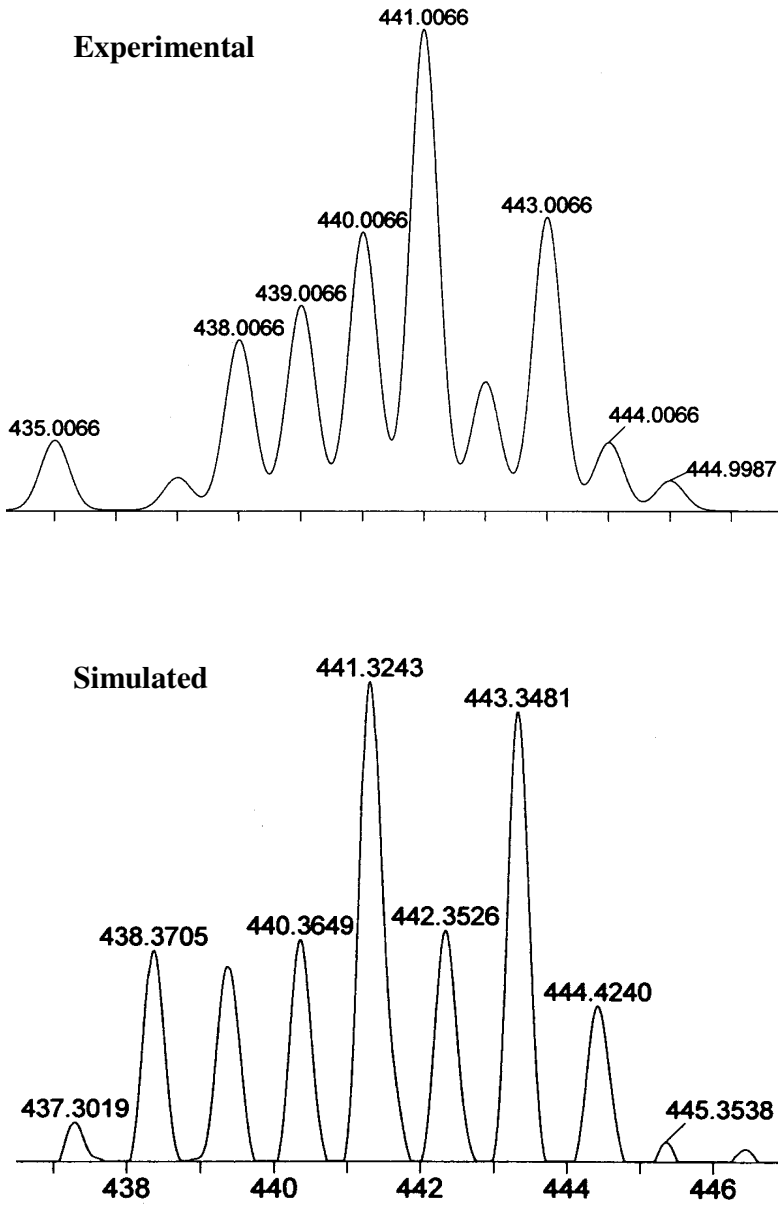
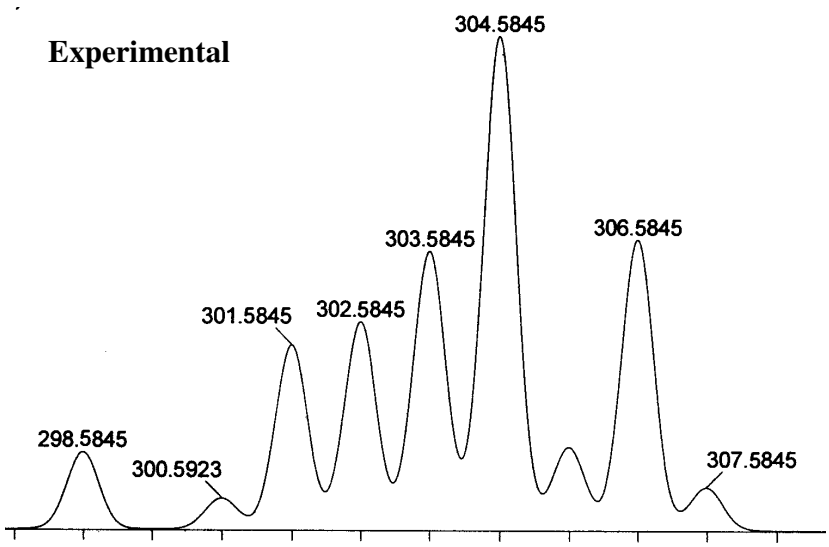


Figure S5. Experimental and simulated ESI-MS spectra of the compound, **5**.



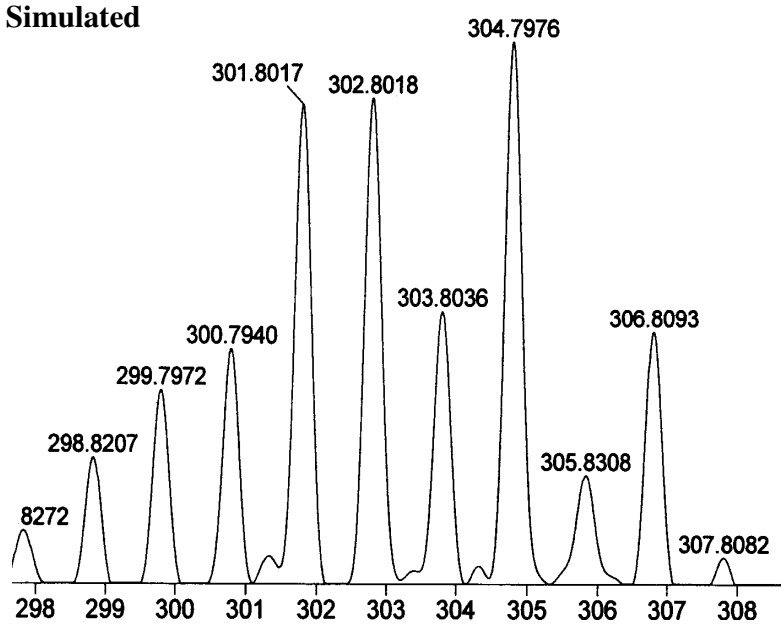


Figure S6. Experimental and simulated ESI-MS spectra of the compound, [**6**]Cl_2.

