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Supporting Information

Functionalized pyridyl diazoles iridium complexes catalyzed FA dehydrogenation: synergistic effect of adjacent versus long-range interaction

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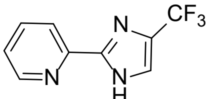
Contents

1. Synthesis of ligands

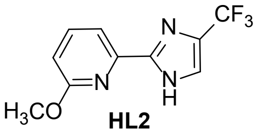
1.1. 2-(4-(trifluoromethyl)-1H-imidazol-2-yl)pyridine (HL1)



HL1

3,3-Dibromo-1,1,1-trifluoropropan-2-one (2.97 g, 0.011 mol) in batches was added to a mixture of sodium acetate (1.805 g, 0.022 mol) dissolved in water (5 mL) and stirred. Heat the resulting mixture at 100 °C for 30 minutes and cool to room temperature. Then add a solution of 2-pyridine formaldehyde (0.95 mL, 0.01 mol) dropwise in concentrated ammonia water (35 %, 10 mL) and methanol (30 mL), and continue stirring at room temperature for 12 hours. The reactant is concentrated under vacuum, dissolved in dichloromethane, and washed with water (30 mL × 3). The organic layer was dried with Na_2SO_4, filtered, and recrystallized with dichloromethane and n-hexane to obtain 1.13 g of lightly yellow crystalline powder with a yield of 53 %. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.50 (s, 1H), 8.66 (d, *J* = 4.8 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.94 (t, *J* = 7.7 Hz, 1H), 7.86 (s, 1H), 7.50 – 7.43 (m, 1H). ^{19}F NMR (376 MHz, DMSO-d6) δ -60.65 (s).

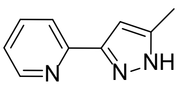
1.2. 2-methoxy-6-(4-(trifluoromethyl)-1H-imidazol-2-yl)pyridine (HL2)



HL2

3,3-Dibromo-1,1,1-trifluoropropan-2-one (2.97 g, 0.011 mol) in batches was added to a mixture of sodium acetate (1.805 g, 0.022 mol) dissolved in water (5 mL) and stirred. Heat the resulting mixture at 100 °C for 30 minutes and cool to room temperature. Then add a solution of 6-methoxy-2-pyridine formaldehyde (1.2 mL, 0.01 mol) dropwise in concentrated ammonia water (35 %, 10 mL) and methanol (30 mL), and continue stirring at room temperature for 12 hours. The reactant is concentrated under vacuum, dissolved in dichloromethane, and washed with water (30 mL × 3). The organic layer was dried with Na_2SO_4, filtered, and recrystallized with dichloromethane and n-hexane to obtain 1.22 g of lightly yellow crystalline powder with a yield of 50%. ^{1}H NMR (400 MHz, DMSO-d6) δ 13.16 (s, 1H), 7.92 (s, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.00 (s, 3H). ^{19}F NMR (376 MHz, DMSO) δ -60.72 (s).

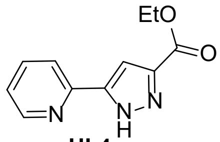
1.3. 2-(5-methyl-1H-pyrazol-3-yl)pyridine (HL3)



HL3

Add acetone (0.95 mL, 13 mmol) to THF (5 mL) suspension of NaH (0.52 g, 13 mmol) at 0 °C. Stir the mixture at room temperature for 20 minutes and then heat to 60 °C. Slowly add ethyl 2-pyridinecarboxylate (1.65 g, 10 mmol) to the mixture in a solution of THF (5 mL). After stirring the mixture at 70 °C for 20 minutes, adjust the pH of the mixture to 8-9 with dilute HCl at 0 °C. The mixture was extracted with ether (5 mL x 4), the organic layer was washed with salt water, dried with $MgSO_4$, and then concentrated under vacuum to obtain a yellow oily substance (1.79 g). Add a solution of EtOH (2 mL) with hydrazine hydrate (0.97 mL, 20 mmol) dropwise to a solution of EtOH (18 mL) with an oily substance (1.79 g). After 1 minute, the dropwise addition is completed. After refluxing the mixture for 1.5 hours, remove the solvent on the evaporator. The residue is dissolved in CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated under vacuum. Wash the residual solid with ether on filter paper and vacuum dry to obtain a white solid (0.97 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.79 – 7.65 (m, 2H), 7.22 (s, 1H), 6.57 (s, 1H), 2.37 (s, 3H).

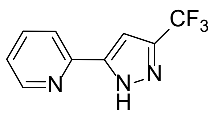
1.4. ethyl 5-(pyridin-2-yl)-1H-pyrazole-3-carboxylate (HL4)



HL4

NaOEt solution (4.1 mL, 21 wt.% in EtOH, 1.1 mmol) was added to EtOH (10 mL) solution of diethyl oxalate (1.4 mL, 10 mmol), followed by a mixture of 2-acetylpyridine (1.15 mL, 10 mmol) in EtOH (2 mL). The mixture was stirred overnight at room temperature. 2.4 N HCl (4 mL) was added to quench the reaction and extracted with EtOAc (2 × 40 mL). The merged organic layer was washed with salt water and dried with $MgSO_4$. After filtration and vacuum concentration, ethyl 2,4-dioxo-4-(pyridin-2-yl)butanoate was obtained as a brown solid (2 g, 90 %). $N_2H_4 \cdot H_2O$ (0.44 mL, 9 mmol) was added to a solution of ethyl 2,4-dioxo-4-(pyridin-2-yl)butanoate (2 g, 9 mmol) in EtOH (15 mL), and reflux the reaction mixture for 3 hours. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was diluted with Et_2O and washed with salt water. The organic layer was dried with $MgSO_4$, filtered, concentrated in vacuum and recrystallized with dichloromethane and n-hexane to obtain ethyl 5-(pyridin-2-yl) -1H-pyrazole-3-carboxylate (1.21 g, 56%) as a off white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.65 (d, J = 4.8 Hz, 1H), 7.84 – 7.69 (m, 2H), 7.29 (dd, J = 6.3, 4.8 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).

1.5. 2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (HL5)

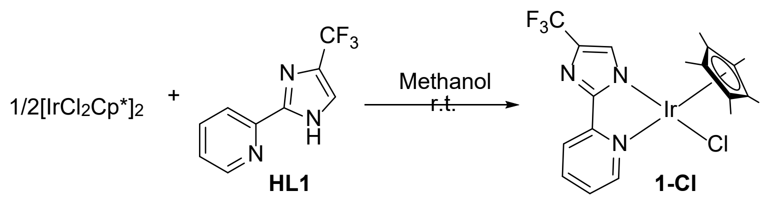


HL5

2-Acetylpyridine (1.00 g, 8.25 mmol) and ethyl trifluoroacetate (2.35 g, 16.51 mmol) was added slowly to the stirred NaH (660 mg, 60 %, 16.51 mol) suspension in THF (20 mL, dry). The mixture was stirred at room temperature for 30 minutes, then heated and refluxed overnight. The reactant is cooled and quenched with water. Adjust the pH of the mixture to 5-6 using dilute HCl (2 M), and extract the water layer with ethyl acetate (60 mL × 3). Merge the organic phase, dry with $MgSO_4$, filter, and vacuum remove the solvent to obtain 1,3-diketone. Diketone was dissolved in ethanol (20 mL) and $N_2H_4{\cdot}H_2O$ (4 mL) was added. Heat and reflux the solution overnight, then cool to room temperature. The solvent was removed by vacuum, and the residue was purified through a silica gel column (hexane: EtOAc=2:1 v/v). The recrystallization was carried out using dichloromethane and n-hexane to obtain 0.95 g of white crystalline powder, with a yield of 54 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.51 (s, 1H), 8.74 (d, J = 4.8 Hz, 1H), 7.82 (td, J = 7.8, 1.1 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.33 (dd, J = 7.1, 5.3 Hz, 1H), 6.97 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.17 (s).

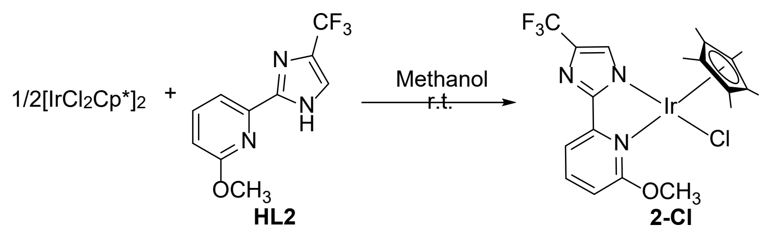
2. Synthesis of complexes

2.1. Synthesis of **1-Cl**



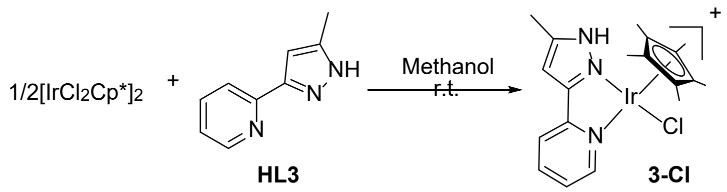
HL1 (21.3 mg, 0.1 mmol) and $[Cp^*IrCl_2]_2$ (39.8 mg, 0.05 mmol) were added to a 10 mL round bottom flask, MeOH (dry, 3 mL) was added, and stirred overnight at room temperature. The color of the solution is yellow. The solvent was spun dry under vacuum and recrystallized with dichloromethane and n-hexane to obtain 47 mg of yellow solid **1-Cl** with a yield of 82 %. ESI-MS (m/z) for $[M-Cl]^+$: found: 540.0758, calc.: 540.1234. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.74 (d, J = 5.6 Hz, 1H), 8.09 – 7.99 (m, 2H), 7.70 (s, 1H), 7.49 (dd, J = 9.2, 3.6 Hz, 1H), 1.67 (s, 15H). ^{19}F NMR (376 MHz, DMSO-d6) δ -59.01 (s).

2.2. Synthesis of **2-Cl**



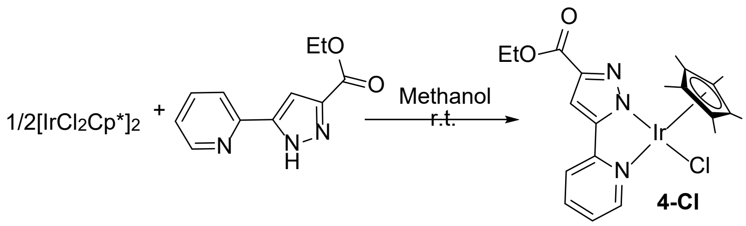
The preparation of **2-Cl** is similar to that of **1-Cl**. The yellow solid **2-Cl** was obtained through recrystallization, with a yield of 50 mg, 83 %. ESI-MS (m/z) for $[M-Cl]^+$: found: 606.0661, calc.: 606.1098. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, J = 7.5 Hz, 1H), 8.04 (t, J = 7.9 Hz, 1H), 7.51 (s, 1H), 7.09 (d, J = 8.4 Hz, 1H), 4.15 (s, 3H), 1.70 (s, 15H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.59 (s).

2.3. Synthesis of **3-Cl**



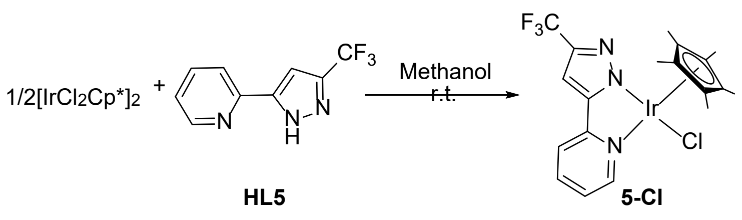
The preparation of **3-Cl** is similar to that of **1-Cl**. The yellow solid **3-Cl** was obtained through recrystallization, with a yield of 48 mg, 86 %. ESI-MS (m/z) for $[M-Cl]^+$: found: 486.0962, calc.: 486.1516. ^{1}H NMR (400 MHz, DMSO-d6) δ 14.26 (s, 1H), 8.87 (d, *J* = 5.4 Hz, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 8.22 (t, *J* = 7.5 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.11 (s, 1H), 2.54 (s, 3H), 1.70 (s, 15H).

2.4. Synthesis of **4-Cl**



The preparation of **4-Cl** is similar to that of **1-Cl**. The yellow solid **4-Cl** was obtained through recrystallization, with a yield of 46 mg, 79 %. ESI-MS (m/z) for $[M-Cl]^+$: found: 580.0592, calc.: 580.1330. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.74 (d, *J* = 5.7 Hz, 1H), 8.03 (dt, *J* = 16.5, 8.0 Hz, 2H), 7.40 (t, *J* = 6.5 Hz, 1H), 7.34 (s, 1H), 4.29 (dd, *J* = 16.4, 9.1 Hz, 2H), 1.66 (s, 15H), 1.31 (t, *J* = 7.1 Hz, 3H).

2.5. Synthesis of **5-Cl**



The preparation of **5-Cl** is similar to that of **1-Cl**. The yellow solid **5-Cl** was obtained with a yield of 40 mg, 70 %. ESI-MS (m/z) for $[M-Cl]^+$: found: 540.0612, calc.: 540.1234. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.5 Hz, 1H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 6.3 Hz, 1H), 6.82 (s, 1H), 1.75 (s, 15H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.44 (s).

3. FA dehydrogenation

3.1. The influence of catalyst types on dehydrogenation performance of formic acid

Table S1. The effect of catalyst types on dehydrogenation of FA

entry	Cat.	T(°C)	TON	TOF(h^{-1})
1	**1-H_2O**	90	1685	6738
2	**2-H_2O**	90	3946	15784
3	**3-H_2O**	90	1225	4901
4	**4-H_2O**	90	2164	8658
5	**5-H_2O**	90	6483	25932

Reaction conditions: catalyst, FA (4 mmol), H_2O (2 mL), and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 15 minutes.

