Supporting Information

(24 pages including the cover page)

Base–Controlled Directed Synthesis of Metal–Methyleneimidazoline (MIz) and Metal–Mesoionic Carbene (MIC) Compounds

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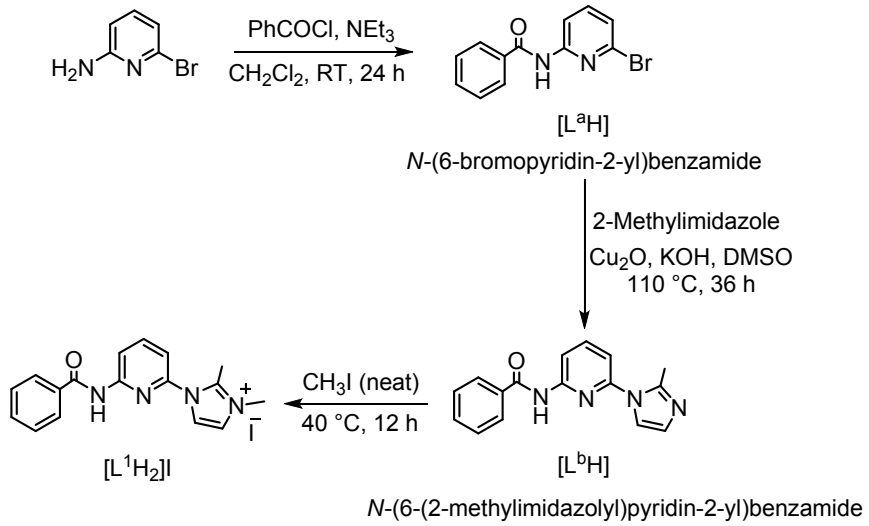
Synthesis of $[L^1H_2]I$



Scheme S1. Synthesis of the ligand **$[L^1H_2]I$**.

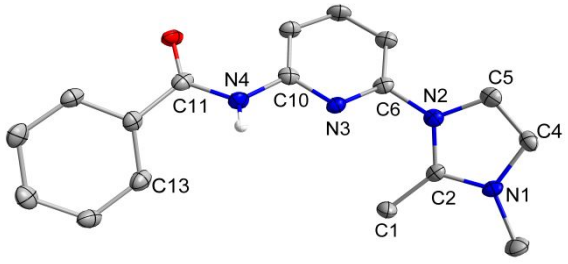
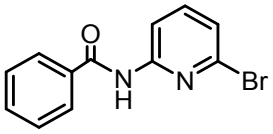


Figure S1. Molecular structure of the cationic unit of **$[L^1H_2]I$**.

Spectroscopy Data:



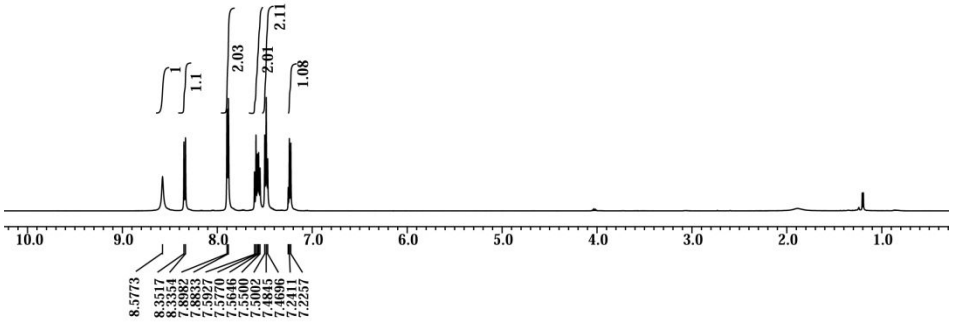


Figure S2. ^{1}H NMR of **[L^{a}H]** in $CDCl_3$.

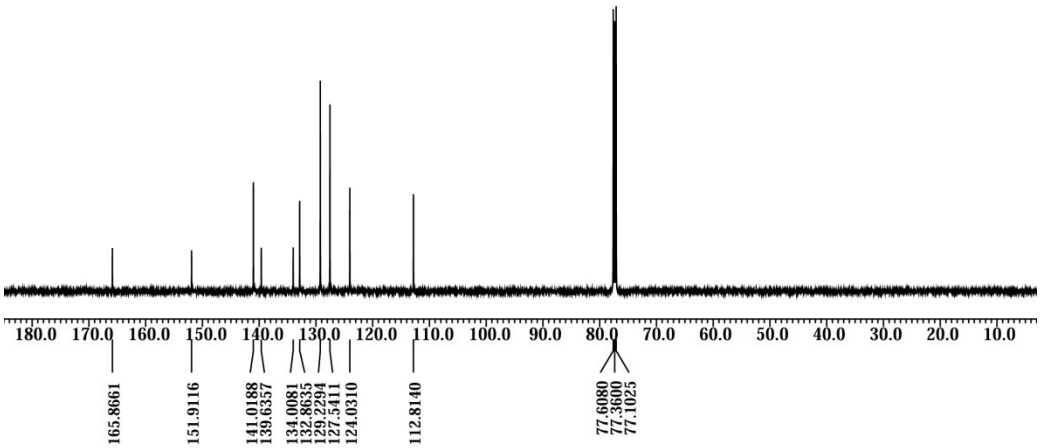


Figure S3. ^{13}C NMR of **[L^{a}H]** in $CDCl_3$.

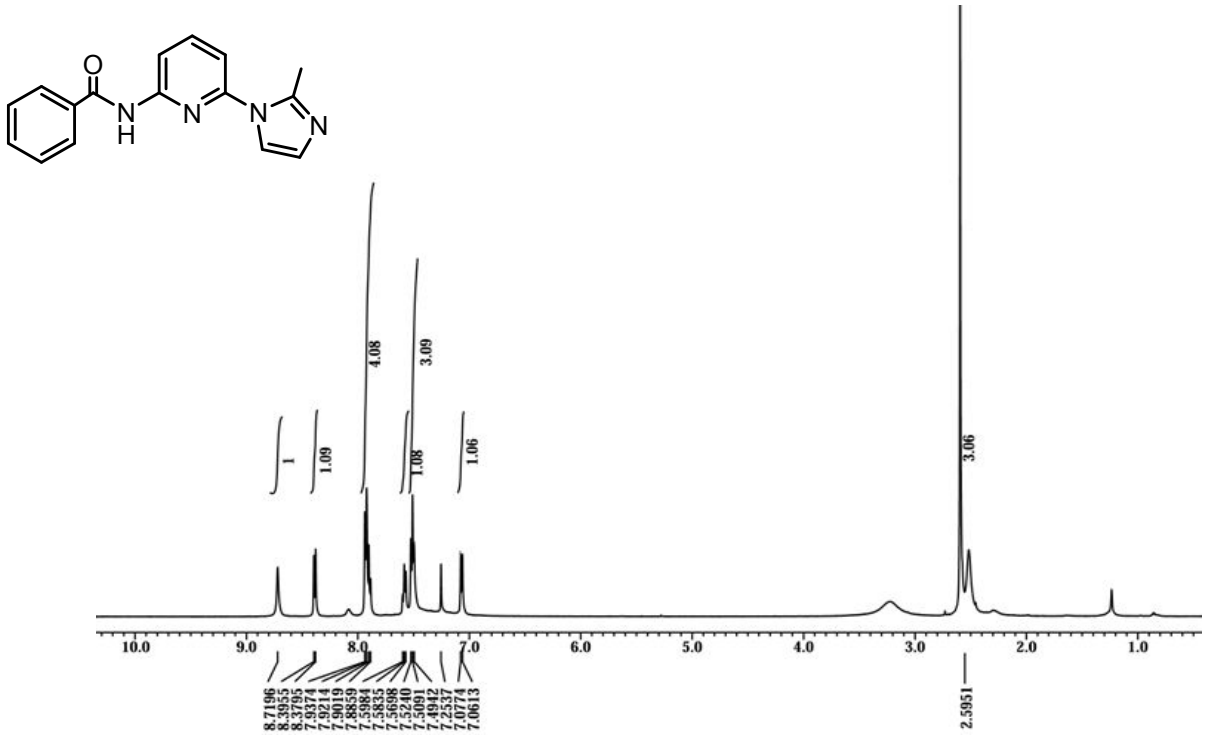


Figure S4. ^{1}H NMR of **[L^{b}H$_2$]** in $CDCl_3$.

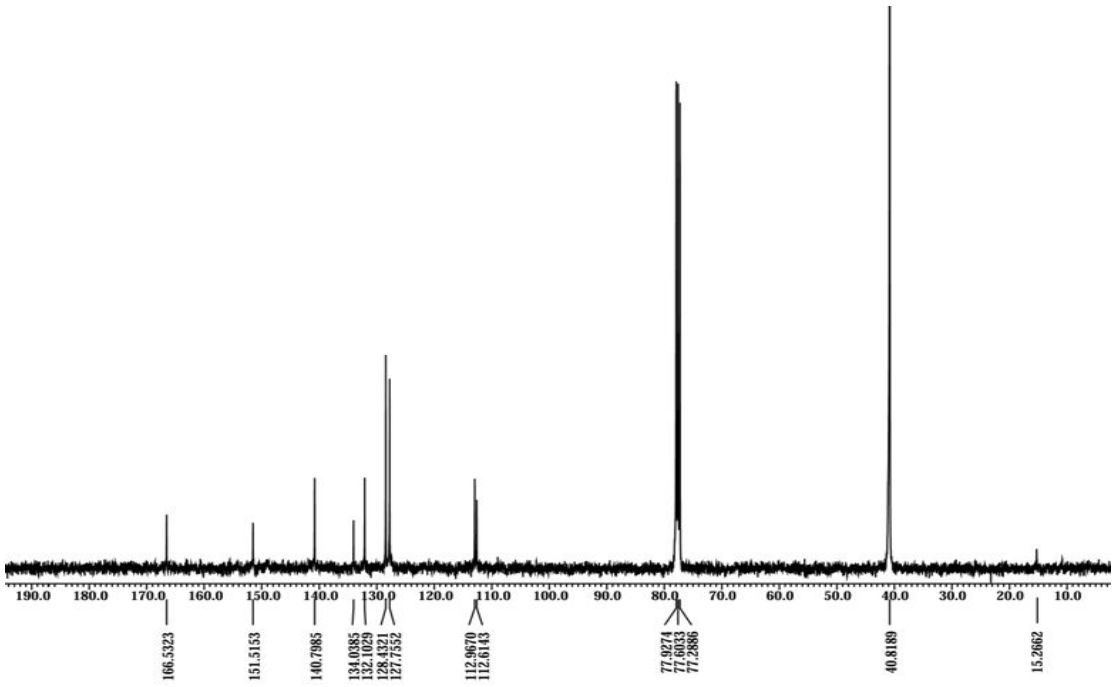


Figure S5. ^{13}C NMR of **[L^{b}H$_2$]** in $CDCl_3$.