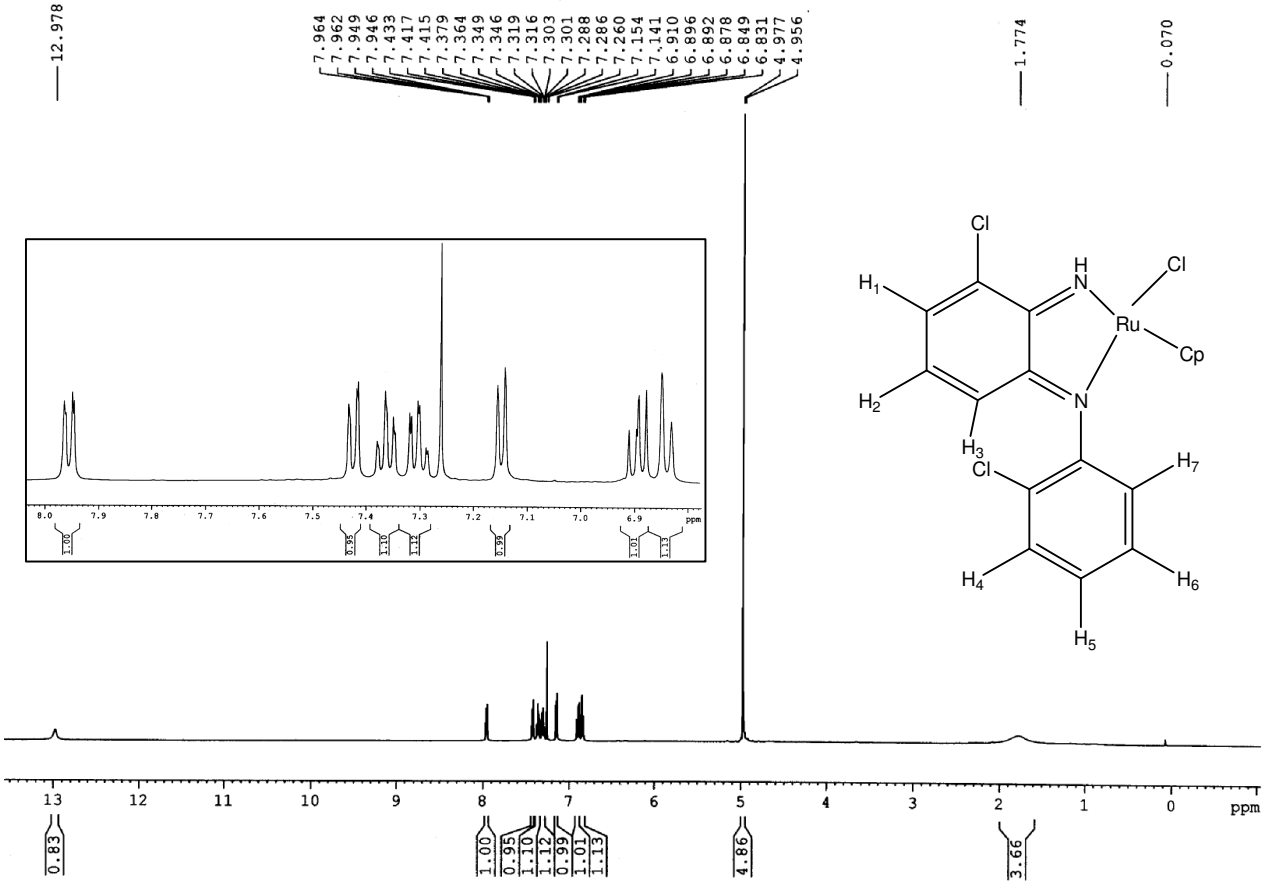


Figure S7. ^{1}H NMR spectrum of the compound, **1** in $CDCl_3$.