3.2. The effect of amount of catalyst on dehydrogenation of FA using **2-H_2O** and **5-H_2O**

3.2.1. The effect of amount of catalyst on dehydrogenation of FA in **2-H_2O**

Table S2. The effect of amount of catalyst on dehydrogenation of FA in **2-H_2O**

entry	$n_{cat.}$(μmol)	T(°C)	TON	TOF(h^{-1})
1	4	90	746	8952
2	0.8	90	1169	14028
3	0.4	90	1475	17700
4	0.2	90	1184	14208

Reaction conditions: catalyst**2-H_2O**, FA (4 mmol), H_2O (2 mL), and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 5 minutes.

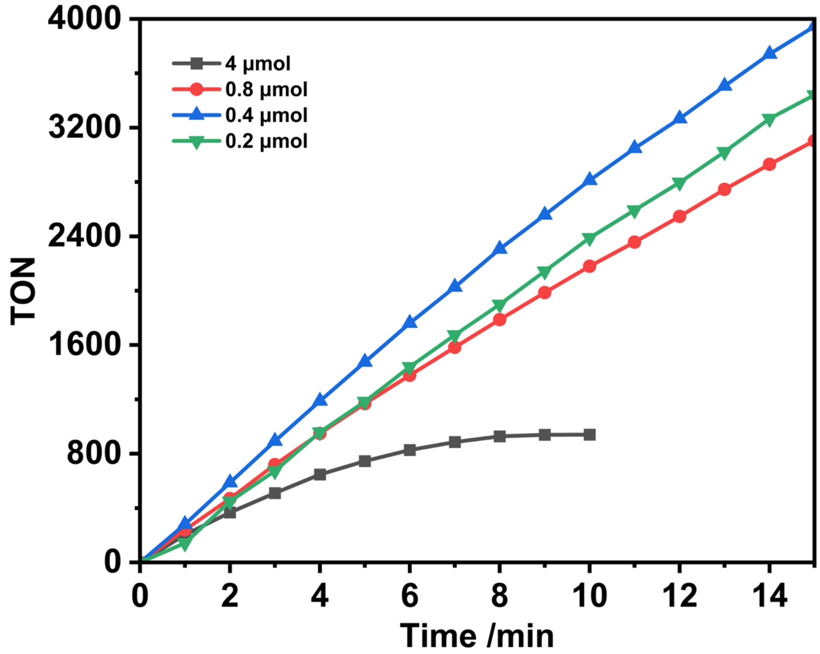


Figure S1. The effect of amount of catalyst on catalytic activity of **2-H_2O**

3.2.2. The effect of amount of catalyst on dehydrogenation of FA in **5-H_2O**

Table S3. The effect of amount of catalyst on dehydrogenation of FA in **5-H_2O**

entry	$n_{cat.}$(μmol)	T(°C)	TON	TOF(h^{-1})
1	1.6	90	1429	17148
2	0.8	90	2149	25788
3	0.4	90	2619	31428
4	0.2	90	2757	33084
5	0.08	90	2425	29100

Reaction conditions: catalyst**5-H_2O**, FA (4 mmol), H_2O (2 mL), and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 5 minutes.

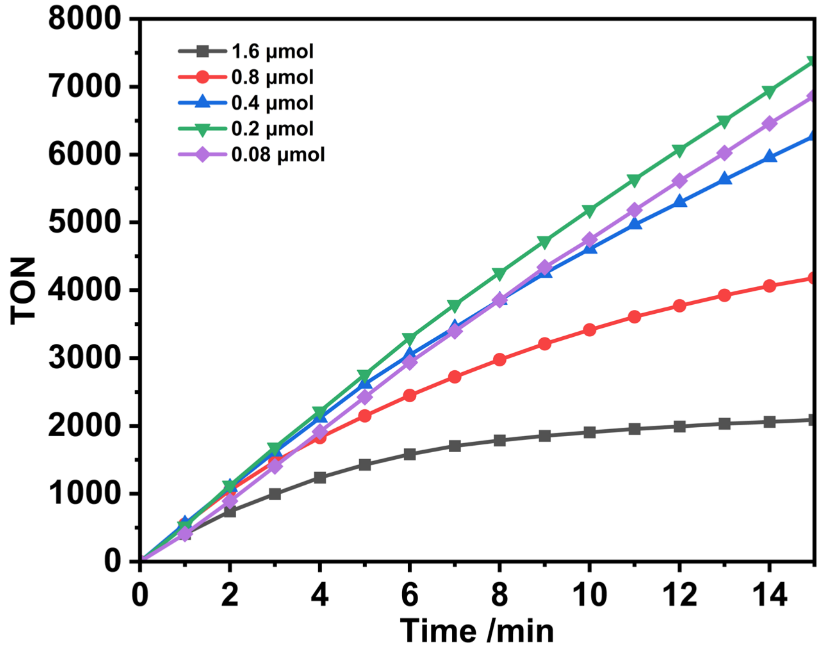


Figure S2. The effect of amount of catalyst on catalytic activity of **5-H_2O**

3.3. The influence of FA concentration on FA dehydrogenation using **2-H_2O** and **5-H_2O**

3.3.1. The influence of FA concentration on FA dehydrogenation in **2-H_2O**

Table S4. The effect of FA concentration on FA dehydrogenation in **2-H_2O**[a]

entry	Cat.	C_{HCOOH}(mol/L)	TON[b]	Time(h)	TON[c]	TOF(h^{-1})	Conv./%
1	**2-H_2O**	0.5	2455	0.35	919	11028	98
2	**2-H_2O**	2	8888	0.77	1475	17700	89
3	**2-H_2O**	4	16999	1.58	1373	16476	85
4	**2-H_2O**	8	13773	3.5	786	9432	34.4
5	**2-H_2O**	25	-	-	-	-	-

[a] **Reaction conditions: 2-H_2O** (0.4 μmol), solution (2 mL), T=90 °C, and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 5 minutes. b is the TON at the end of the reaction, and c is the TON at 5 minutes of the reaction.

3.3.2. The influence of FA concentration on FA dehydrogenation in **5-H_2O**

Table S5. The effect of FA concentration on FA dehydrogenation in **5-H_2O**[a]

entry	Cat.	C_{HCOOH}(mol/L)	TON[b]	Time(h)	TON[c]	TOF(h^{-1})	Conv./%
1	**5-H_2O**	0.5	2700	0.38	1511	18132	100
2	**5-H_2O**	2	9597	0.6	2619	31428	96
3	**5-H_2O**	4	19169	1.08	2379	28548	96
4	**5-H_2O**	8	37919	2.67	1531	18377	95
5	**5-H_2O**	25	-	-	-	-	-

[a] **Reaction conditions: 5-H_2O** (0.4 μmol), solution (2 mL), T=90 °C, and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 5 minutes. b is the TON at the end of the reaction, and c is the TON at 5 minutes of the reaction.

3.4. The influence of pH on dehydrogenation of FA using **2-H_2O** and **5-H_2O**

3.4.1. The influence of pH on dehydrogenation of FA in **2-H_2O**

Table S6. The influence of pH on dehydrogenation of FA in **2-H_2O**

entry	Cat.	pH	TON	TOF(h^{-1})
1	**2-H_2O**	1.46	1475	17700
2	**2-H_2O**	3.04	2348	28176
3	**2-H_2O**	3.60	1123	13476
4	**2-H_2O**	4.18	332	3984
5	**2-H_2O**	7.25	-	-

Reaction conditions: catalyst **2-H_2O** (0.4 μmol), solution (2 mL), T=90 °C, and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 5 minutes.

3.4.2. The influence of pH on dehydrogenation of FA in **5-H_2O**

Table S7. The influence of pH on dehydrogenation of FA in **5-H_2O**

entry	Cat.	pH	TON	TOF(h^{-1})
1	**5-H_2O**	1.46	2619	31428
2	**5-H_2O**	3.04	766	9192
3	**5-H_2O**	3.60	265	3185
4	**5-H_2O**	4.18	46	551
5	**5-H_2O**	7.25	-	-

Reaction conditions: catalyst **5-H_2O** (0.4 μmol), solution (2 mL), T=90 °C, and TON=$n_{released\ gas}/2n_{catalyst}$. TOF is based on the released gas in the first 5 minutes.

3.5. The effect of temperature on the catalytic activity of formic acid dehydrogenation using **2-H_2O** and **5-H_2O**

3.5.1. The effect of temperature on the catalytic activity of formic acid dehydrogenation in **2-H_2O**

Table S8. The effect of temperature on the catalytic activity of formic acid in **2-H_2O**

entry	T(K)	TON	TOF(h^{-1})
1	333.15	919	3732
2	343.15	1833	8820
3	353.15	2624	14700
4	363.15	4155	28176

Reaction conditions: catalyst **2-H_2O** (0.4 μmol), solution (2 mL), pH=3.04 and TON=$n_{released\ gas}/2n_{catalyst}$. TON is based on the released gas in the first 15 minutes. TOF is based on the released gas in the first 5 minutes.

3.5.2. The effect of temperature on the catalytic activity of formic acid dehydrogenation in **5-H_2O**

Table S9. The effect of temperature on the catalytic activity of formic acid in **5-H_2O**

entry	T(K)	TON	TOF(h^{-1})
1	333.15	1154	4778
2	343.15	2404	10291
3	353.15	4191	20522
4	363.15	6274	31428

Reaction conditions: catalyst **5-H_2O** (0.4 μmol), solution (2 mL), pH=1.46 and TON=$n_{released\ gas}/2n_{catalyst}$. TON is based on the released gas in the first 15 minutes. TOF is based on the released gas in the first 5 minutes.

4. Characterization analysis

4.1. ^{1}H NMR and ^{19}F NMR spectra

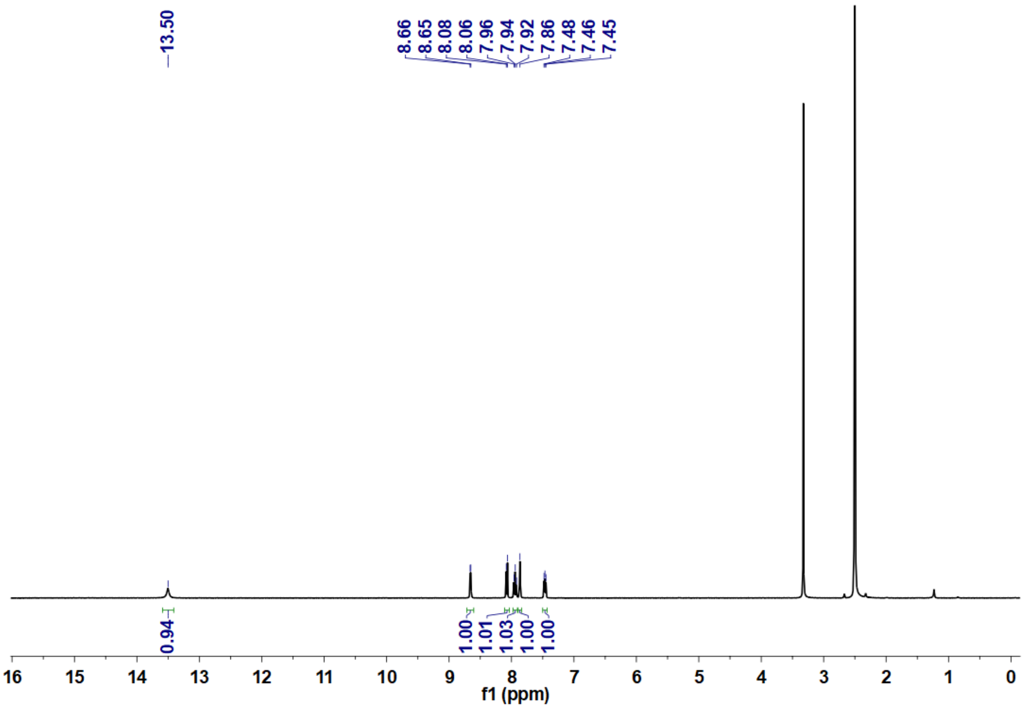


Figure S3. ^{1}H NMR of HL1 (DMSO-d6)

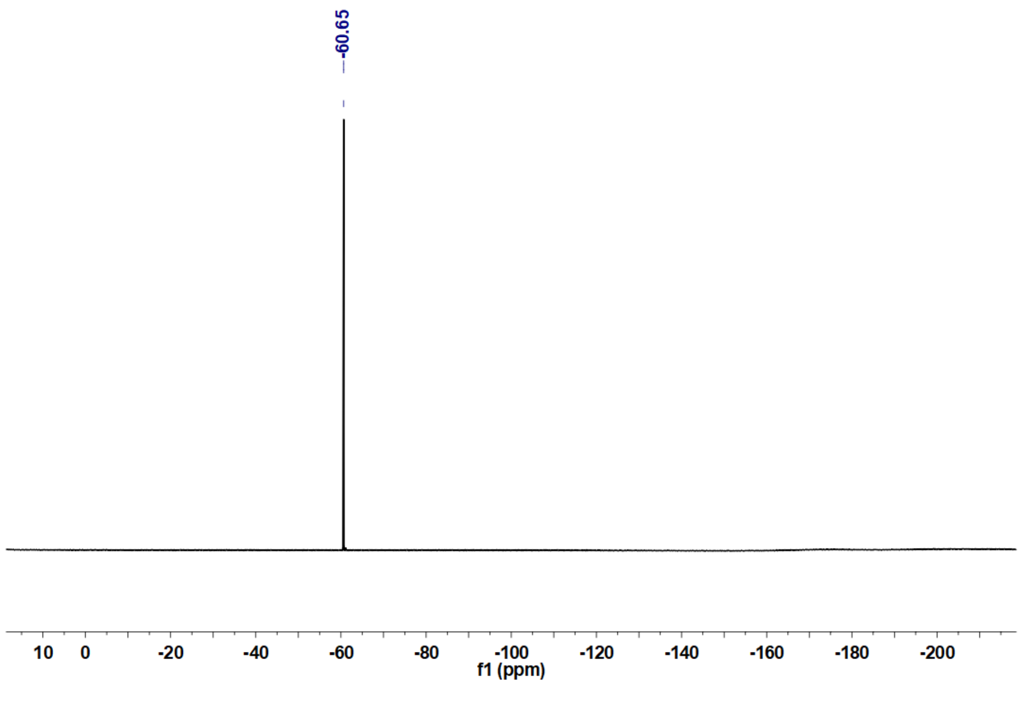


Figure S4. ^{19}F NMR of HL1 (DMSO-d6)