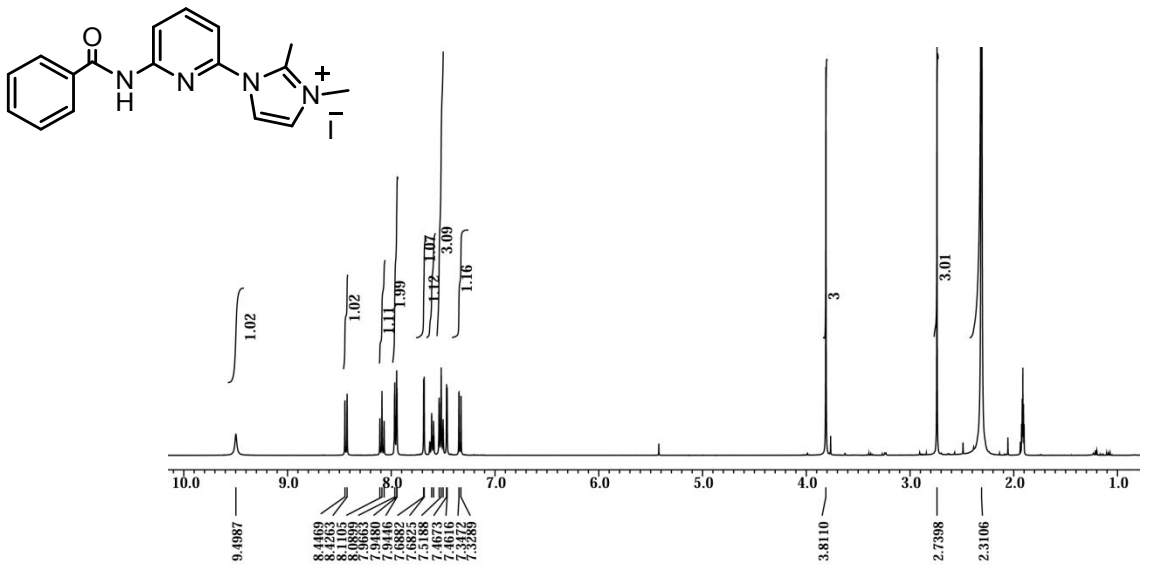


Figure S6. ^{1}H NMR of **[L^{1}H$_2$]I** in CD_3CN.

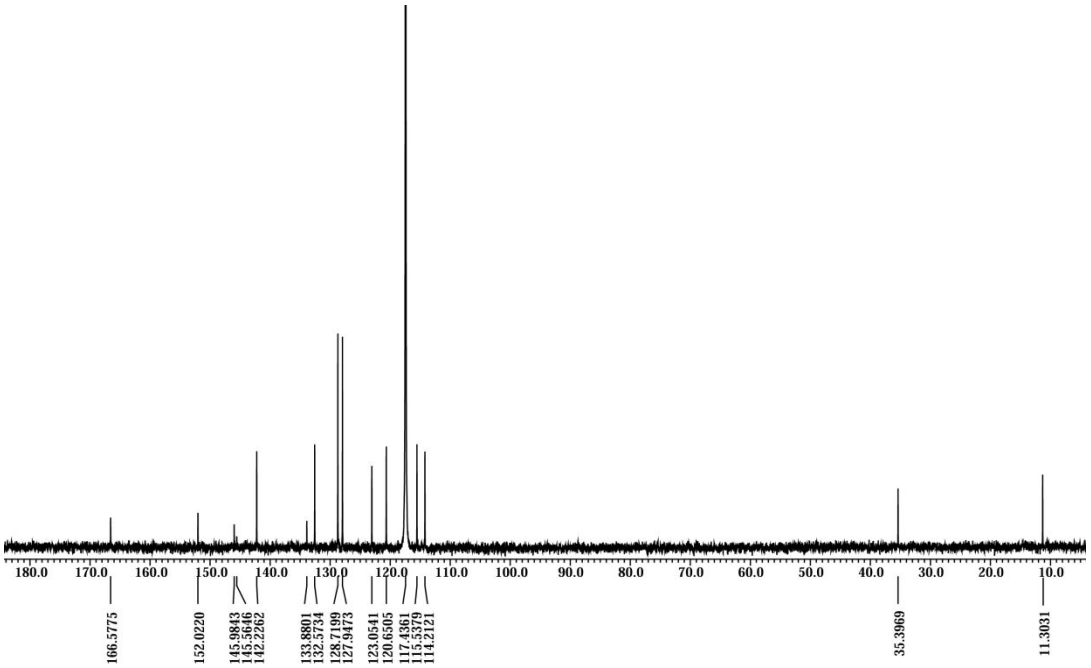


Figure S7. ^{13}C NMR of **[L^{1}H$_2$]I** in CD_3CN.

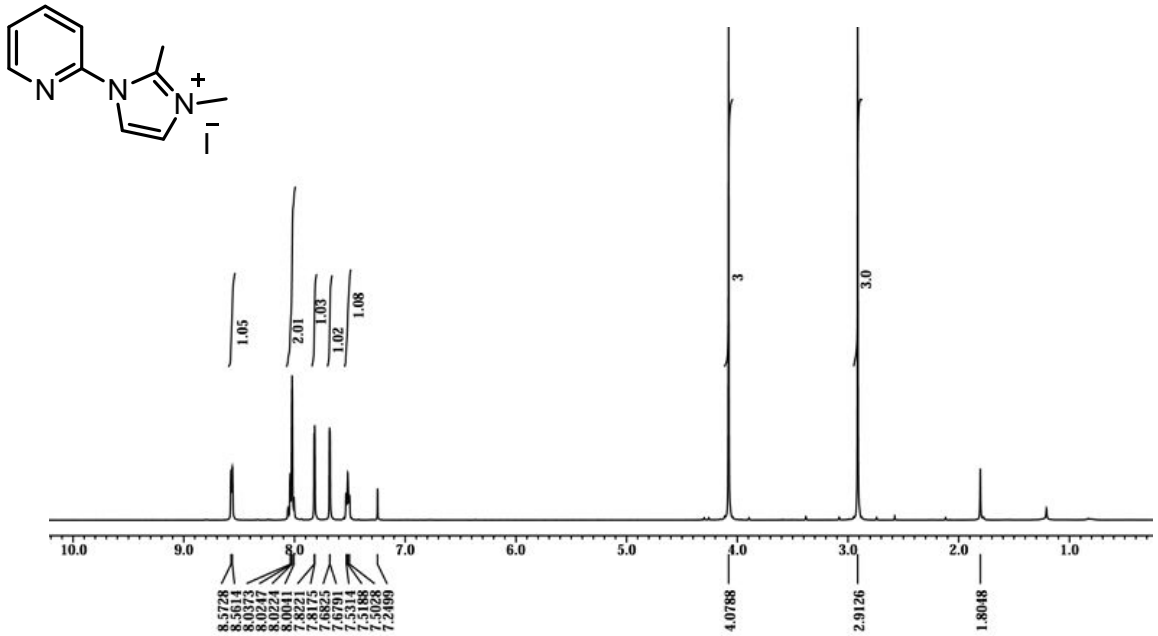


Figure S8. ^{1}H NMR of **[L^{2}H]I** in $CDCl_3$.

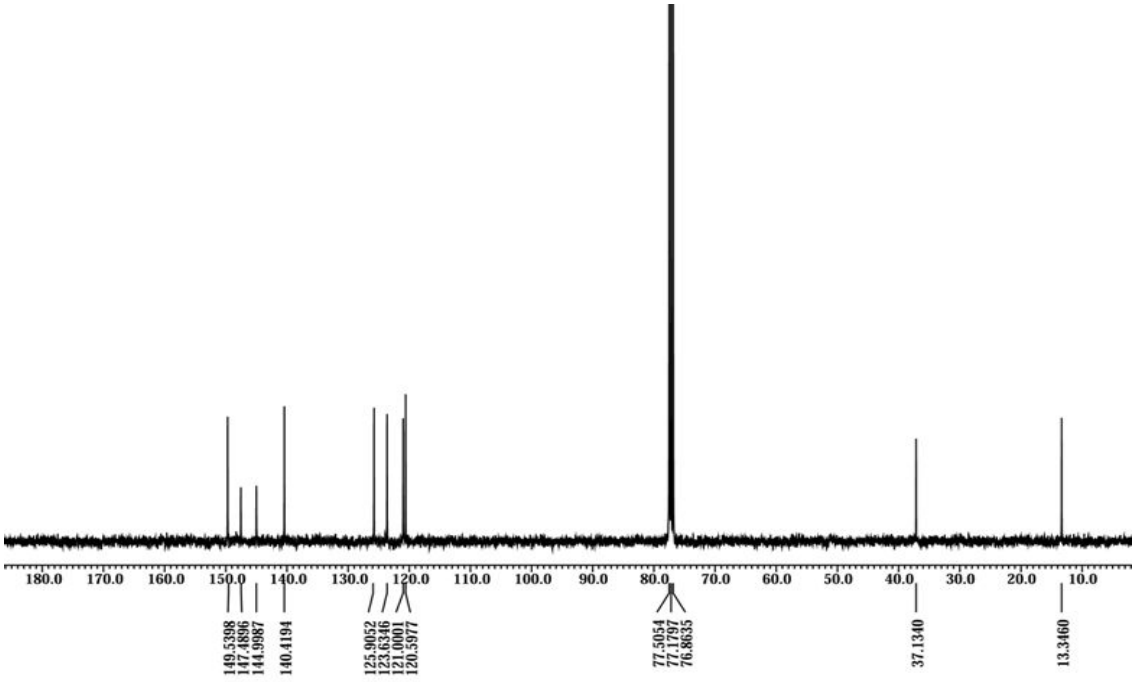


Figure S9. ^{13}C NMR spectrum for **[L^{2}H]I** in $CDCl_3$.

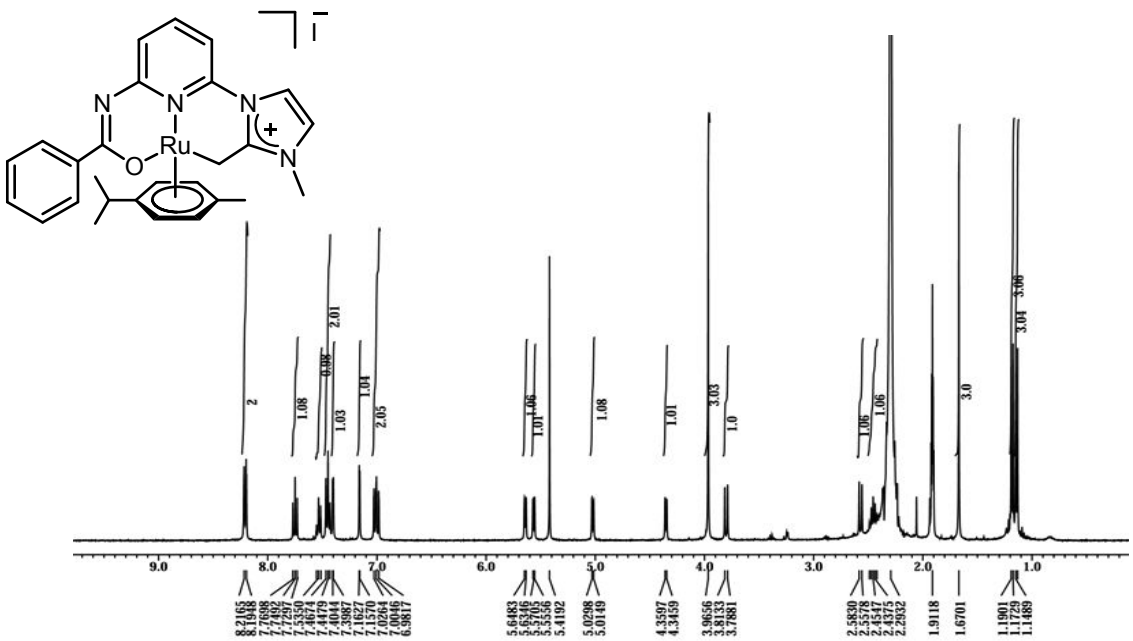


Figure S10. ^{1}H NMR of **1** in CD_3CN.