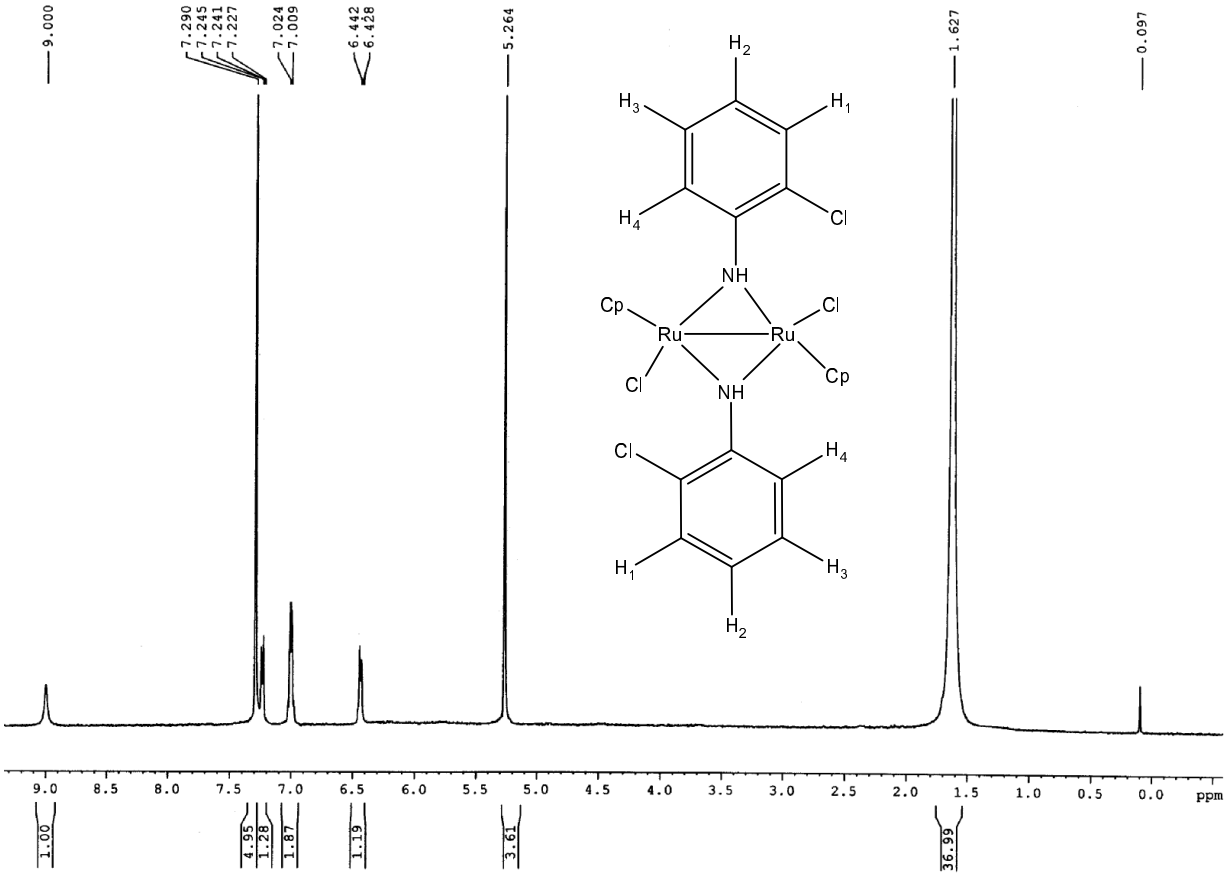


Figure S8. ^{1}H NMR spectrum of the compound, **2** in $CDCl_3$.

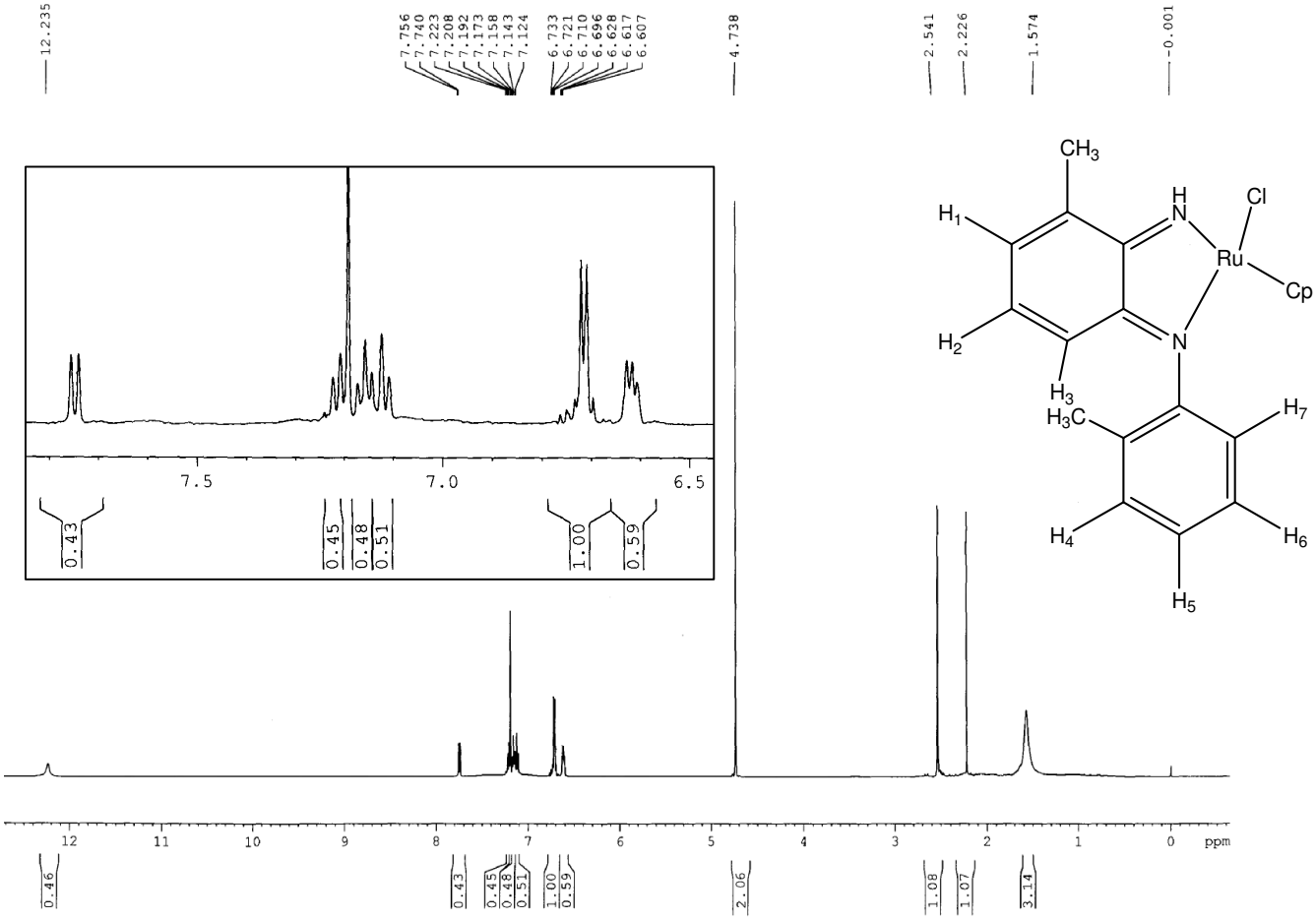


Figure S9. ^{1}H NMR spectrum of the compound, **3** in $CDCl_3$.