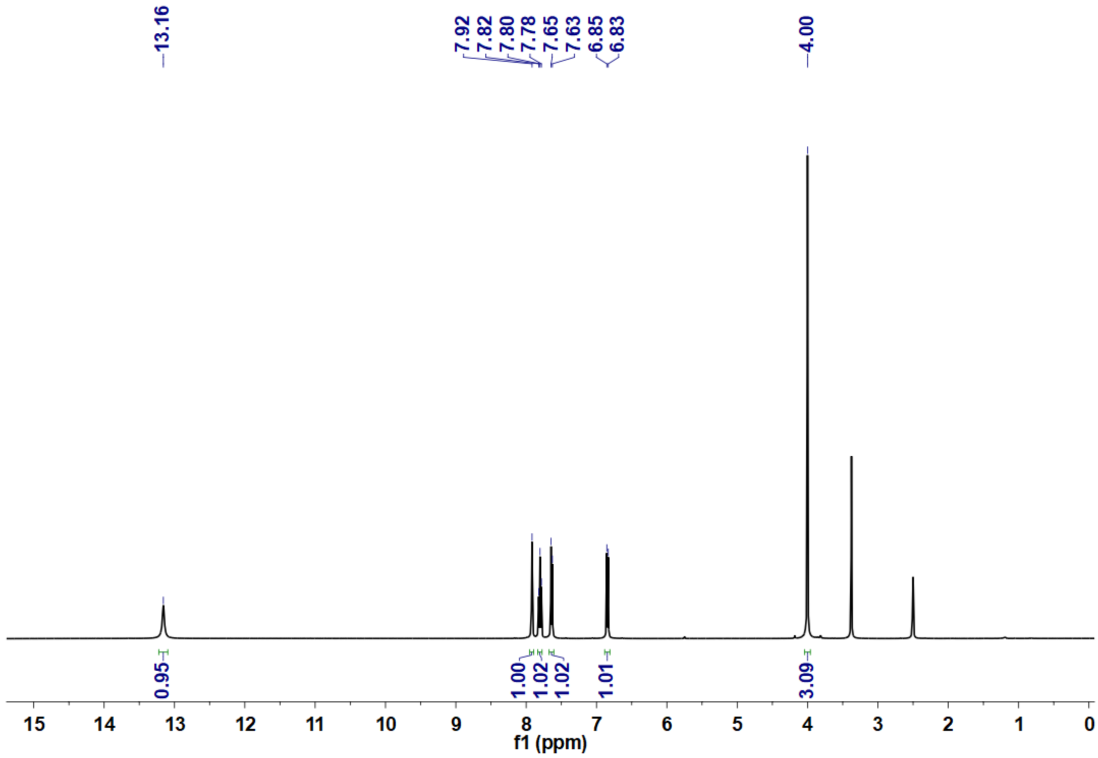


Figure S5. ^{1}H NMR of HL2 (DMSO-d6)

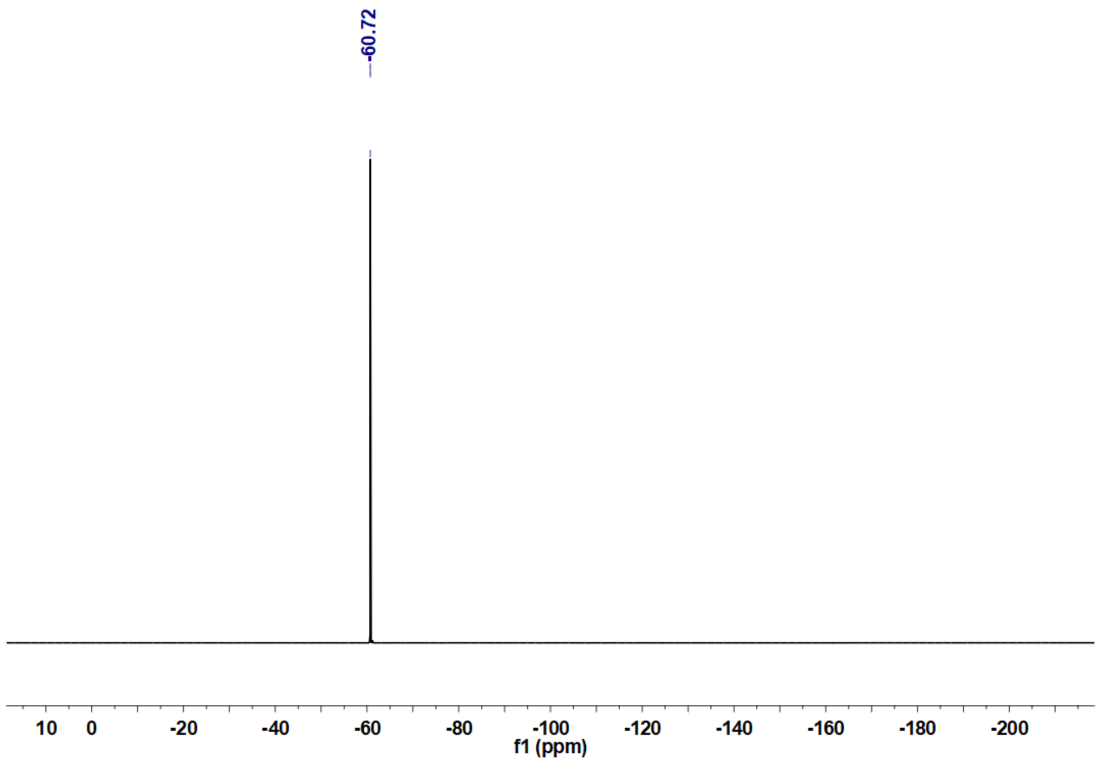


Figure S6. ^{19}F NMR of HL2 (DMSO-d6)

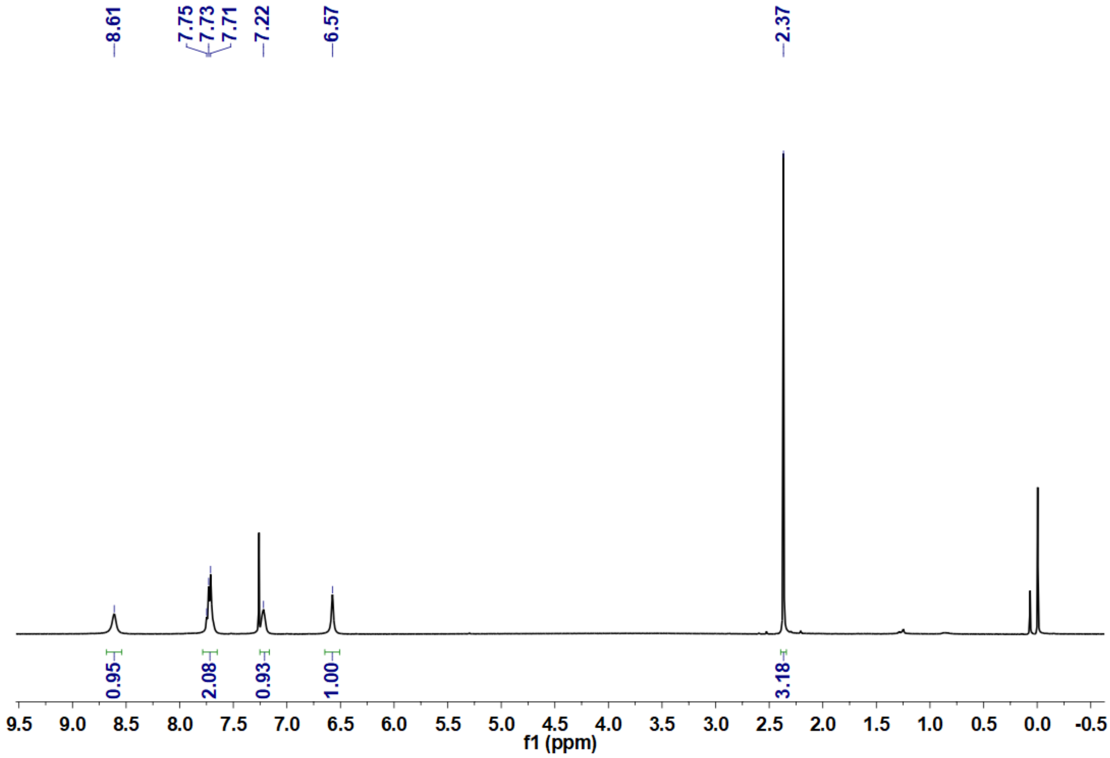


Figure S7. ^{1}H NMR of HL3 ($CDCl_3$)

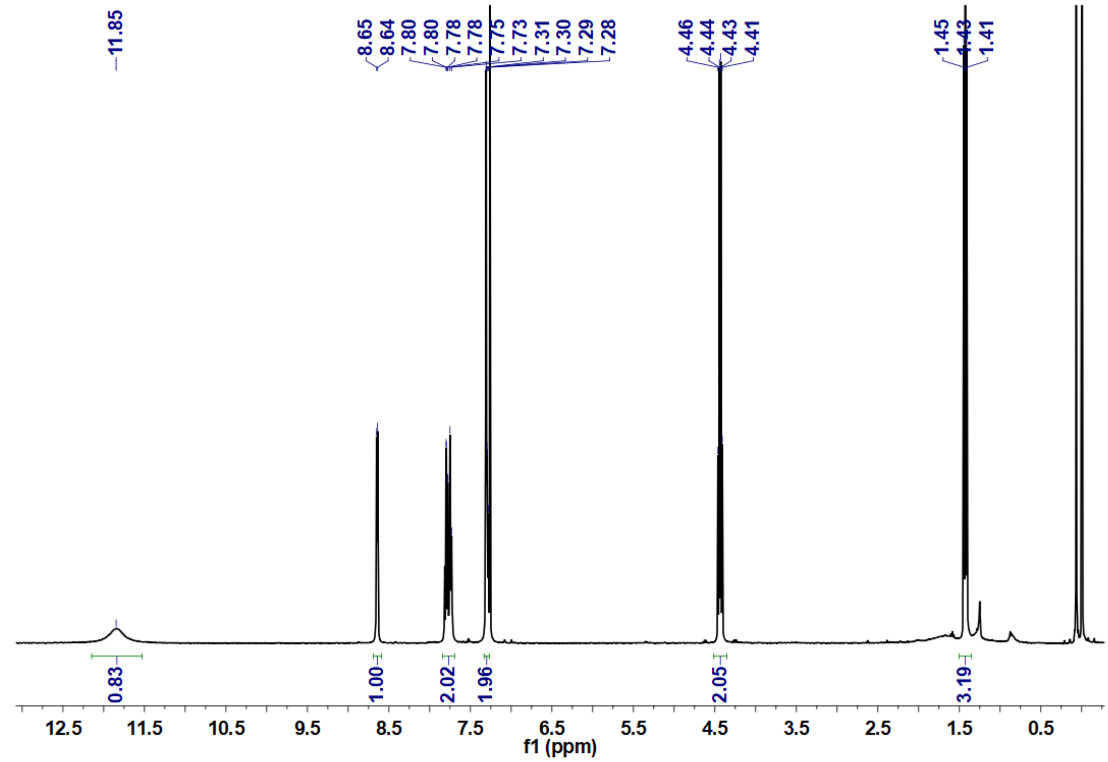


Figure S8. ^{1}H NMR of HL4 ($CDCl_3$)

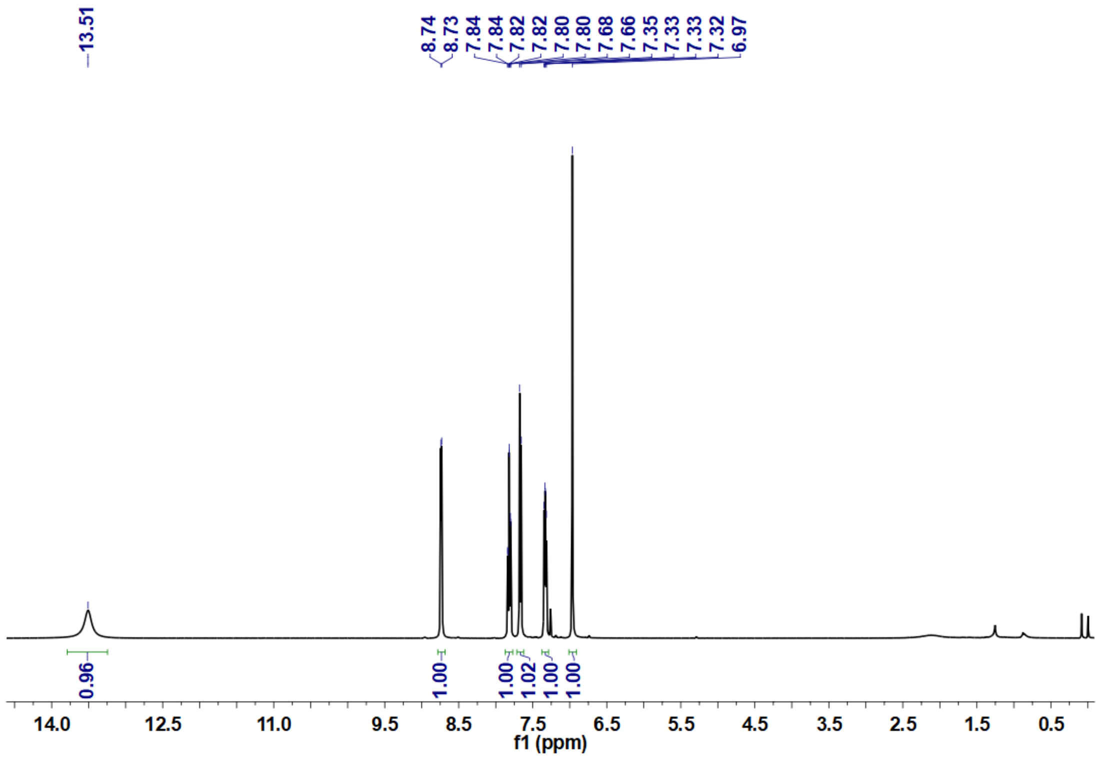


Figure S9. ^{1}H NMR of HL5 ($CDCl_3$)