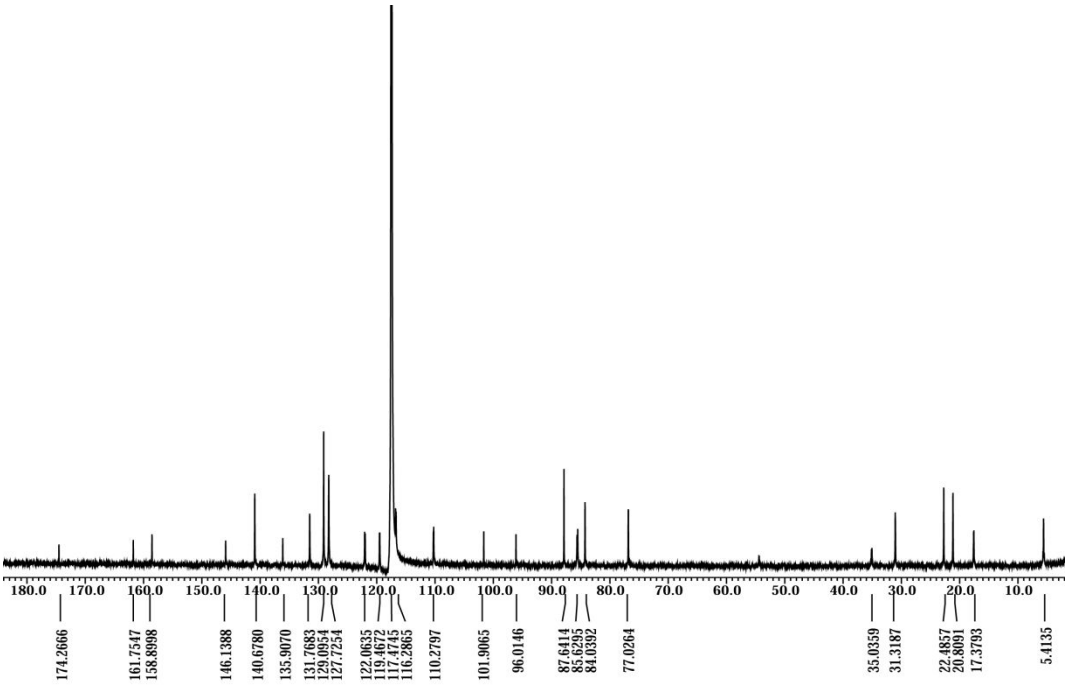


Figure S11. ^{13}C NMR of **1** in CD_3CN.

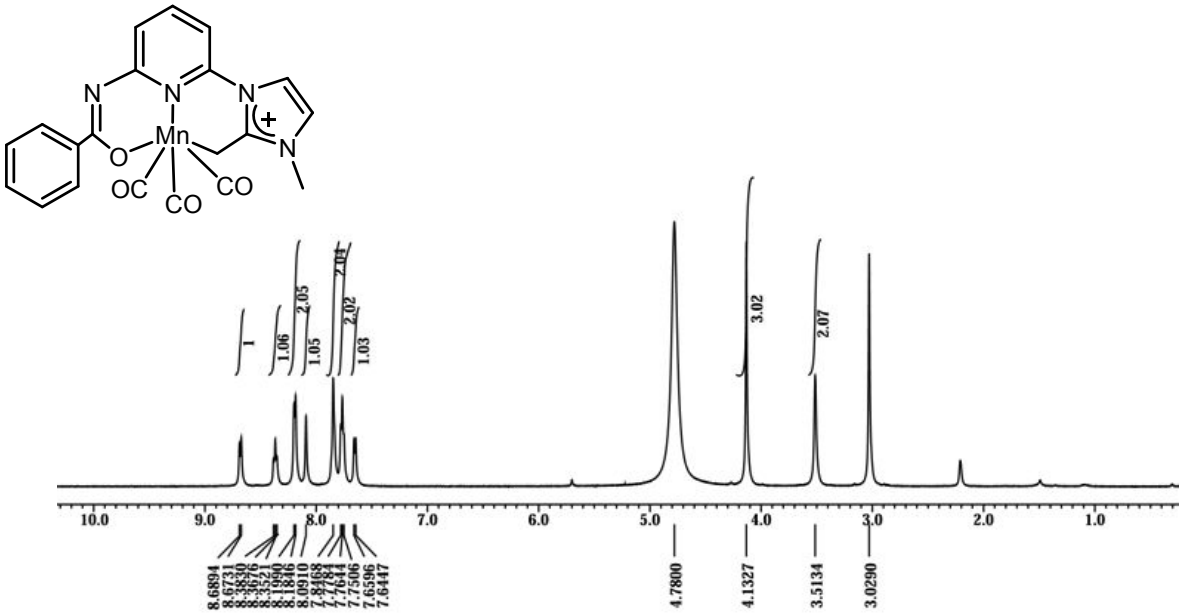


Figure S12. ^{1}H NMR of **2** in CD_3OD.

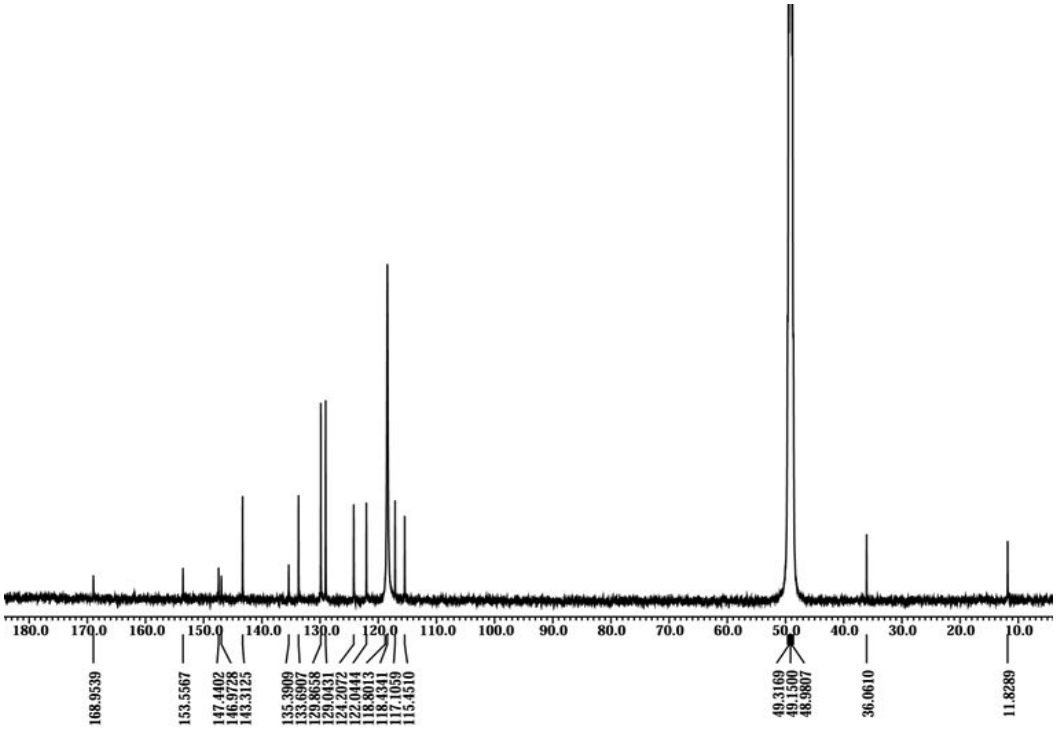


Figure S13. ^{13}C NMR of **2** in CD_3OD.

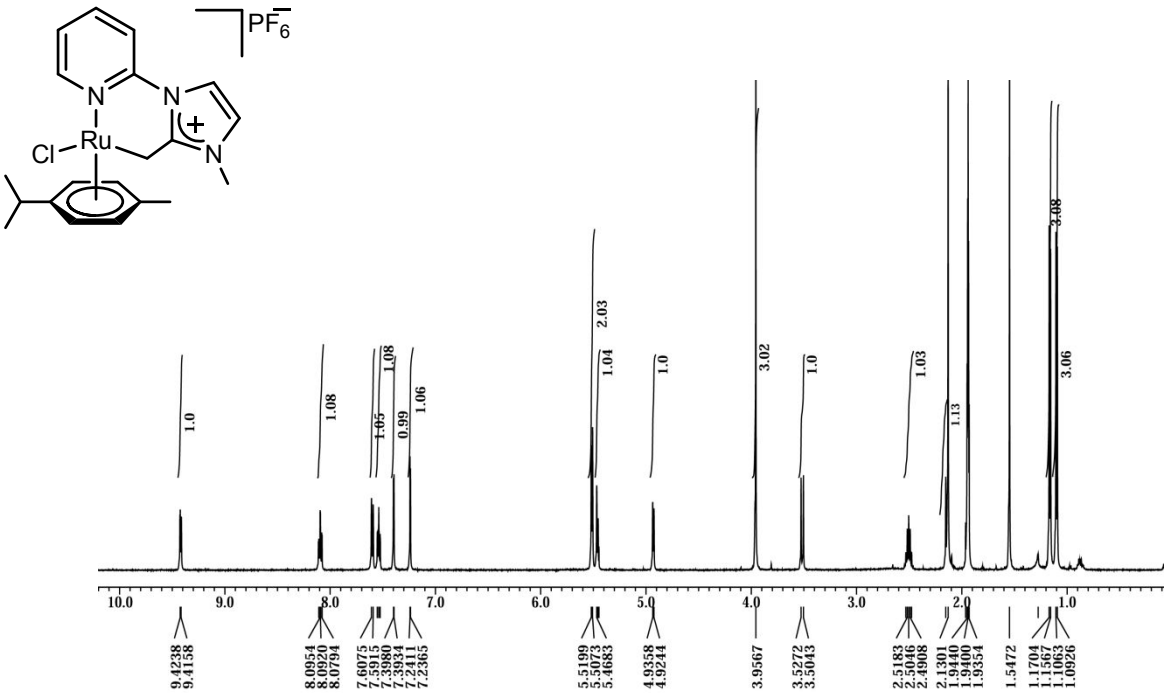


Figure 14. ^{1}H NMR of **3** in CD_3CN.