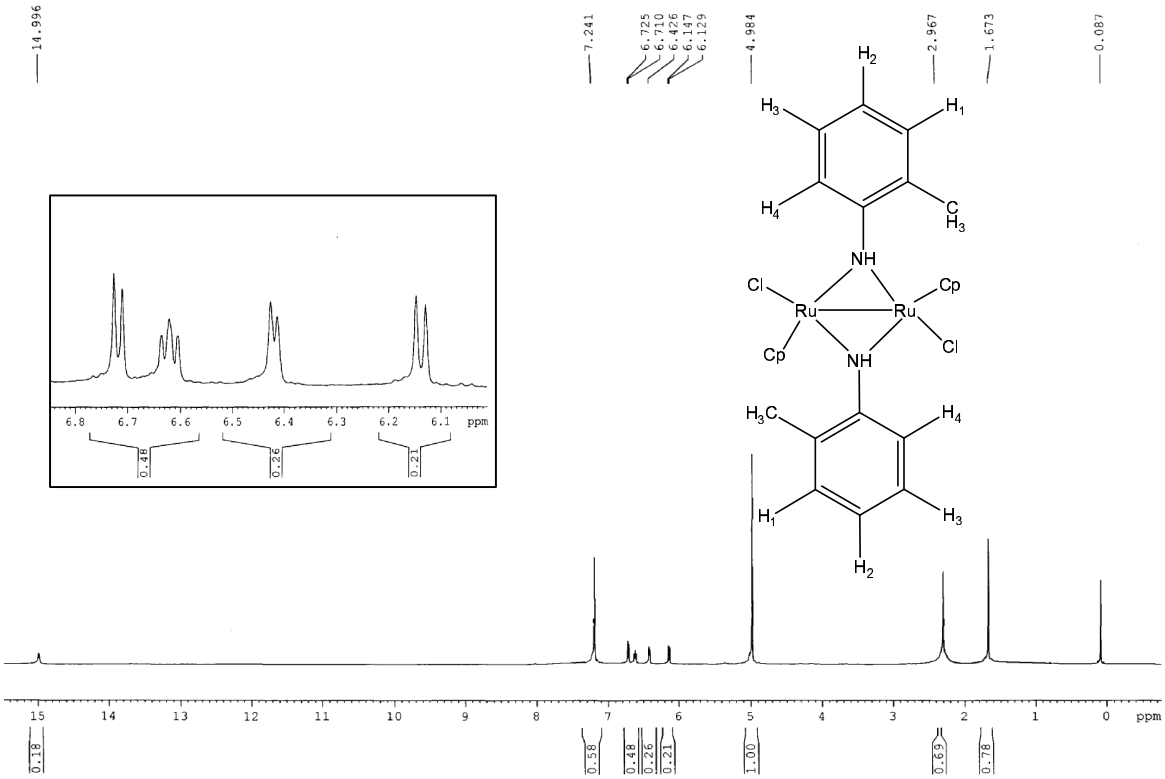


Figure S10. ^{1}H NMR spectrum of the compound, **4** in $CDCl_3$.