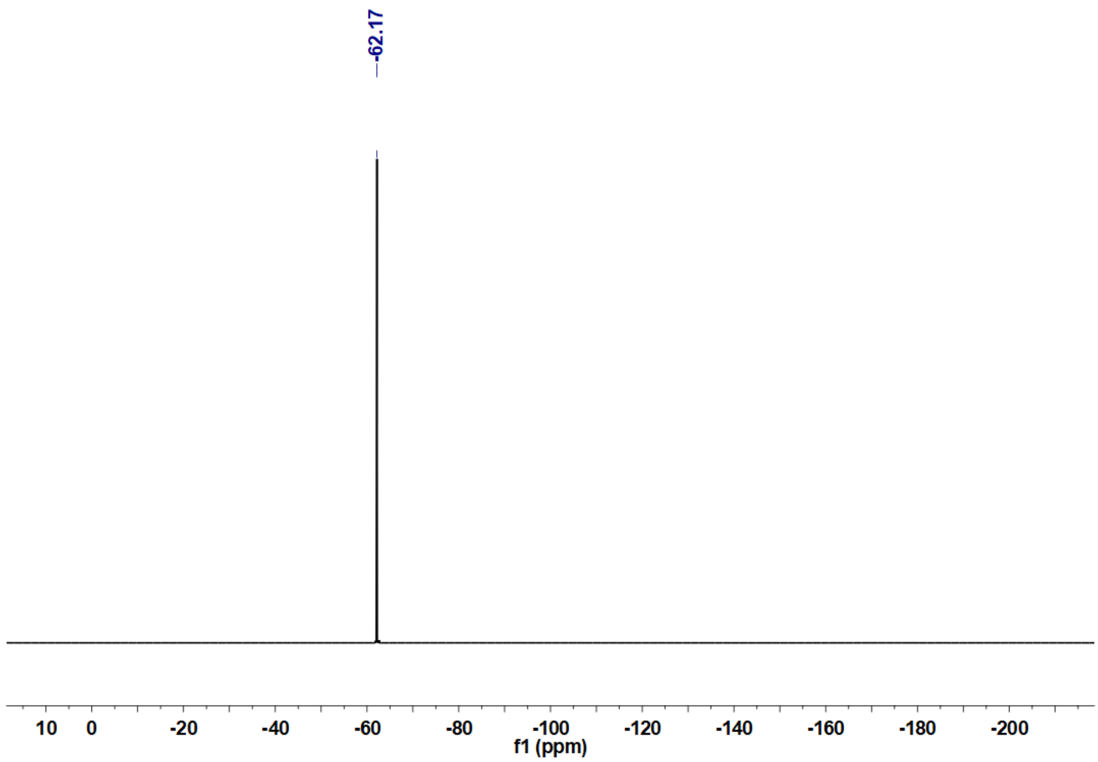


Figure S10. ^{19}F NMR of HL2 (DMSO-d6)

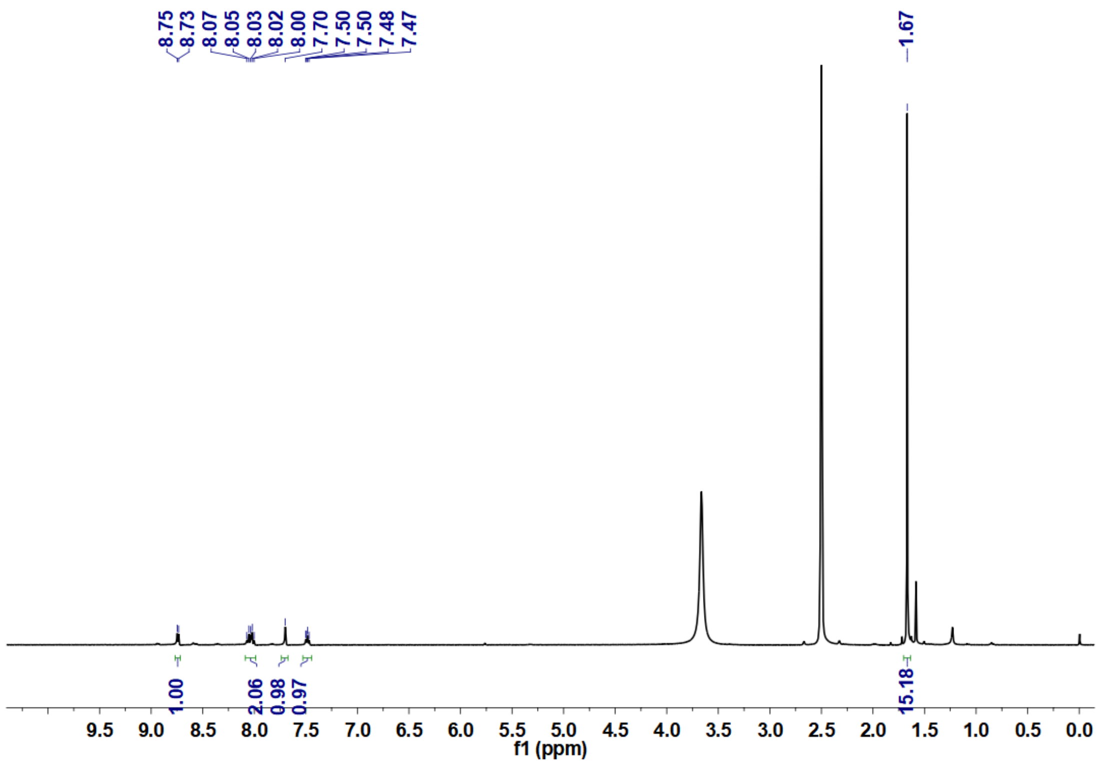


Figure S11. ^{1}H NMR of complex **1-Cl** (DMSO-d6)

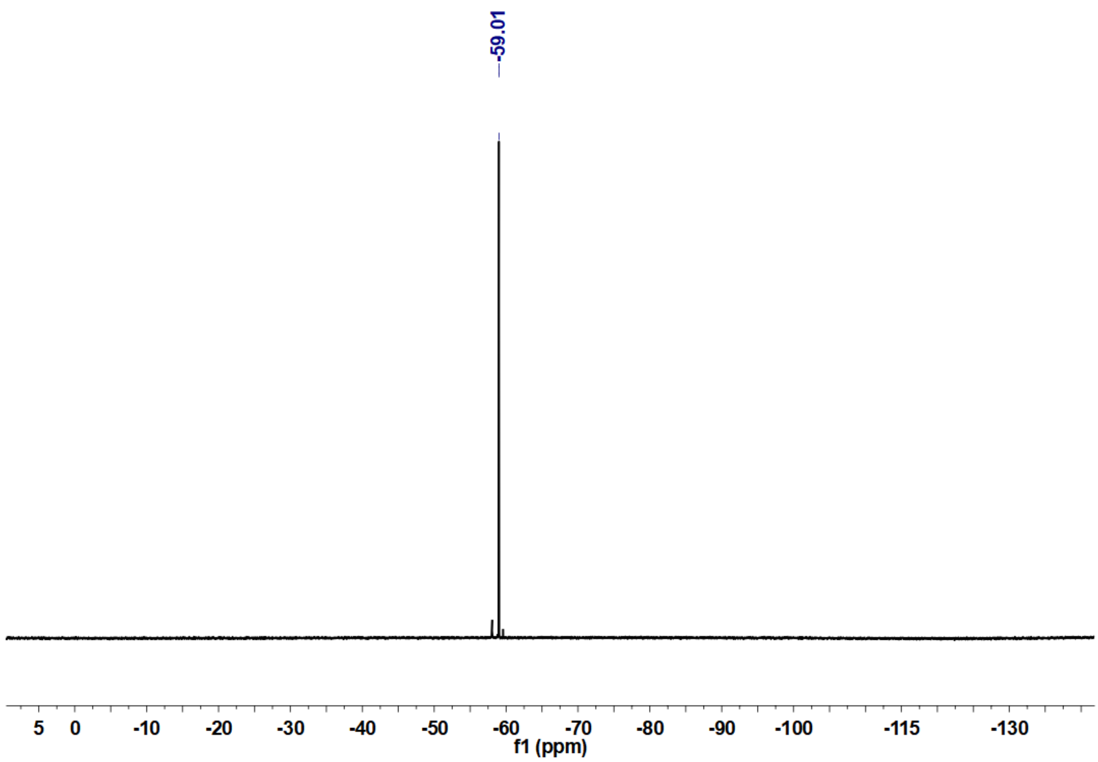


Figure S12. ^{19}F NMR of complex **1-Cl** (DMSO-d6)

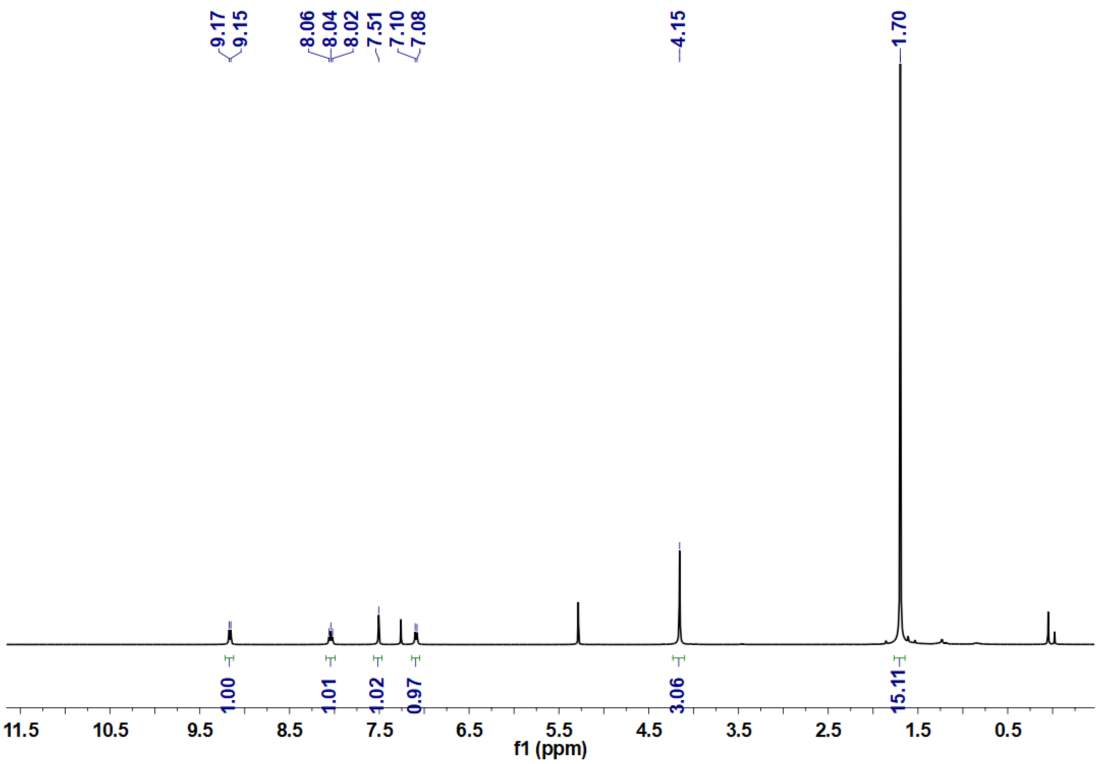


Figure S13. ^{1}H NMR of complex **2-Cl** ($CDCl_3$)

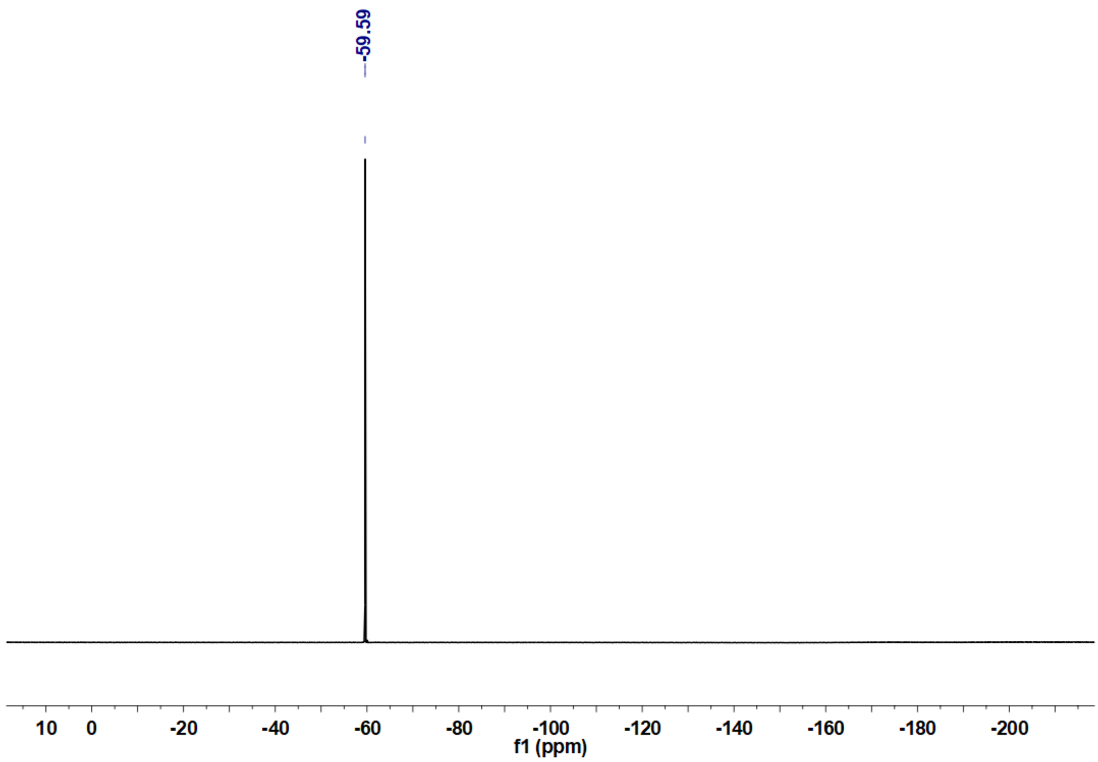


Figure S14. ^{19}F NMR of complex **2-Cl** ($CDCl_3$)