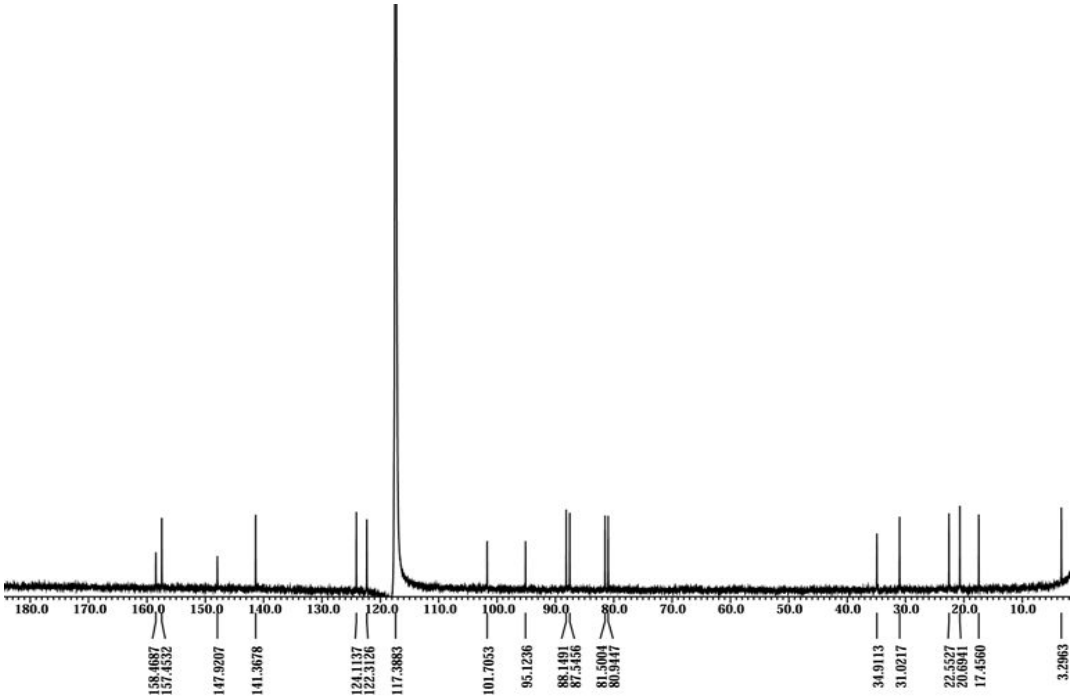


Figure S15. ^{13}C NMR of **3** in CD_3CN.

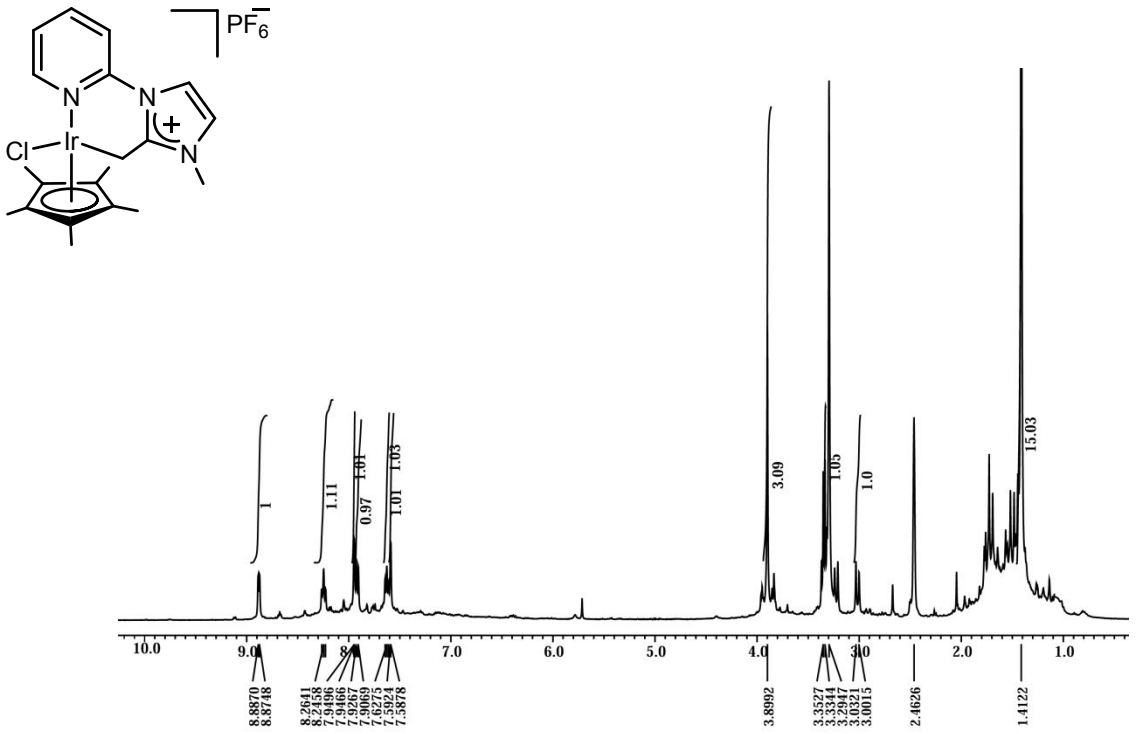


Figure 16. ^{1}H NMR of **4** in DMSO−d_6.

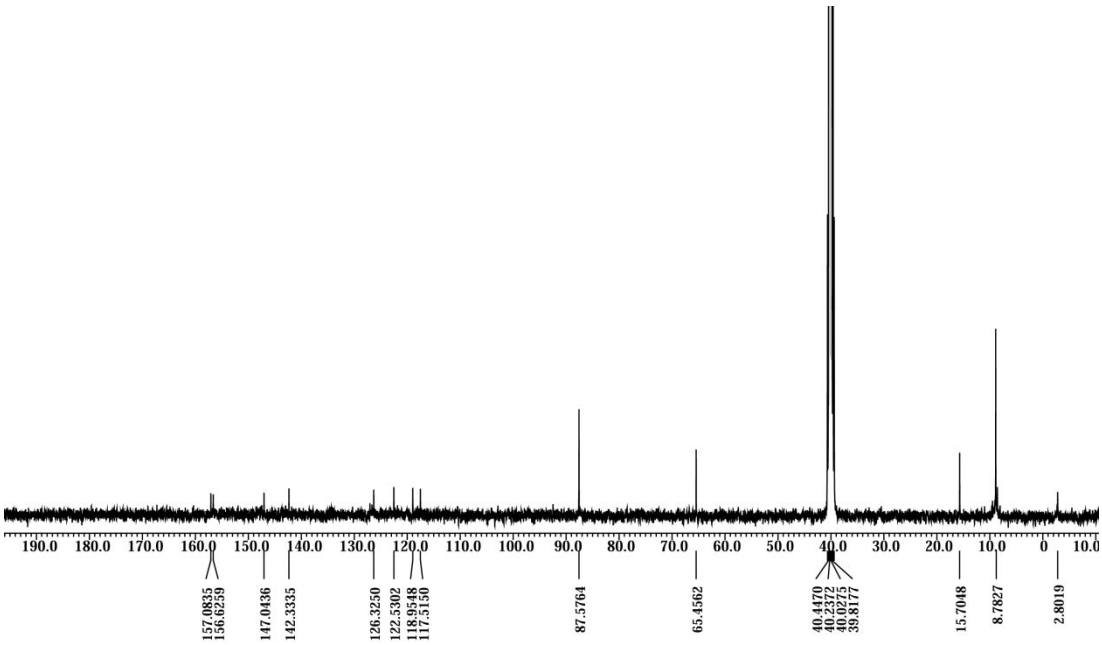


Figure 17. ^{13}C NMR of **4** in DMSO−d_6.

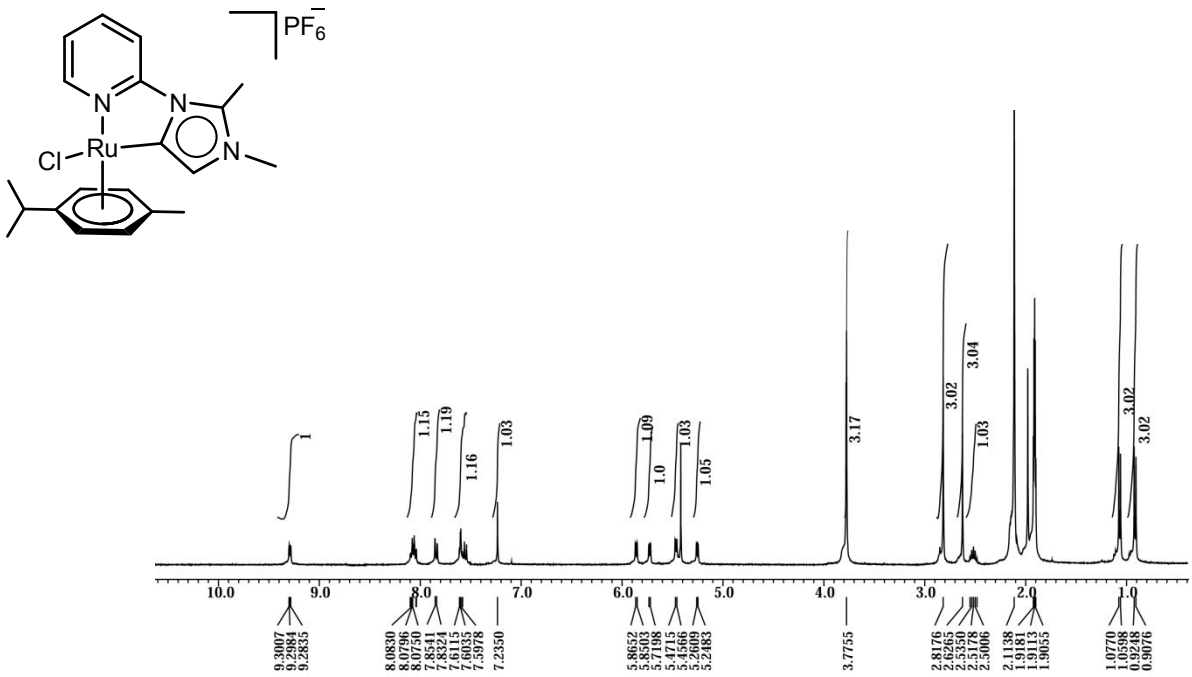


Figure S18. ^{1}H NMR of **5** in CD_3CN.