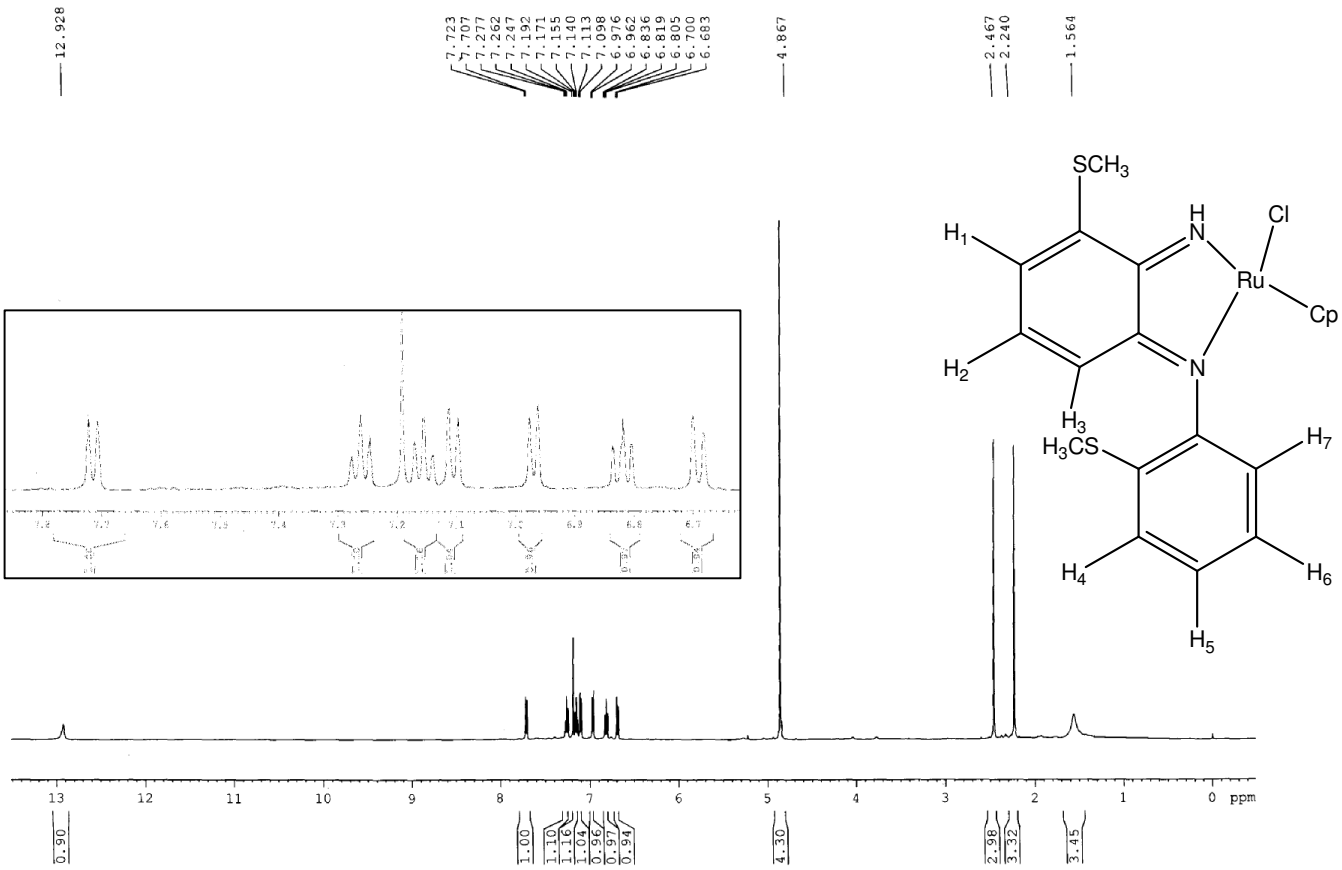


Figure S11. ^{1}H NMR spectrum of the compound, **5** in $CDCl_3$.

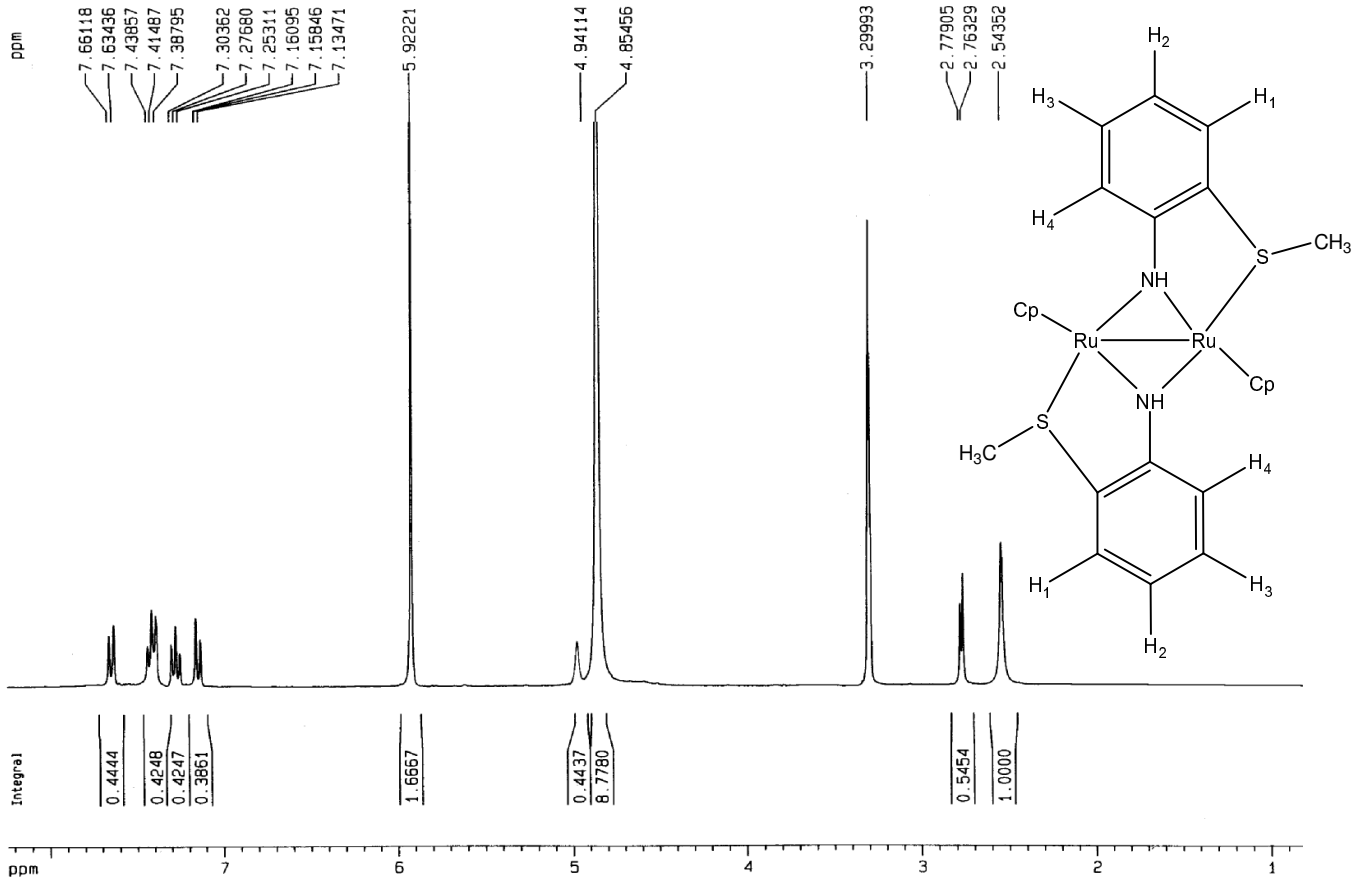


Figure S12. ^{1}H NMR spectrum of the compound, [**6**]Cl_2 in CD_3OD.