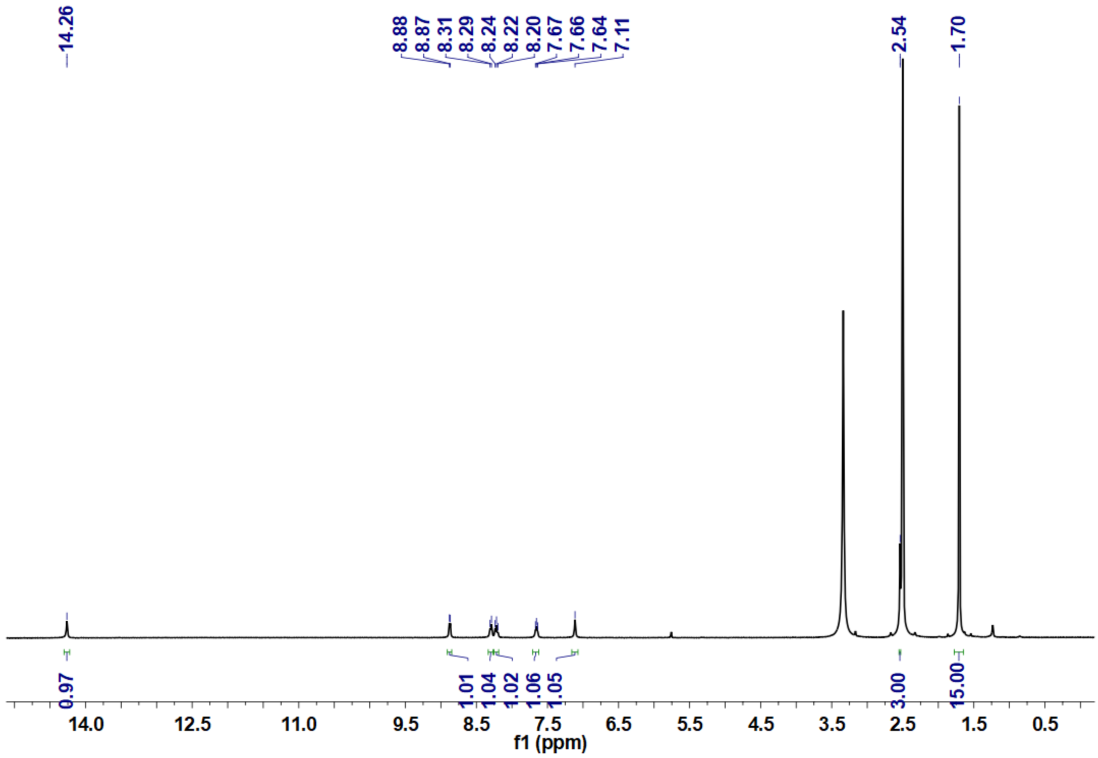


Figure S15. ^{1}H NMR of complex **3-Cl** (DMSO-d6)

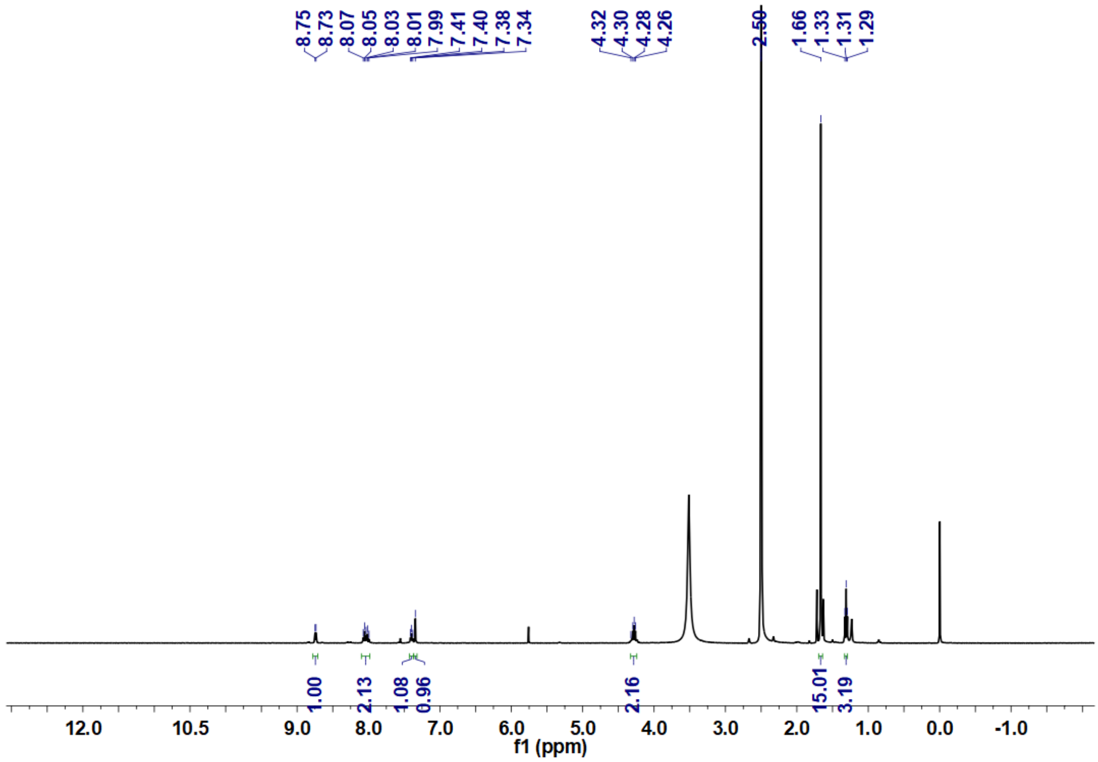


Figure S16. ^{1}H NMR of complex **4-Cl** (DMSO-d6)

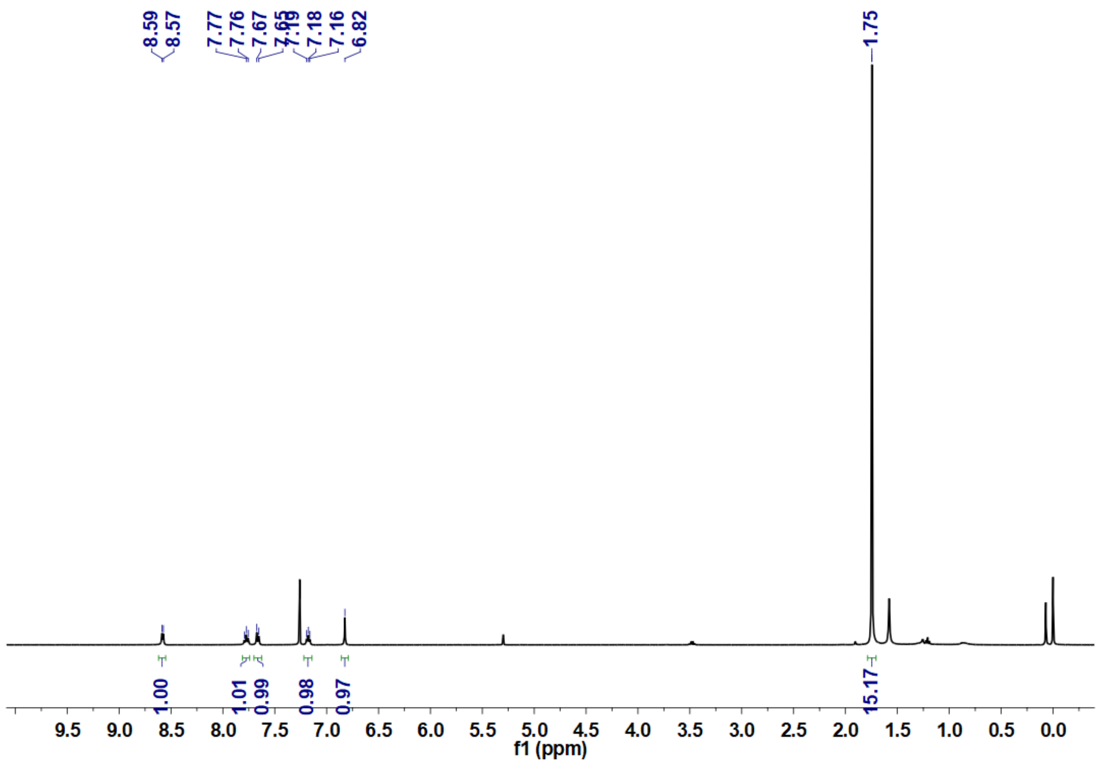


Figure S17. ^{1}H NMR of complex **5-Cl** ($CDCl_3$)

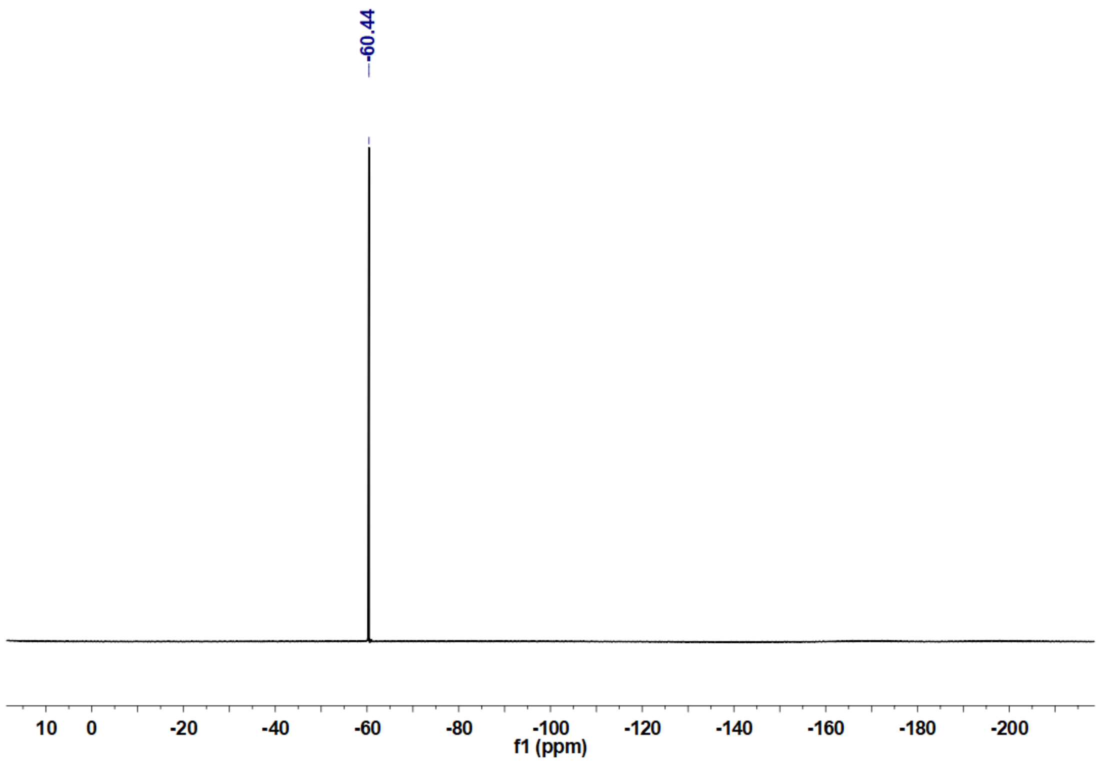


Figure S18. ^{19}F NMR of complex **5-Cl** ($CDCl_3$)

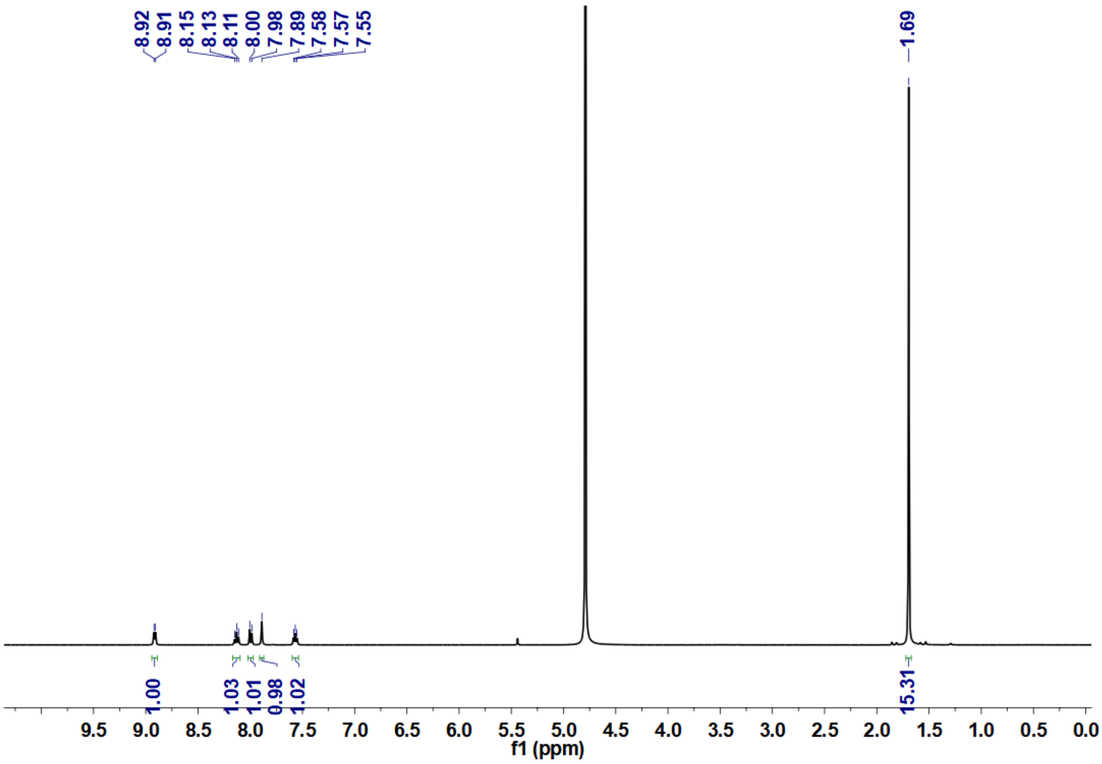


Figure S19. ^{1}H NMR of complex **1-H$_2$O** (D_2O)