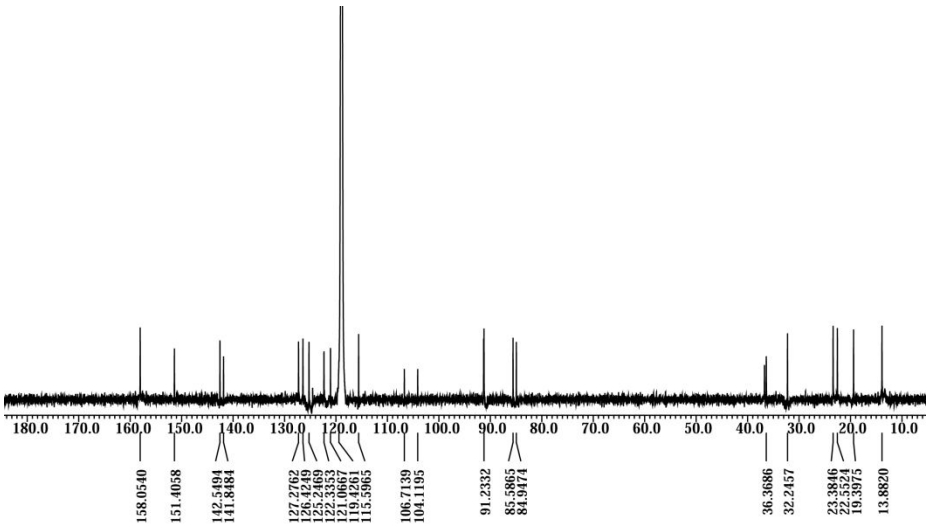


Figure S19. ^{13}C NMR of **5** in CD_3CN.

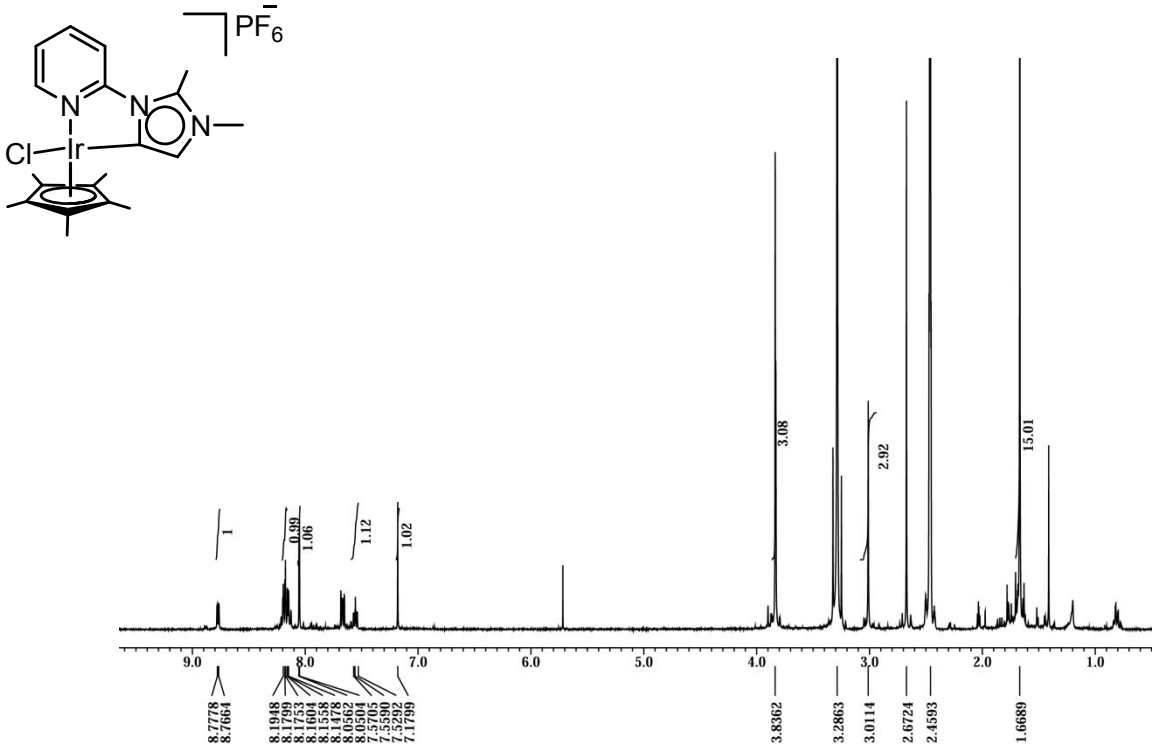


Figure S20. ^{1}H NMR of **6** in DMSO−d_6.

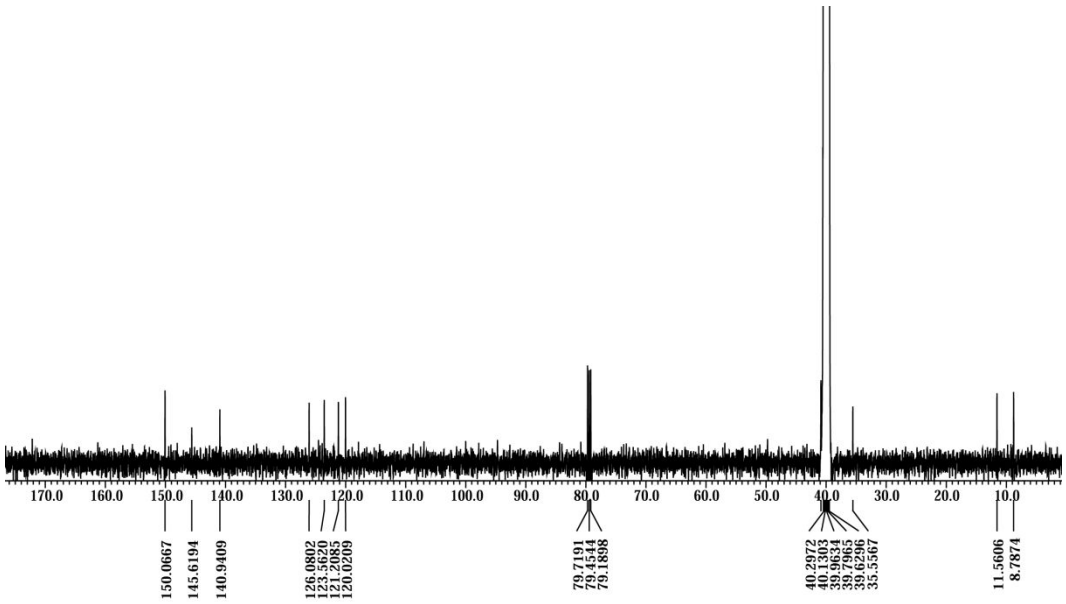


Figure S21. ^{13}C NMR of **6** in CD_3OD.

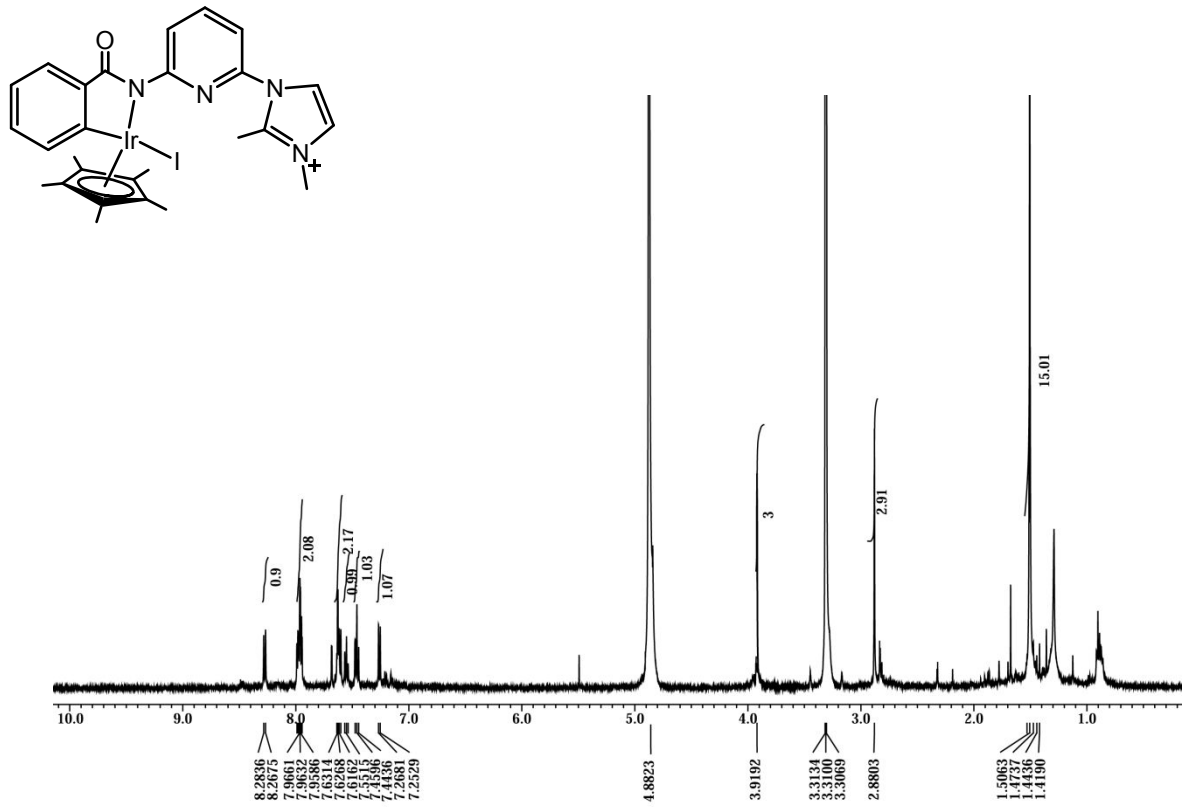


Figure S22. ^{1}H NMR of **7** in CD_3OD.

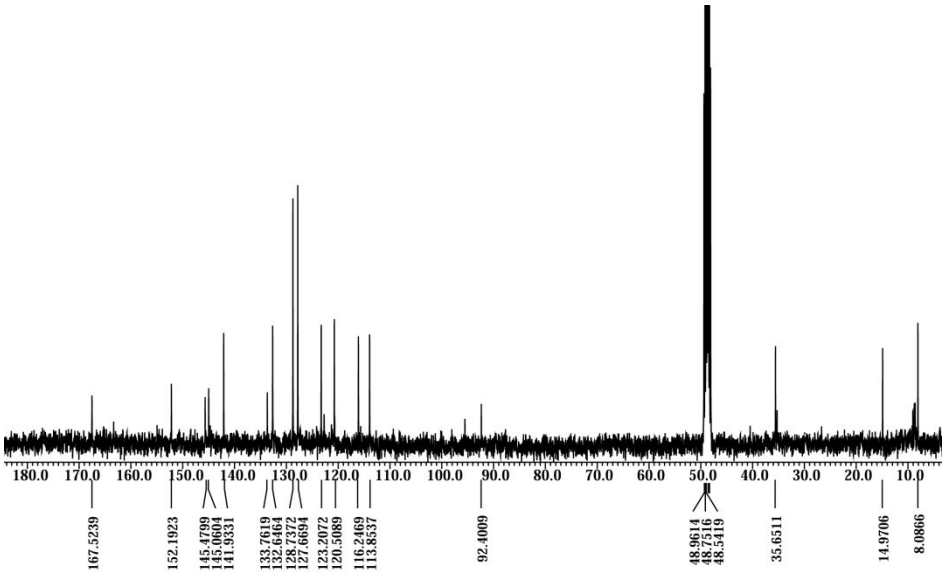


Figure S23. ^{13}C NMR of **7** in CD_3OD.