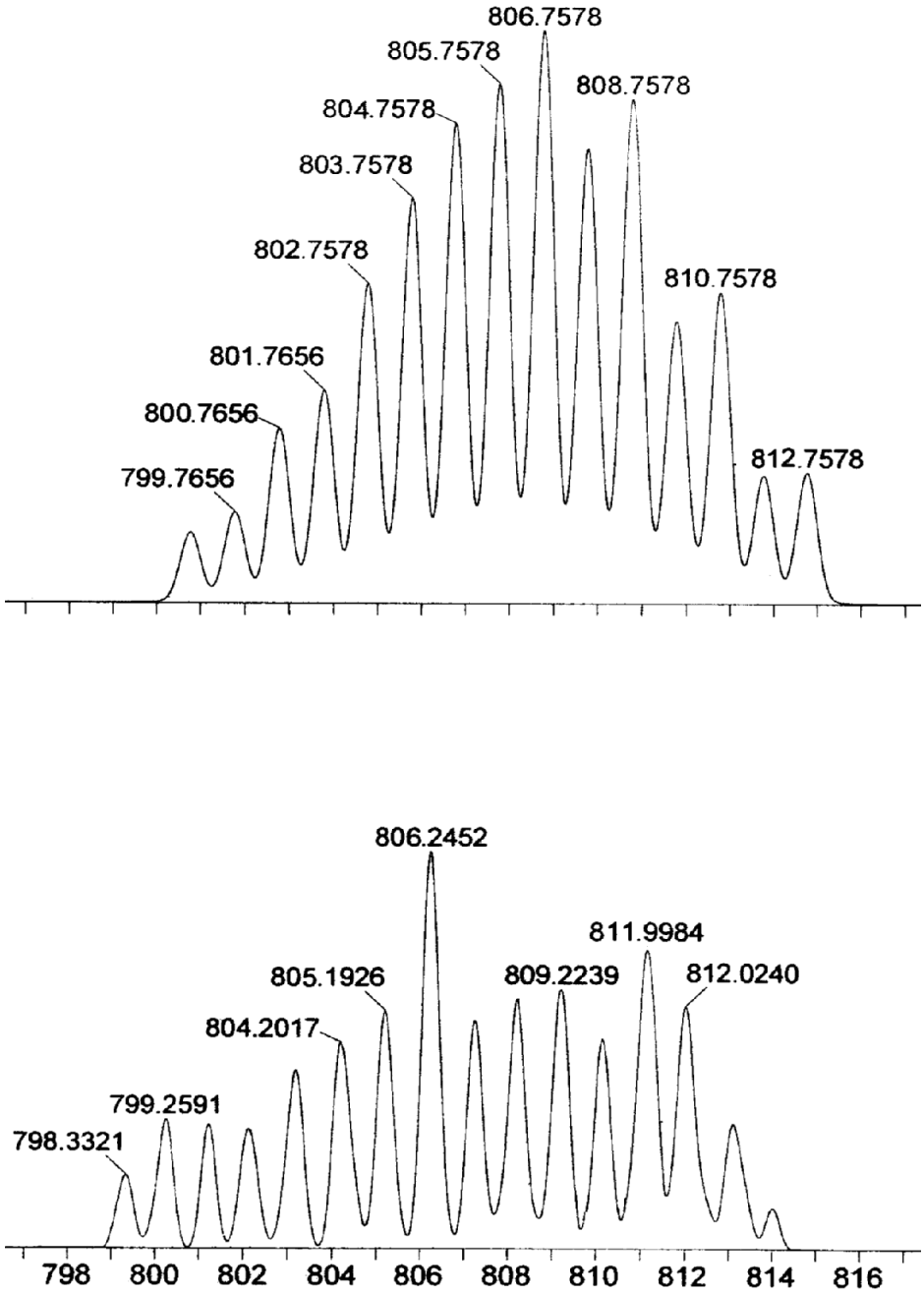


Figure S13. Experimental and simulated ESI-MS spectra of the compound, [**7**]Cl.