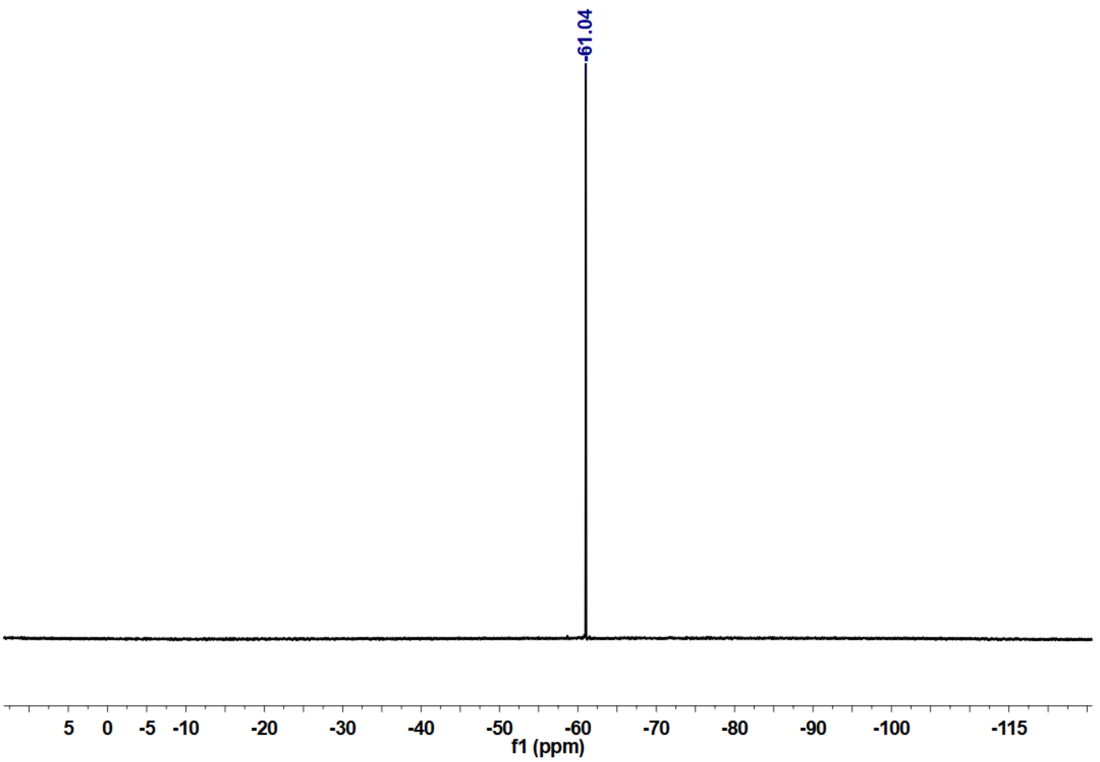


Figure S20. ^{19}F NMR of complex **1-H$_2$O** (D_2O)

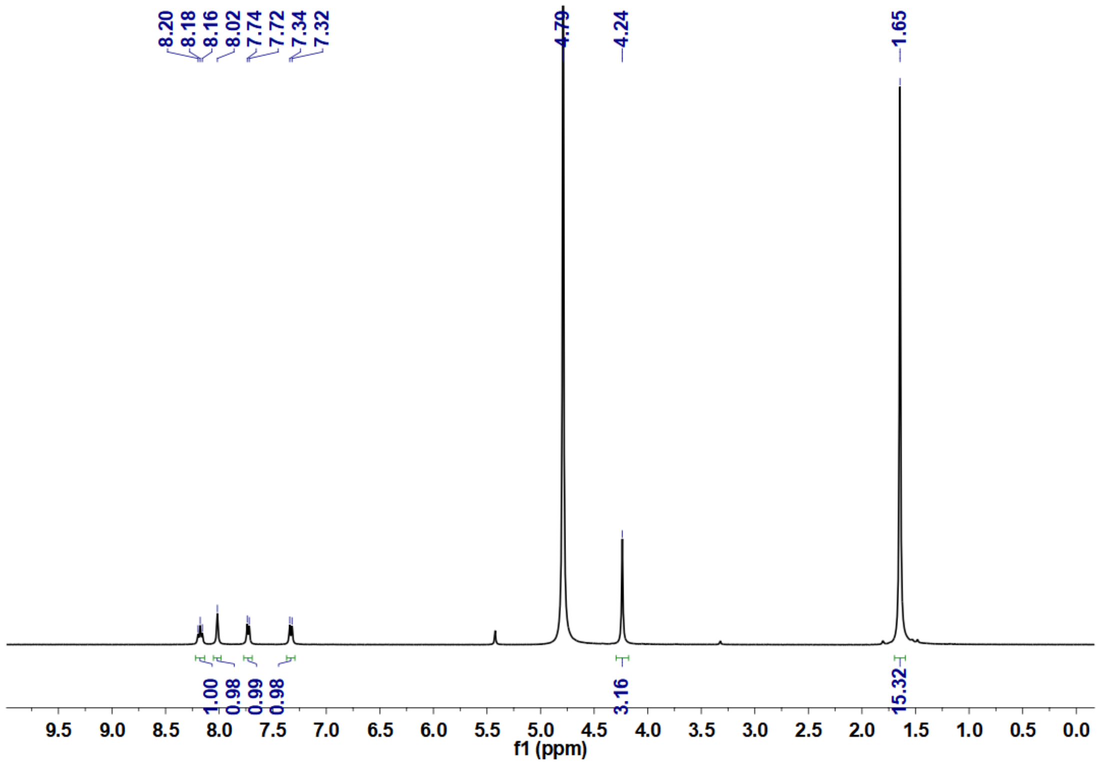


Figure S21. ^{1}H NMR of complex **2-H₂O** (D_2O)

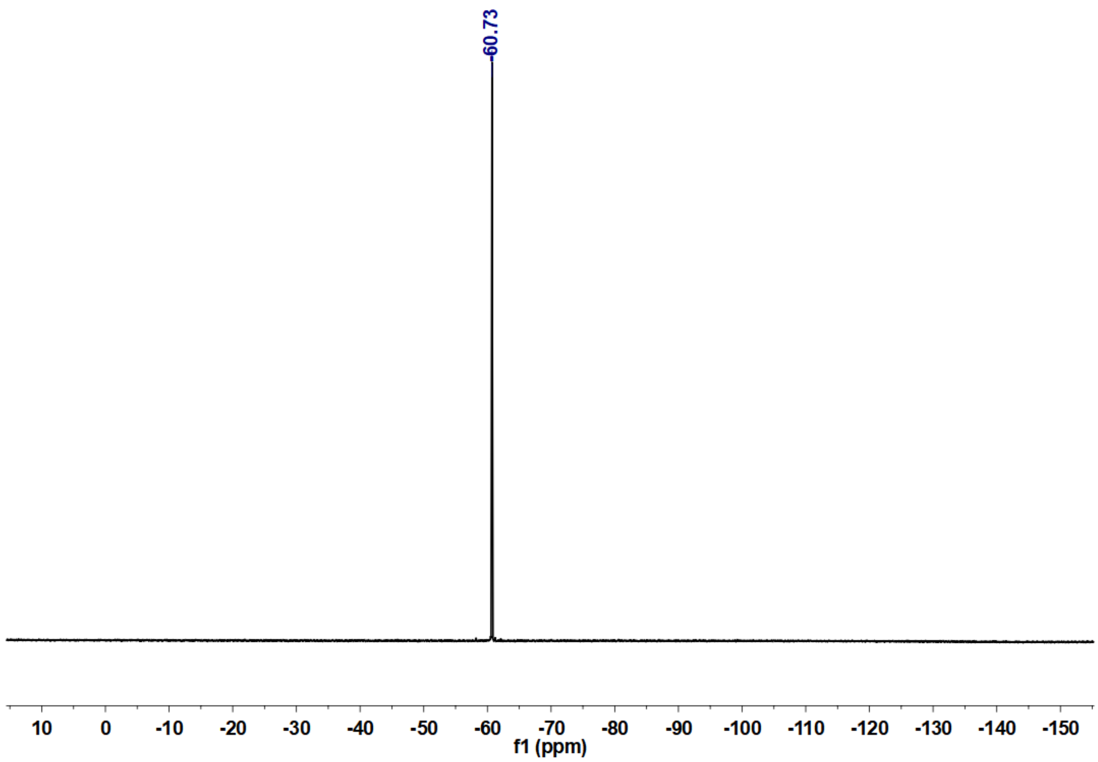


Figure S22. ^{19}F NMR of complex **2-H₂O** (D_2O)

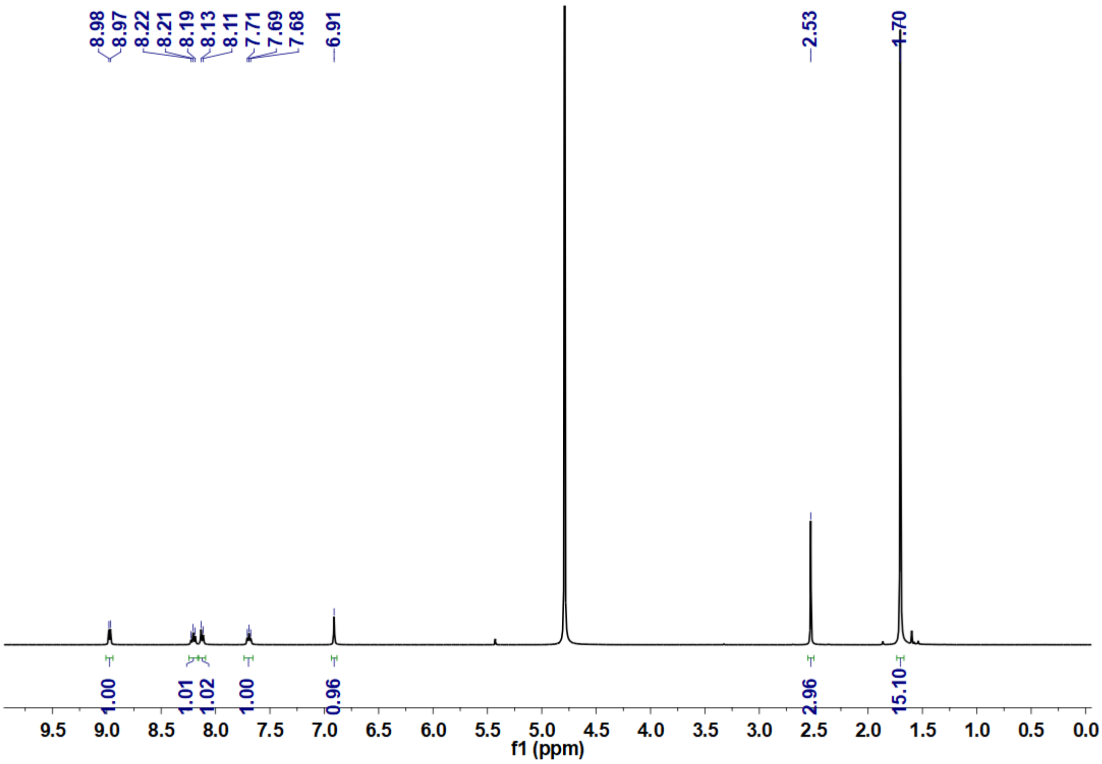


Figure S23. ^{1}H NMR of complex **3-H_2O** (D_2O)

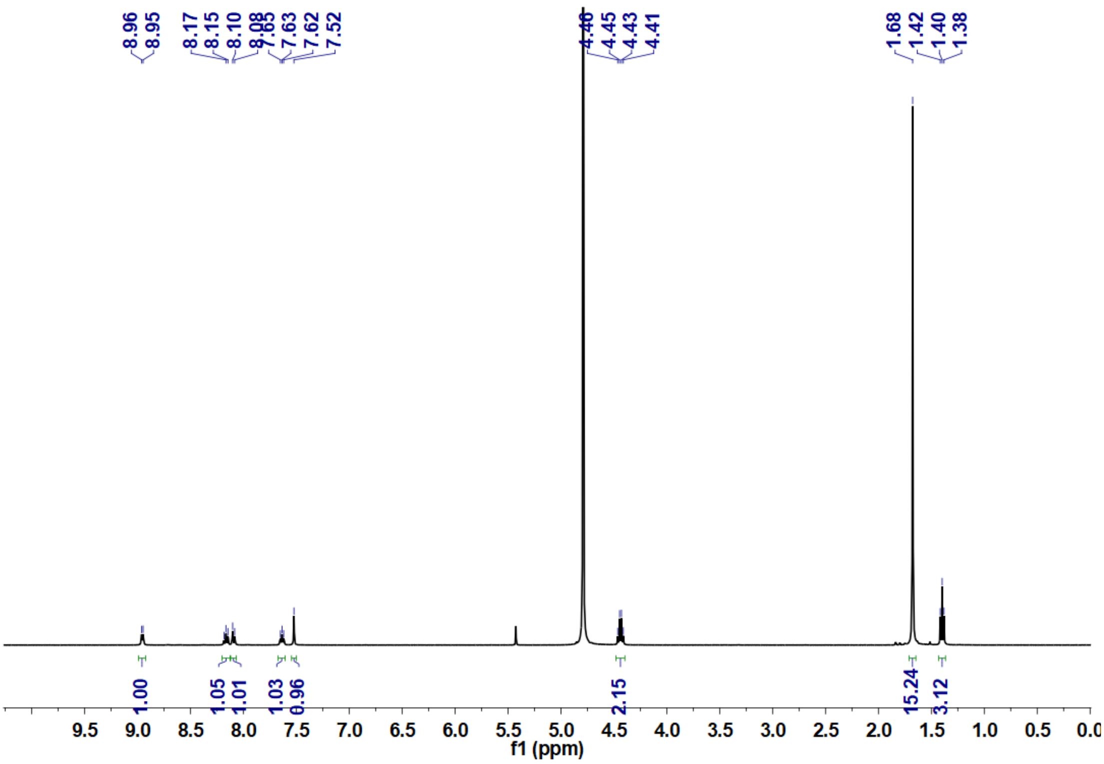


Figure S24. ^{1}H NMR of complex **4-H_2O** (D_2O)