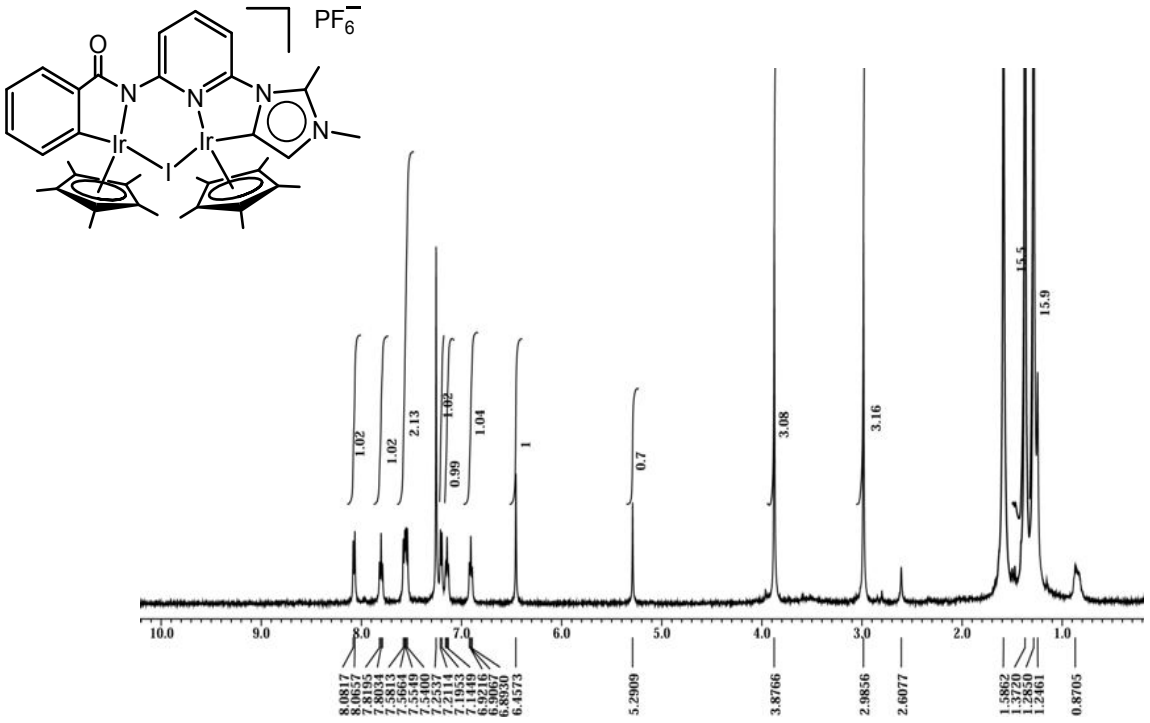


Figure S24. ^{1}H NMR of **8** in $CDCl_3$.

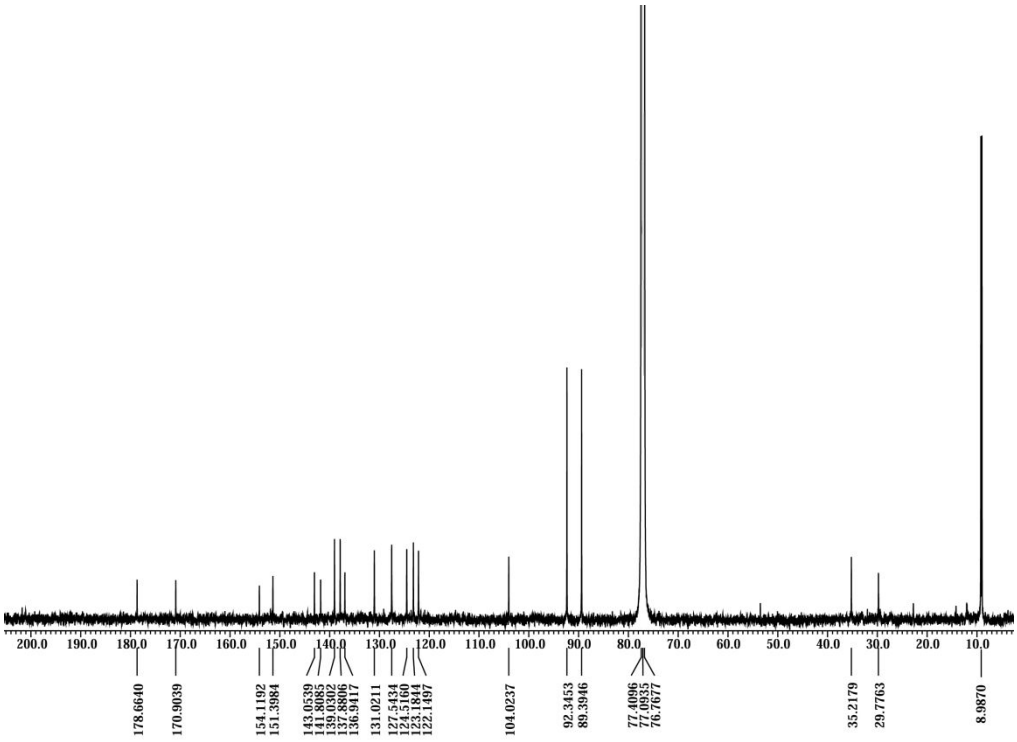
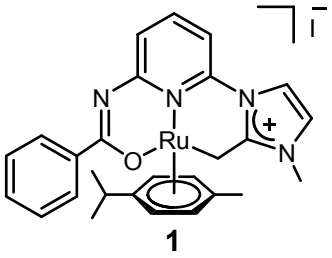


Figure S25. ^{13}C NMR of **8** in $CDCl_3$.



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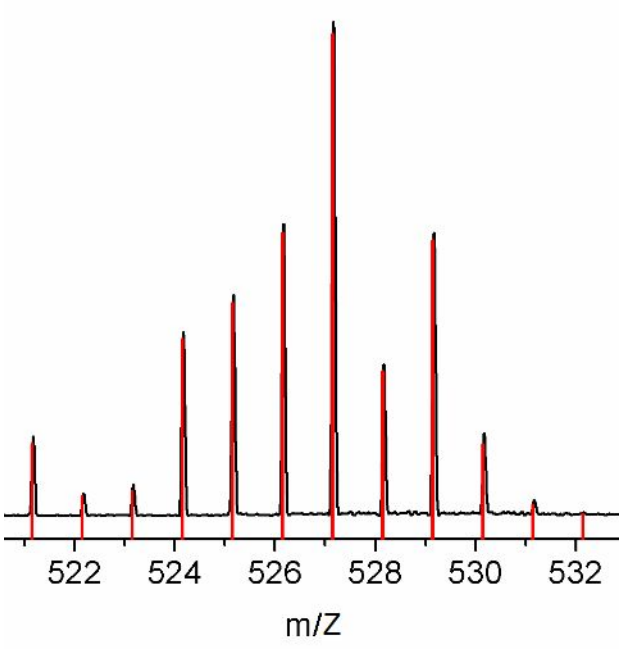
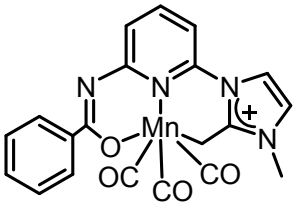


Figure S26. Experimental (black) and simulated (red) ESI-MS of [**1** – I]$^+$.



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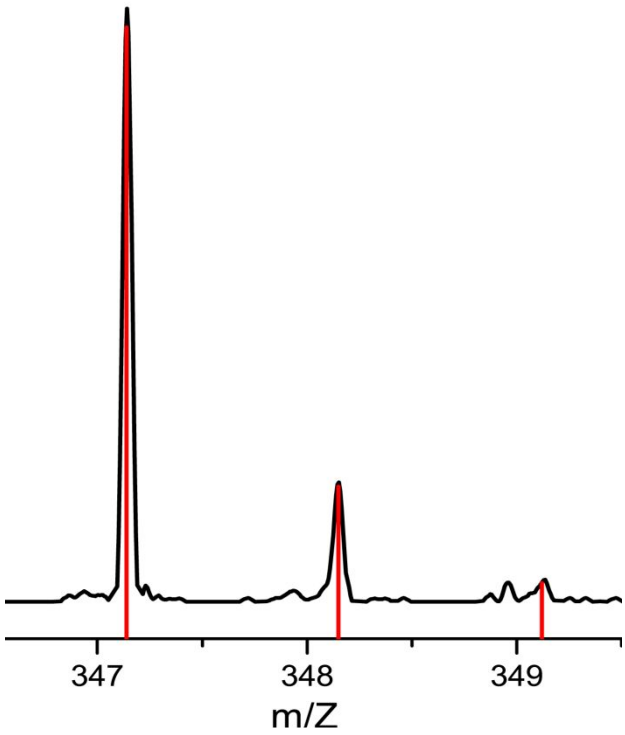


Figure S27. Experimental (black) and simulated (red) ESI-MS of [**2** – 3CO + H]$^+$.

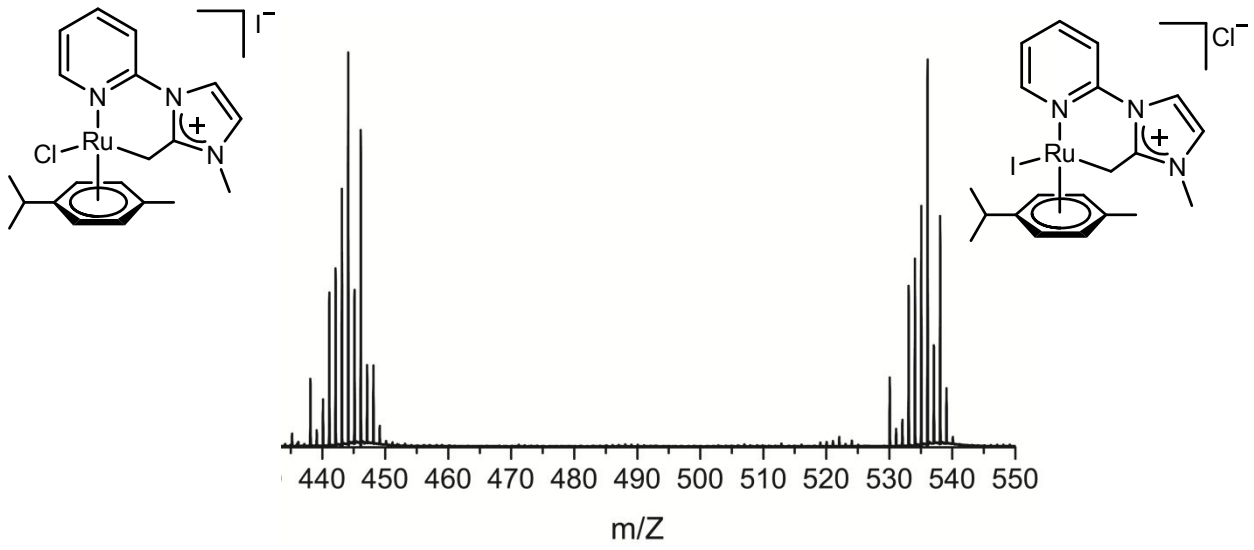
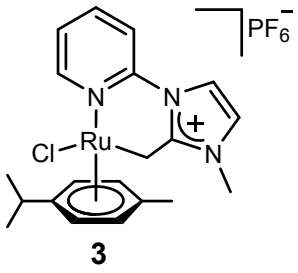


Figure S28. ESI-MS spectrum of [RuL^2(*p*-cymene)Cl]$^+$ (left) and [RuL^2(*p*-cymene)I]$^+$ (right).