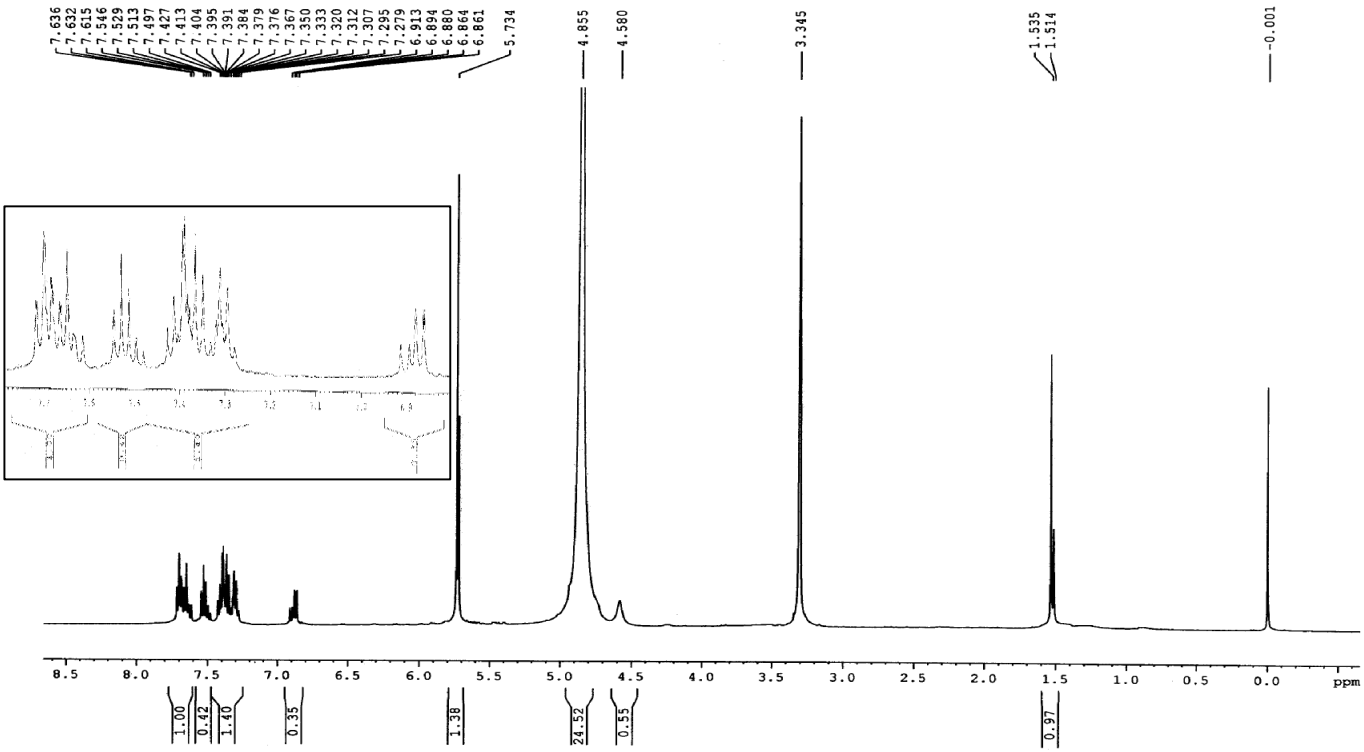


Figure S14. ^{1}H NMR spectrum of the compound, [**7**]Cl in CD_3OD.

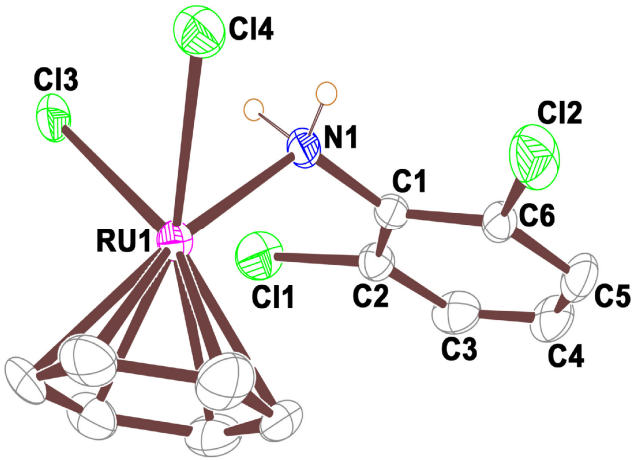


Figure S15. ORTEP and atom numbering scheme of the compound, **8**.