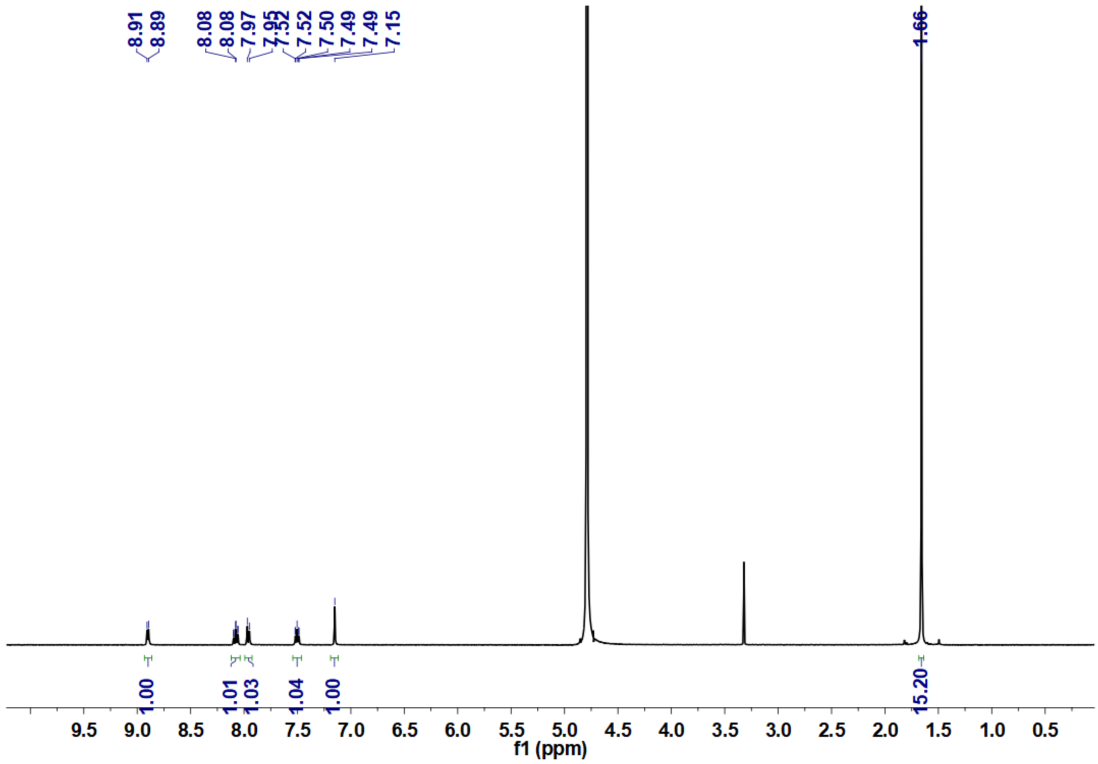


Figure S25. ^{1}H NMR of complex **5-H₂O** (D_2O)

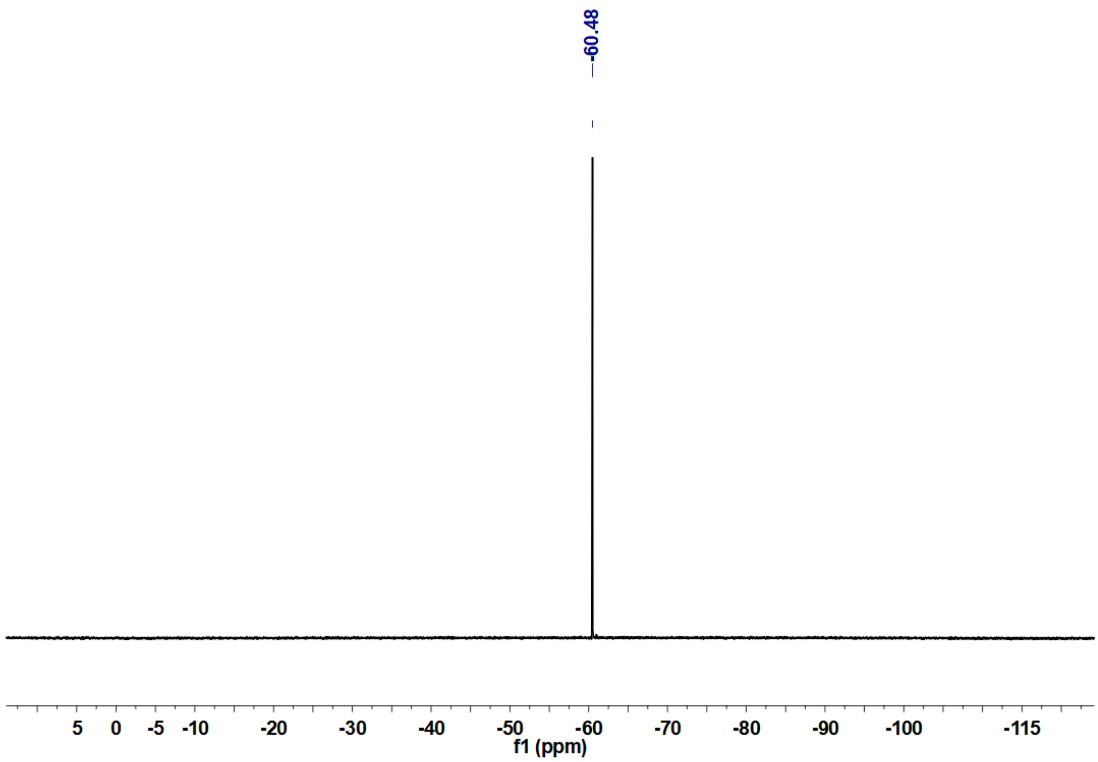


Figure S26. ^{19}F NMR of complex **5-H₂O** (D_2O)