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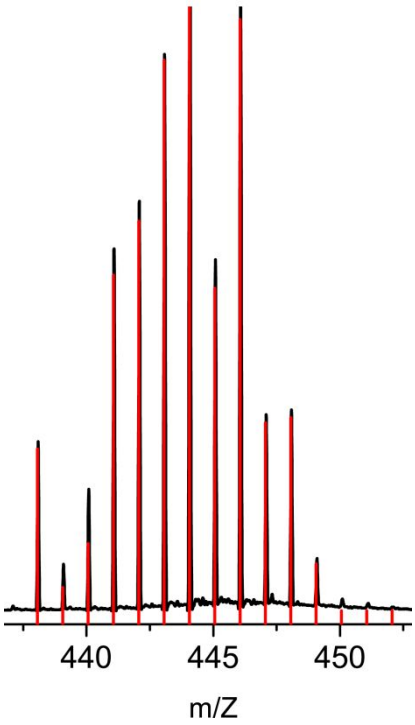


Figure S29 Experimental (black) and simulated (red) ESI-MS spectrum of [**3** – PF_6]$^+$.

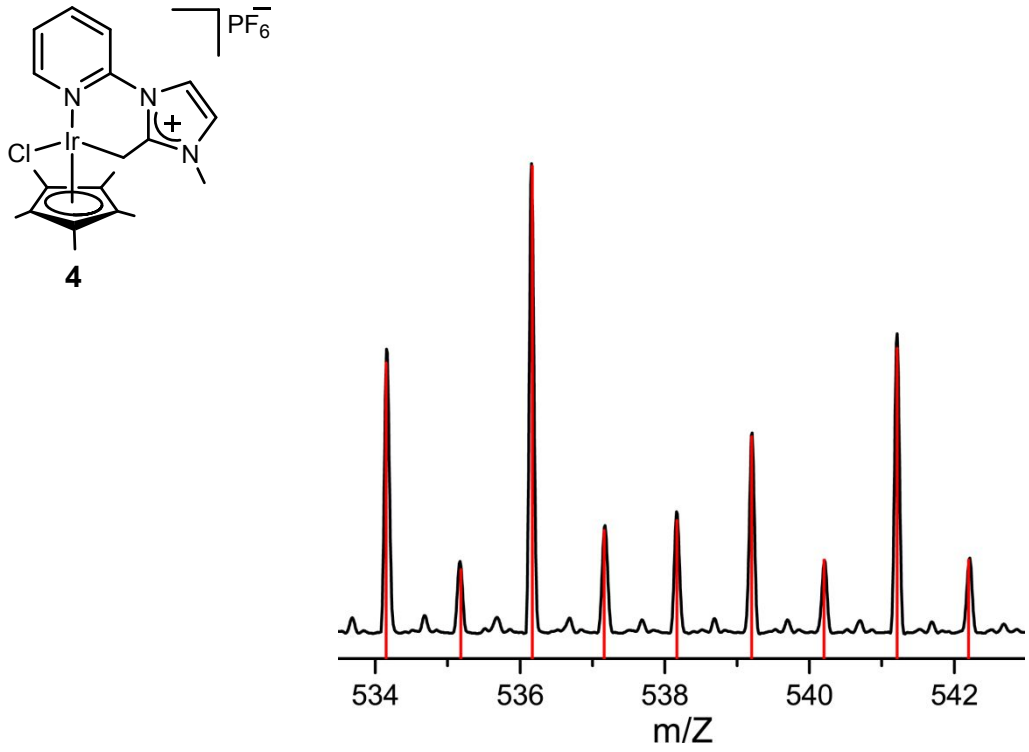


Figure S30. Experimental (black) and simulated (red) ESI-MS spectrum of [**4** – PF_6]$^+$.

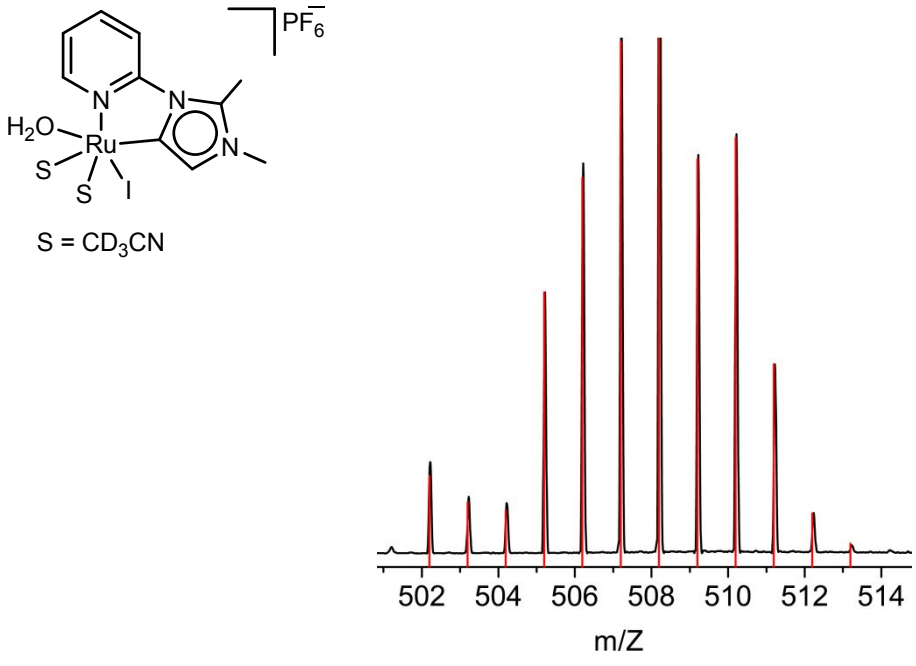


Figure S31. Experimental (black) and simulated (red) ESI-MS spectrum of [$RuL^2(CD_3CN)_2(H_2O)I$]$^+$.

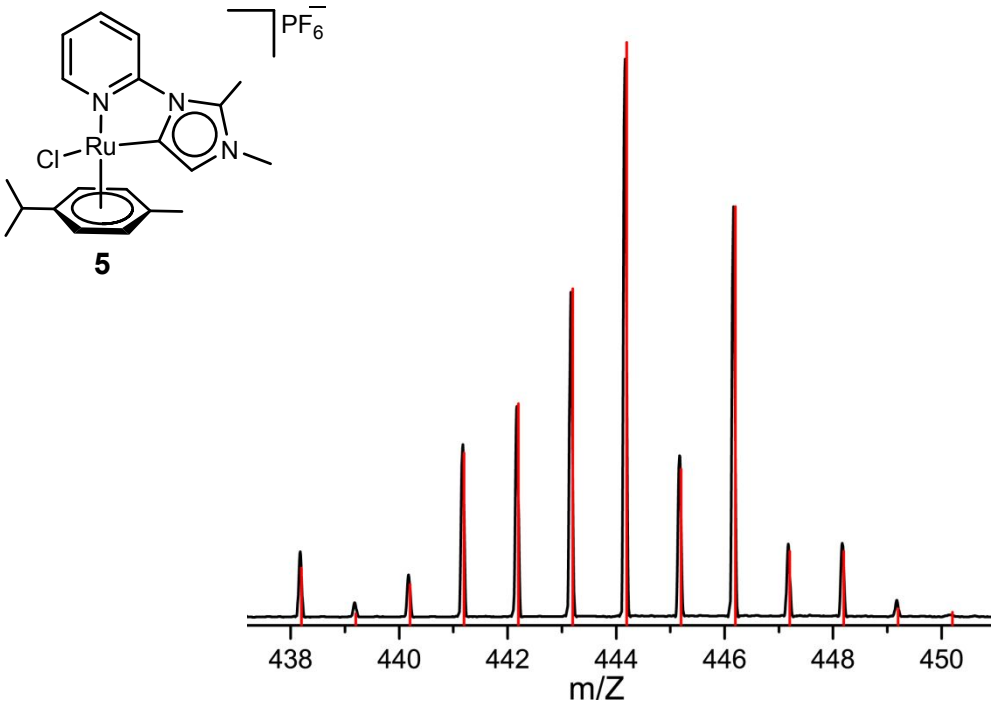


Figure S32. Experimental (black) and simulated (red) ESI-MS spectrum of [**5** – PF_6]$^+$.

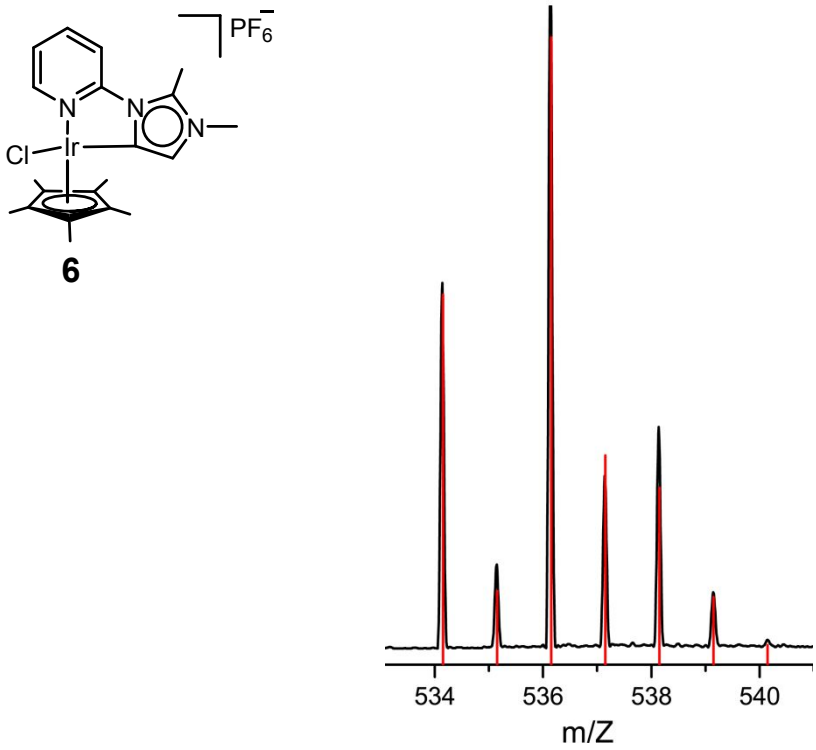
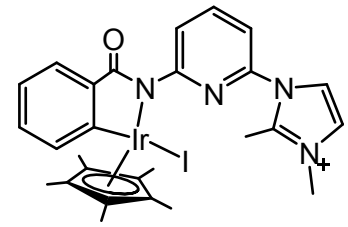


Figure S33 Experimental (black) and simulated (red) ESI-MS spectrum of [**6** – PF_6]$^+$.