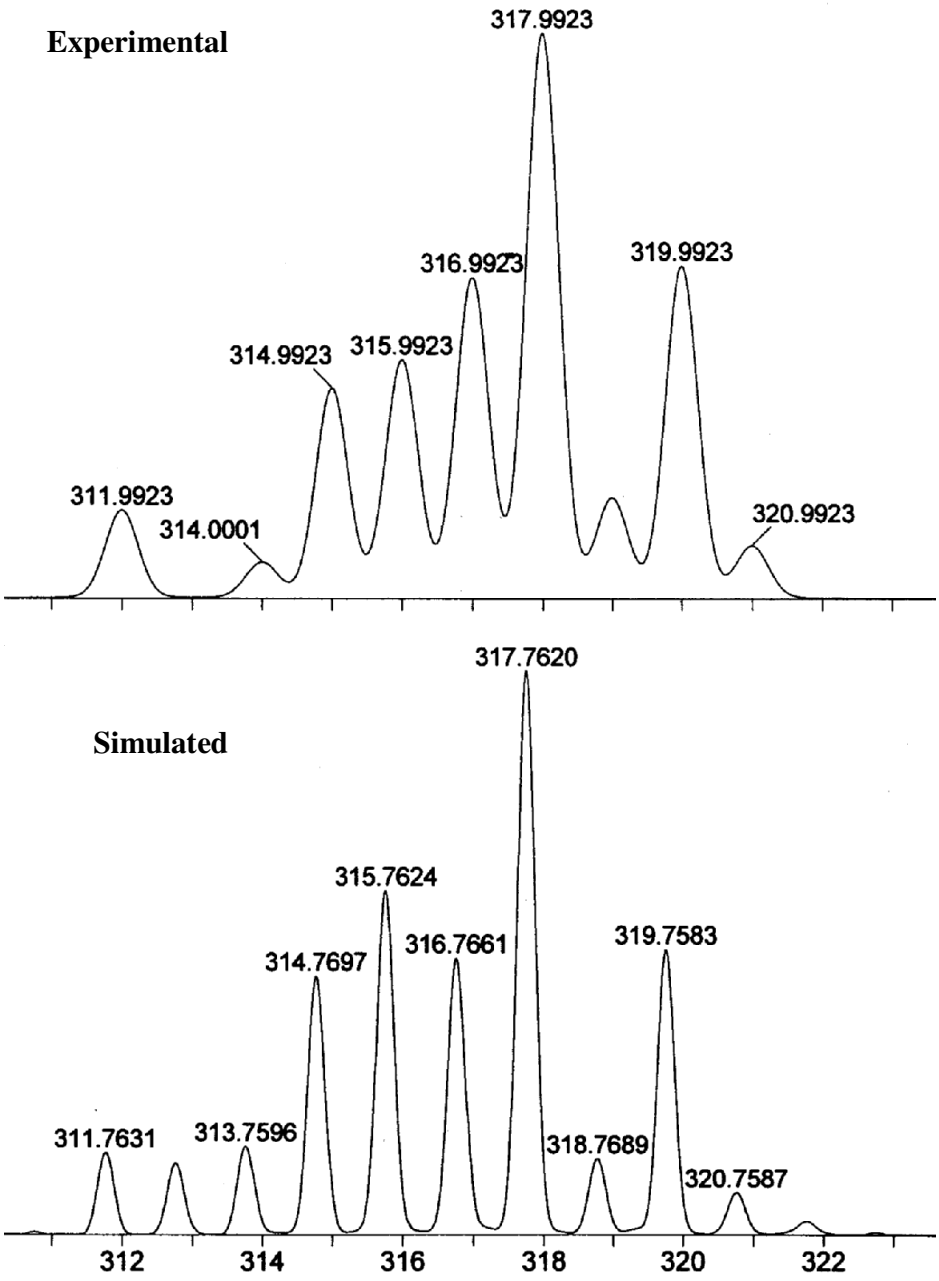


Figure S16. Experimental and simulated ESI-MS spectra of the compound, [**9**]Cl_2.

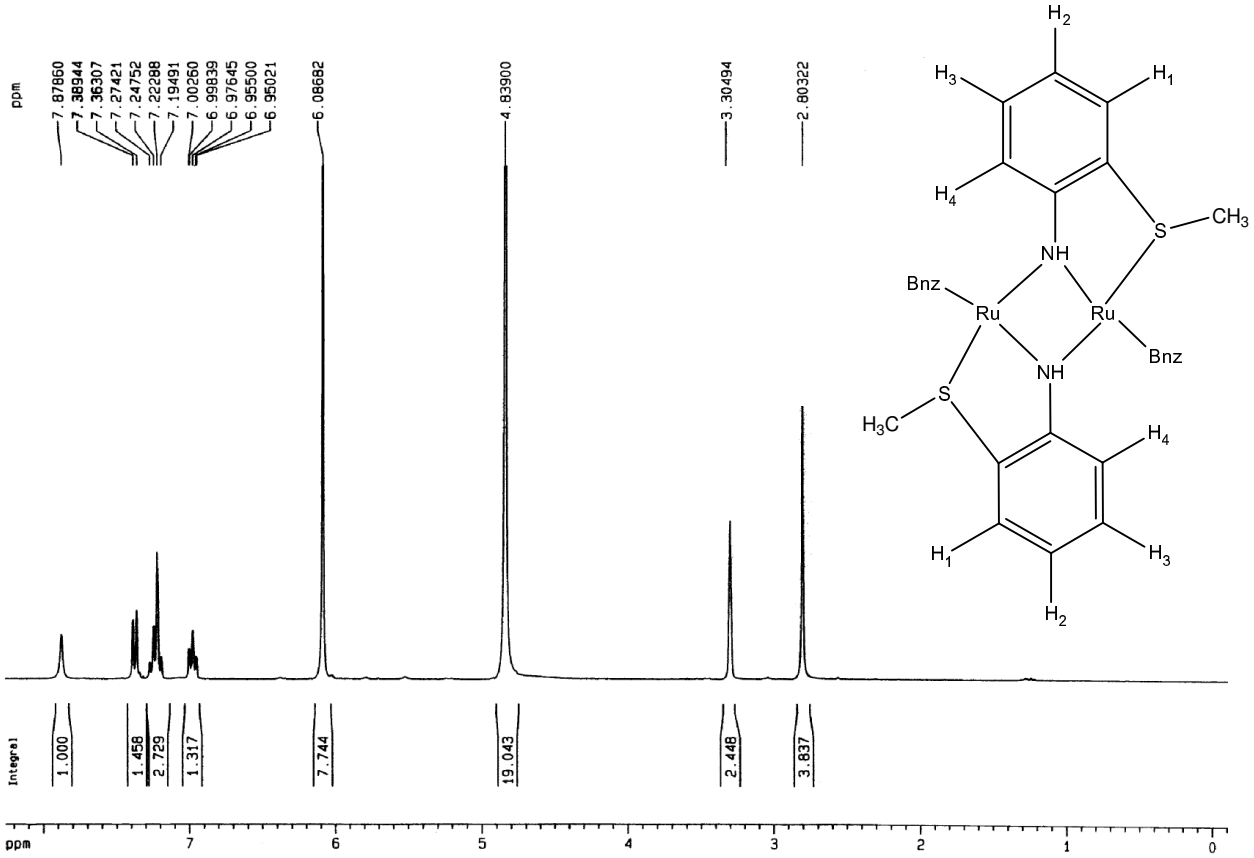


Figure S17. ^{1}H NMR spectrum of the compound, [**9**]Cl_2 in CD_3OD.

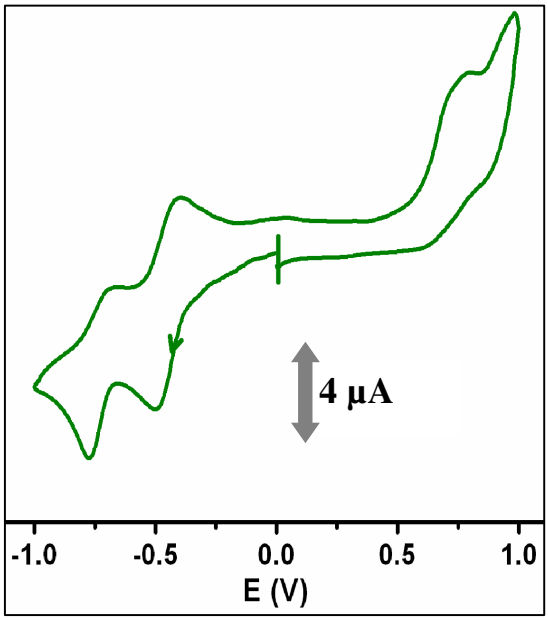


Figure S18. Cyclic voltammogram of complex [**6**]Cl_2 in CH_3CN/0.1 M NEt_4ClO_4.