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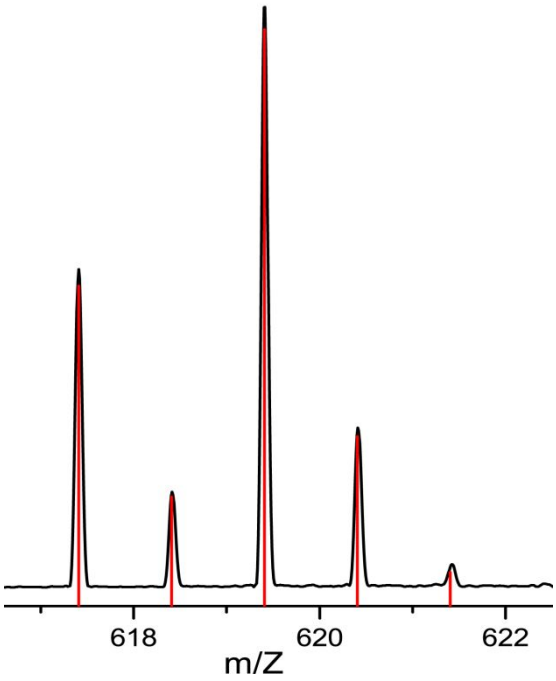
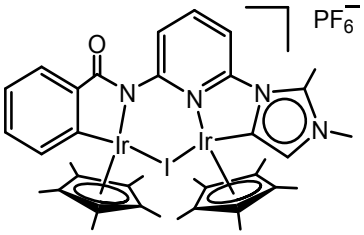


Figure S34. Experimental (black) and simulated (red) ESI-MS spectrum of [**7** – I]$^+$.



8

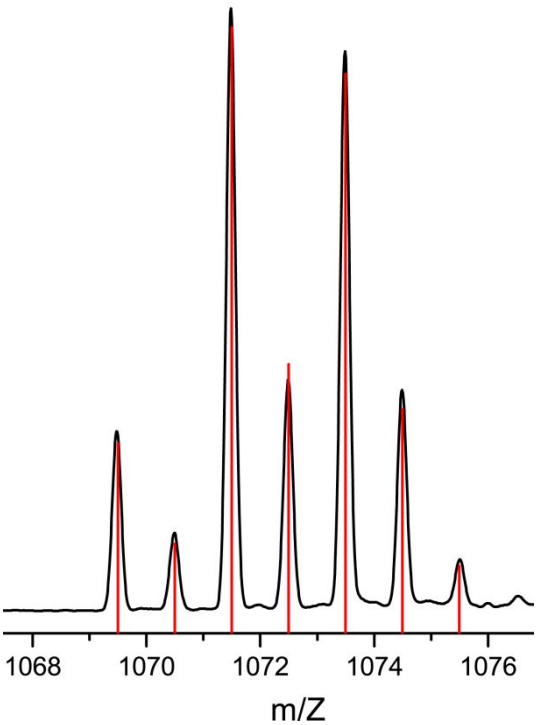


Figure S35. Experimental (black) and simulated (red) ESI-MS spectrum of [**8** – PF_6]$^+$.

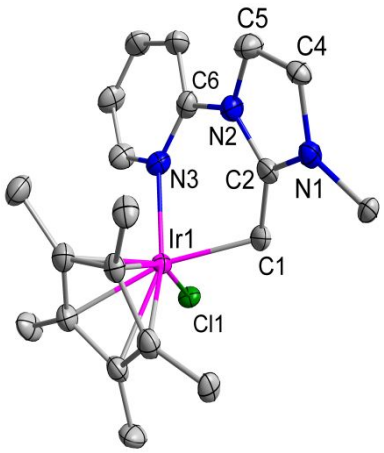


Figure S36. Molecular structure of the cationic unit of **4** with important atoms labeled. All hydrogens are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): Ir1–C1 2.115(4), Ir1–N3 2.110(4), Ir1–Cl 2.4042(11), N3–Ir1–C1 83.13(17), Ir1–C1–C2 107.1(3).

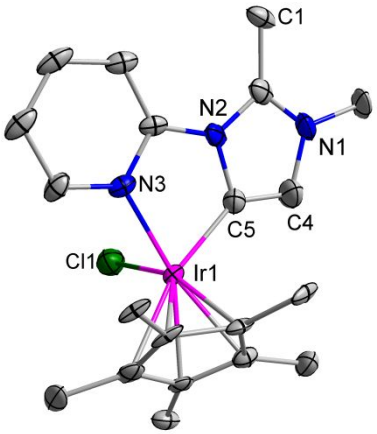


Figure S37. Molecular structure of the cationic unit of **6** with important atoms labeled. All hydrogens are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°):Ir1–C5 2.006(9), Ir1–N3 2.087(7), Ir1–Cl1 2.5200(18), N3–Ir1–C5 76.9(3).

Table S1. Crystallographic Data and Pertinent Refinement Parameters for **1, 2, 3** and **5**

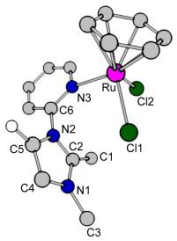
	1.CH_2Cl_2	**2**	**3**	**5.CH_2Cl_2**
Empirical formula	$C_{28}H_{27}N_4OICl_2Ru_1$	$C_{22}H_{15}N_3O_4Mn_1$	$C_{20}H_{25}ClF_6N_3PRu_1$	$C_{21}H_{27}Cl_3N_3F_6PRu_1$
Formula Weight	734.40	428.04	588.92	673.84
Crystal System	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space Group	*P2(1)/c*	*Pbca*	*Pbcm*	*P121/c1*
a (Å)	11.0142(7)	7.9705(5)	19.694(2)	7.8856(5)
b (Å)	19.7894(12)	19.0173(12)	8.8003(11)	10.7768(7)
c (Å)	13.2530(9)	23.8833(16)	12.8643(16)	30.1846(18)
α (deg)	90.00	90.00	90.00	90
β (deg)	94.325(2)	90.00	90.00	94.147(2)
γ (deg)	90.00	90.00	90.00	90
V (Å^3)	2880.5(3)	3620.2(4)	2229.5(5)	2558.4(3)
Z	4	8	4	4
ρ_{calcd} (g cm^{-3})	1.693	1.579	1.754	1.749
μ (mm^{-1})	1.830	0.766	0.958	1.049
F(000)	1448	1760	1184	1352
Reflections				
Collected	28811	26607	32452	39891
Independent	7158	3209	5570	6360
Observed [I >2σ (I)]	5749	2103	5140	5716
No. of variables	338	263	293	358
GooF	1.023	1.021	1.111	1.048
R_{int}	0.0484	0.1367	0.0507	0.0378
Final R indices	R1 = 0.0386	R1 = 0.0567	R1 = 0.0261	R1 = 0.0307
[I > 2σ(I)][a]	wR2 = 0.0861	wR2 = 0.1050	wR2 = 0.0594	wR2 = 0.0744
R indices (all data)[a]	R1 = 0.0567	R1 = 0.1080	R1 = 0.0314	R1 = 0.0361
	wR2 = 0.0925	wR2 = 0.1221	wR2 = 0.0700	wR2 = 0.0785

[a] $R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

Table S2. Crystallographic Data and Pertinent Refinement Parameters for **7**, **8** and **$[L^1H_2]I$**

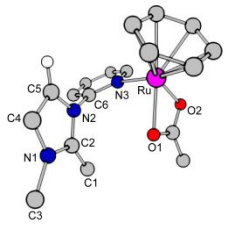
	$7.CH_2Cl_2.H_2O$	**$8.CH_2Cl_2$**	**$[L^1H_2]I$**
Empirical formula	$C_{28}H_{34}Cl_2IN_4O_2Ir_1$	$C_{75}H_{88}Cl_2F_{12}I_2N_8O_2P_2Ir_4$	$C_{17}H_{16}N_4OI$
Formula Weight	848.59	2516.97	419.24
Crystal System	Triclinic	Orthorhombic	Monoclinic
Space Group	*P-1*	*Pna21*	*P2(1)/c*
a (Å)	9.1694(6)	16.823(13)	13.1794(7)
b (Å)	10.7369(7)	10.9581(8)	7.0717(4)
c (Å)	15.2555(10)	43.218(3)	18.3002(10)
α (deg)	83.758(10)	90.00	90
β (deg)	84.308(10)	90.00	100.693(2)
γ (deg)	74.161(10)	90.00	90
V (Å^3)	1432.53(16)	7967.4(10)	1675.98(16)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.967	2.098	1.662
μ (mm^{-1})	5.958	7.621	1.920
F(000)	820	4784	828.0
Reflections			
Collected	16891	71312	24649
Independent	7114	19372	4162
Observed [I >2σ (I)]	6659	15760	3426
No. of variables	348	938	210
GooF	1.031	1.035	1.112
R_{int}	0.0236	0.0715	0.0567
Final R indices	R1 = 0.0215	R1 = 0.0459	0.0394
[I > 2σ(I)][a]	wR2 = 0.0503	wR2 = 0.0958	0.0697
R indices (all data)[a]	R1 = 0.0242	R1 = 0.0665	0.0550
	wR2 = 0.0513	wR2 = 0.1025	0.0761

[a] $R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$



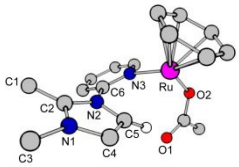
A

Ru—N3 = 2.299
Ru—Cl1 = 2.448
Ru—Cl2 = 2.423
E = -1799.043391



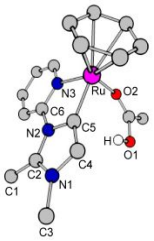
B

Ru—N3 = 2.185
Ru—O2 = 2.115
Ru—O1 = 2.156
ϕ N3–C6–N2–C5 = 86.1°
E = -1106.926124



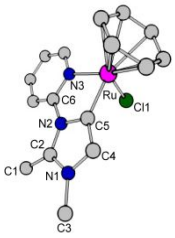
C

Ru—N3 = 2.170
Ru—C5 = 2.721
Ru—O2 = 2.046
Ru—H = 2.474
ϕ N3–C6–N2–C5 = -39.6
∠C5–Ru–H = 24.3
E = -1106.899217



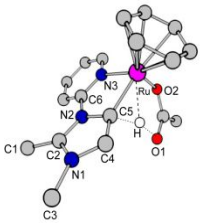
D

Ru—N3 = 2.118
Ru—C5 = 2.031
Ru—O2 = 2.170
O—H = 0.979
E = -1106.933355



E

Ru—N3 = 2.109
Ru—C5 = 2.005
Ru—Cl1 = 2.427
E= -1338.232583



TS—CD

Ru—N3 = 2.112
Ru—O2 = 2.102
Ru—C5 = 2.119
Ru—H = 2.026
O1—H = 1.500
C5—H = 1.485
E = -1106.890301

Figure S38. Optimized structures of the intermediates and the transition state (TS). Selected bond lengths (Å), bond angles (°) and energies (RB3LYP, Hartree) are given below each structure.