4.2. Mass spectra

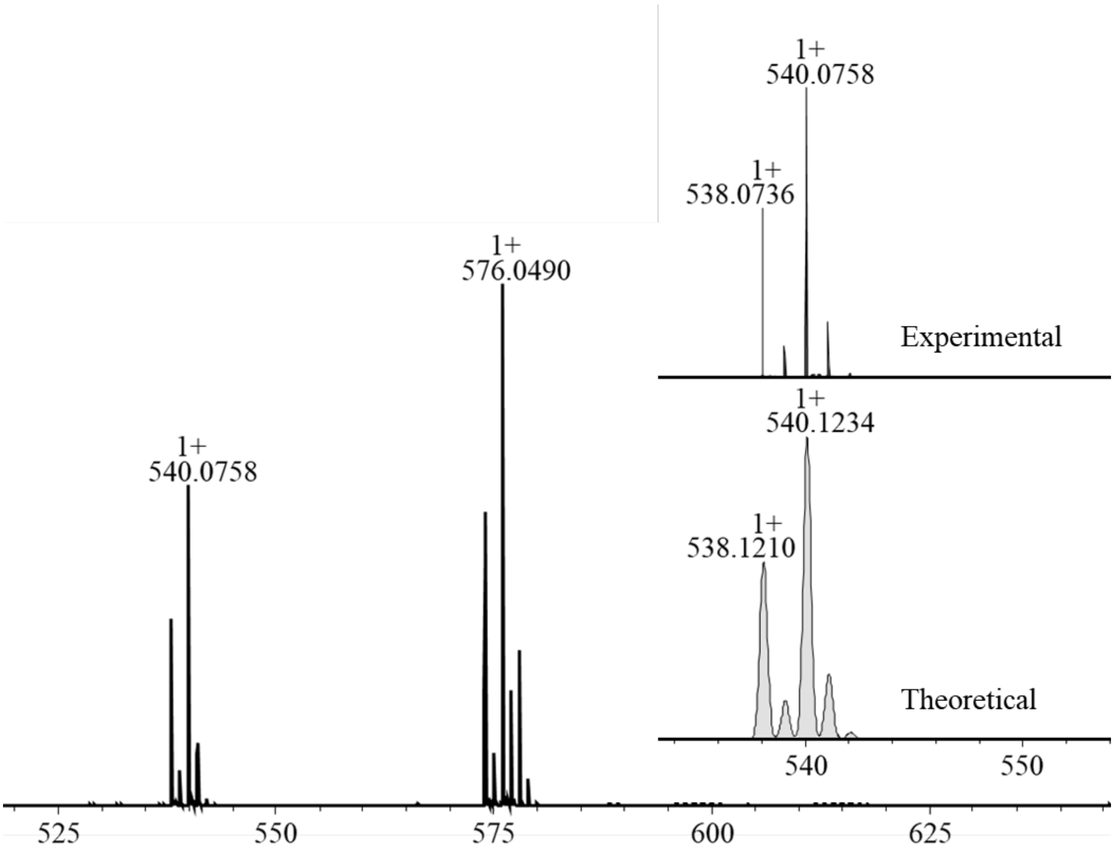


Figure S27. ESI-MS spectrum of complex **1-Cl**

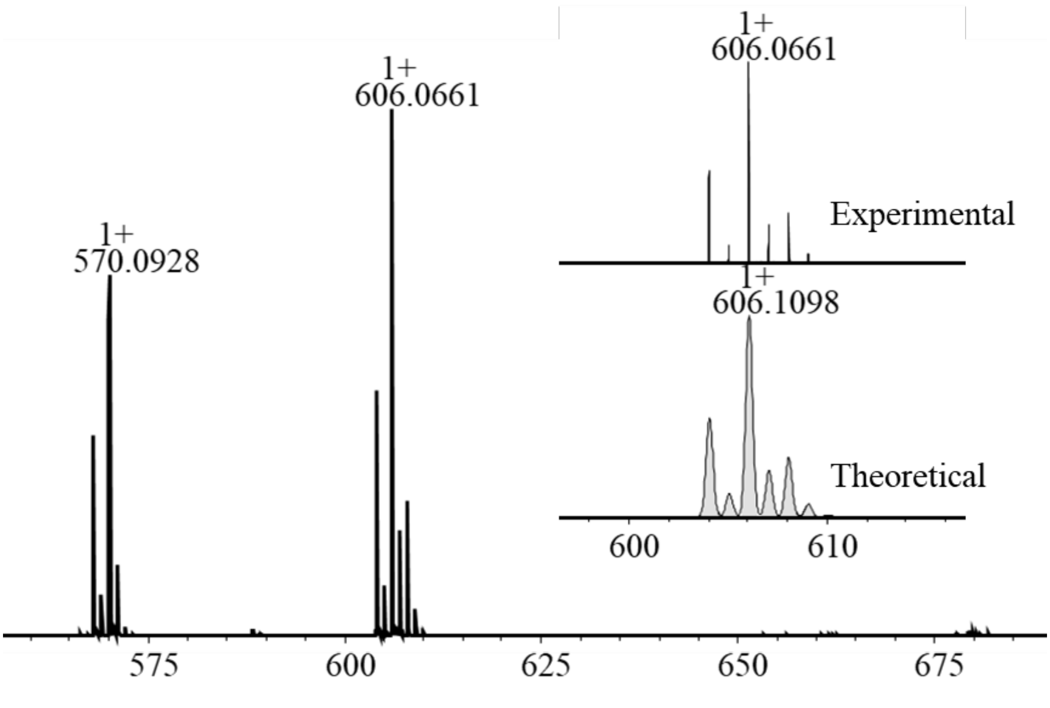


Figure S28. ESI-MS spectrum of complex **2-Cl**

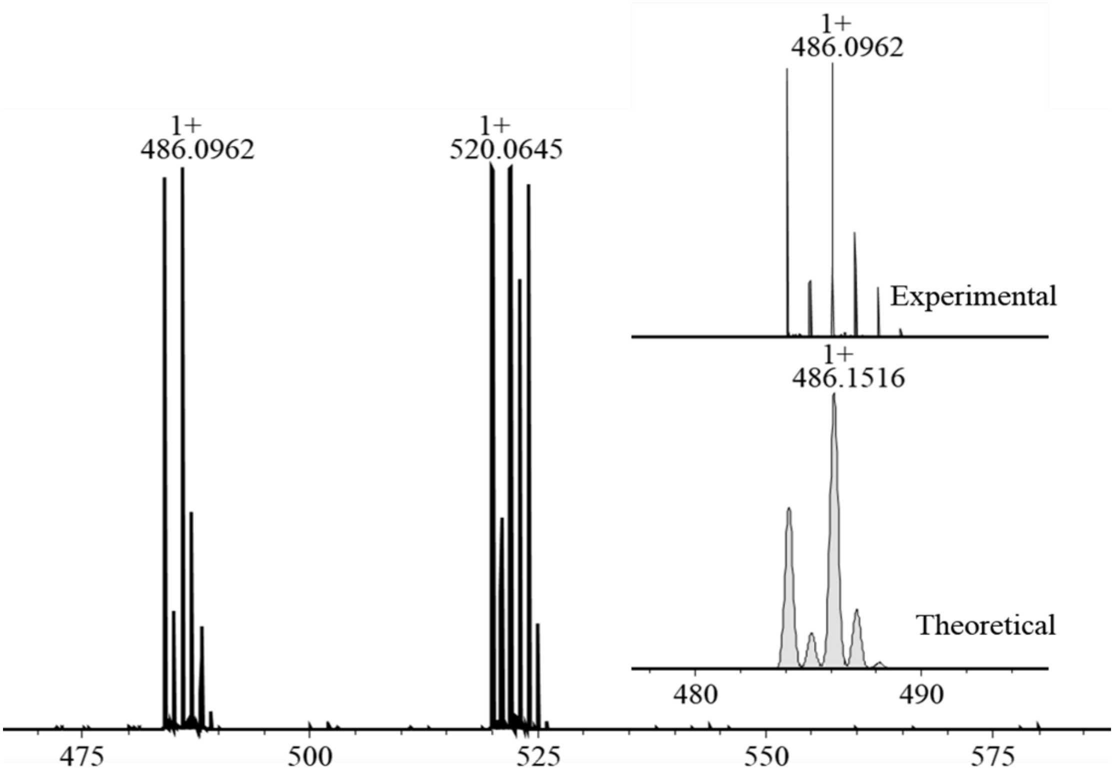


Figure S29. ESI-MS spectrum of complex **3-Cl**

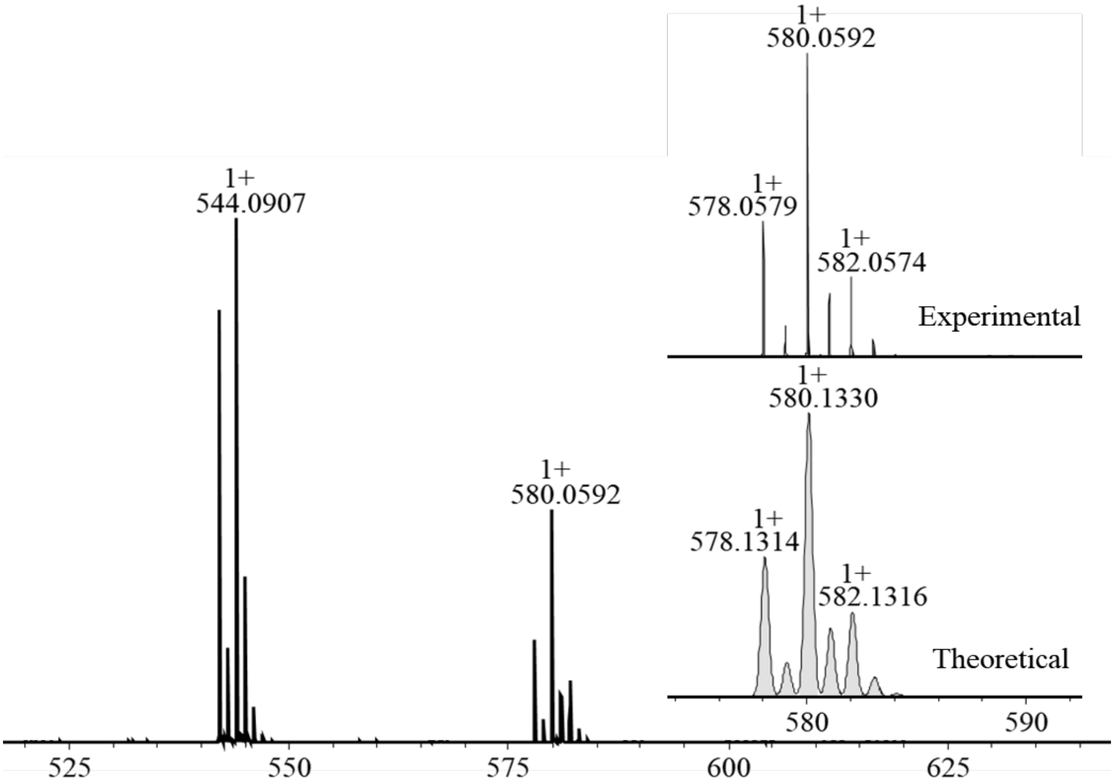


Figure S30. ESI-MS spectrum of complex **4-Cl**

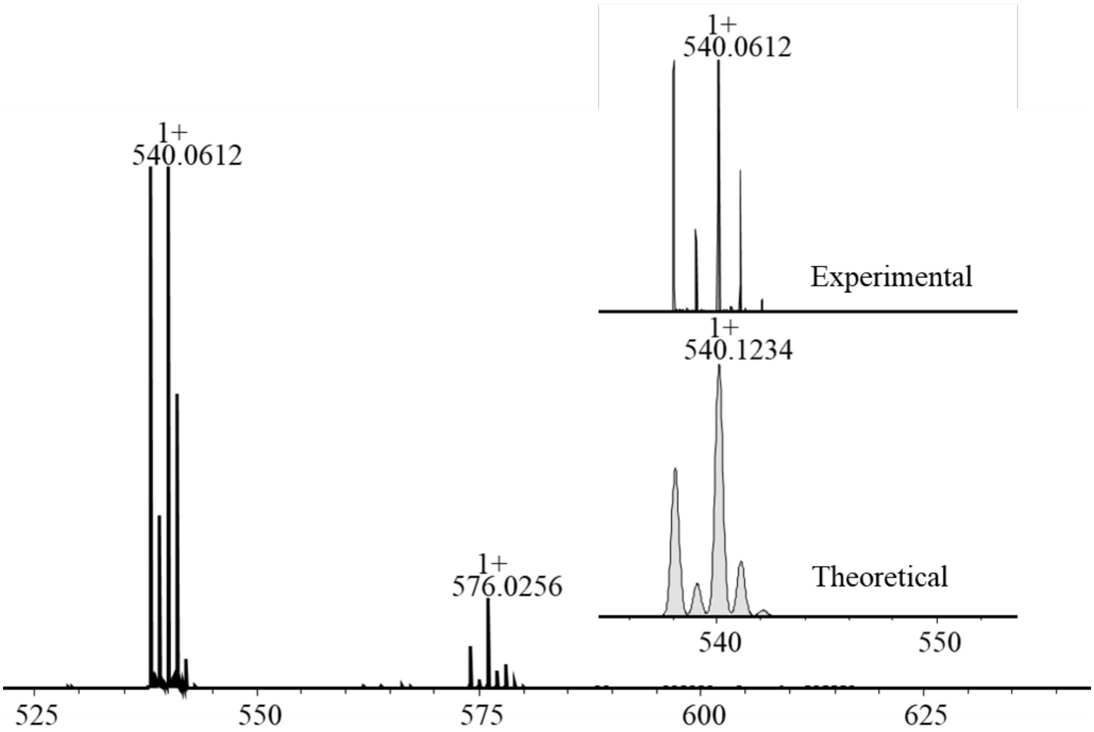


Figure S31. ESI-MS spectrum of complex **5-Cl**

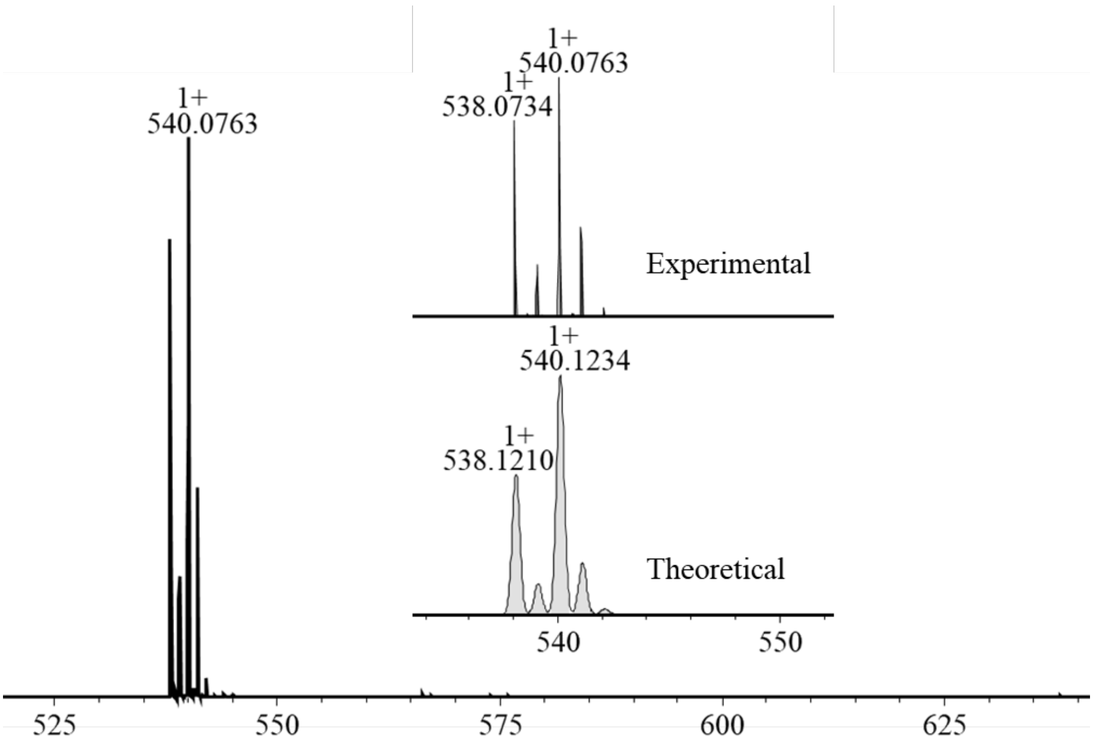


Figure S32. ESI-MS spectrum of complex **1-H_2O**

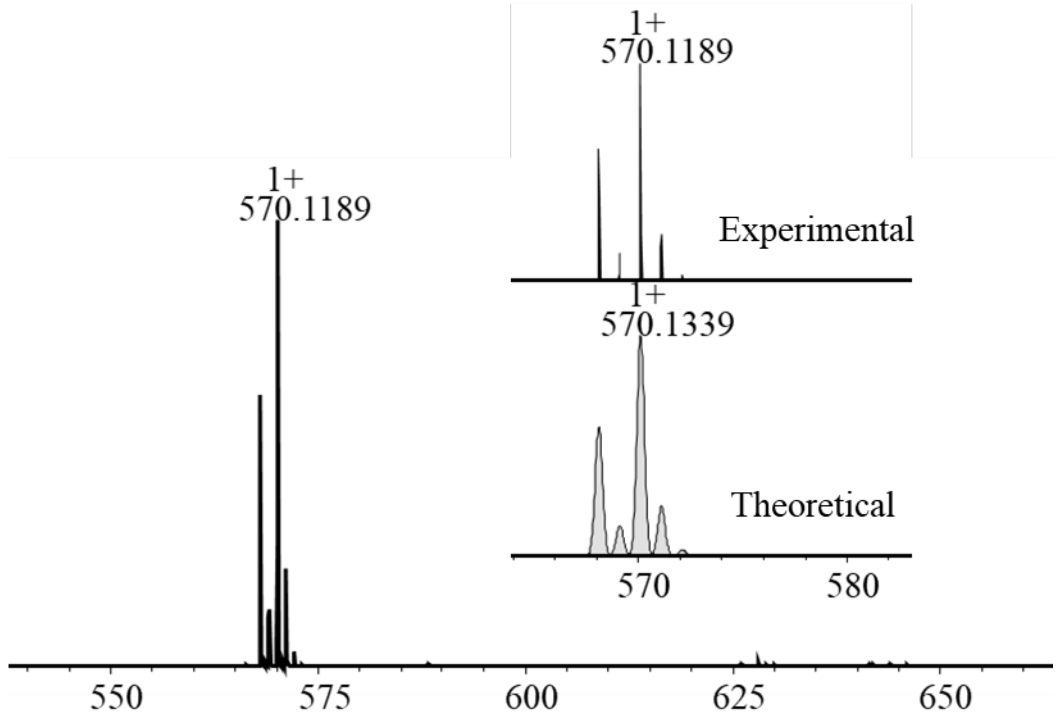


Figure S33. ESI-MS spectrum of complex **2-H_2O**

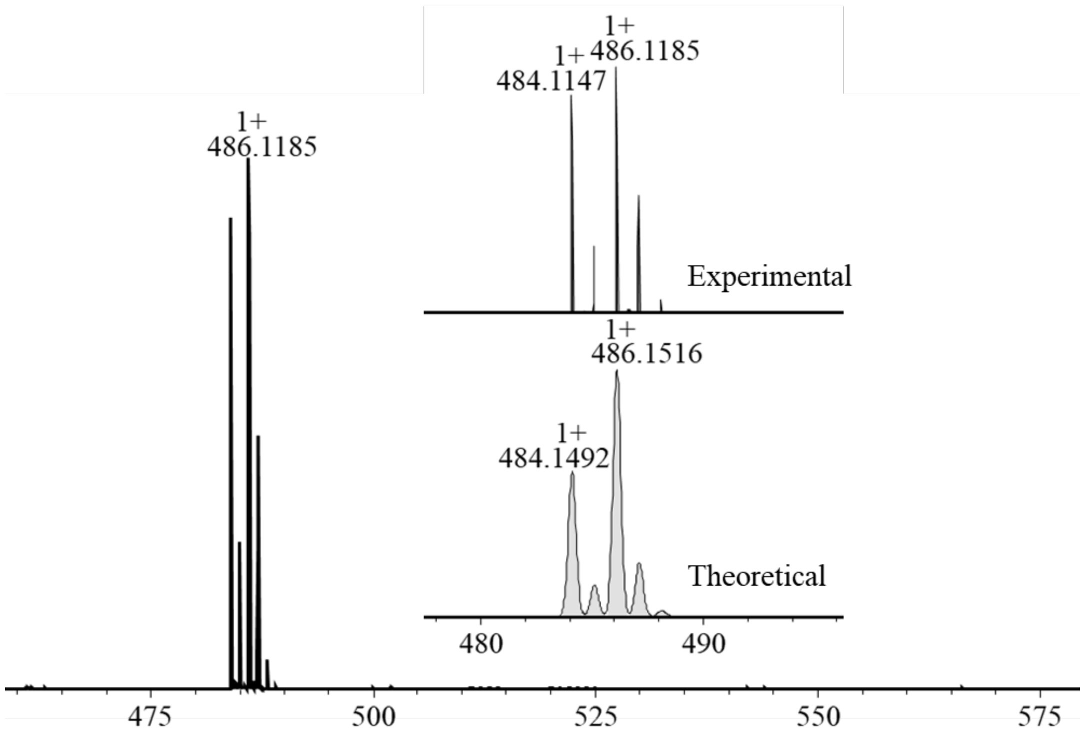


Figure S34. ESI-MS spectrum of complex **3-H_2O**

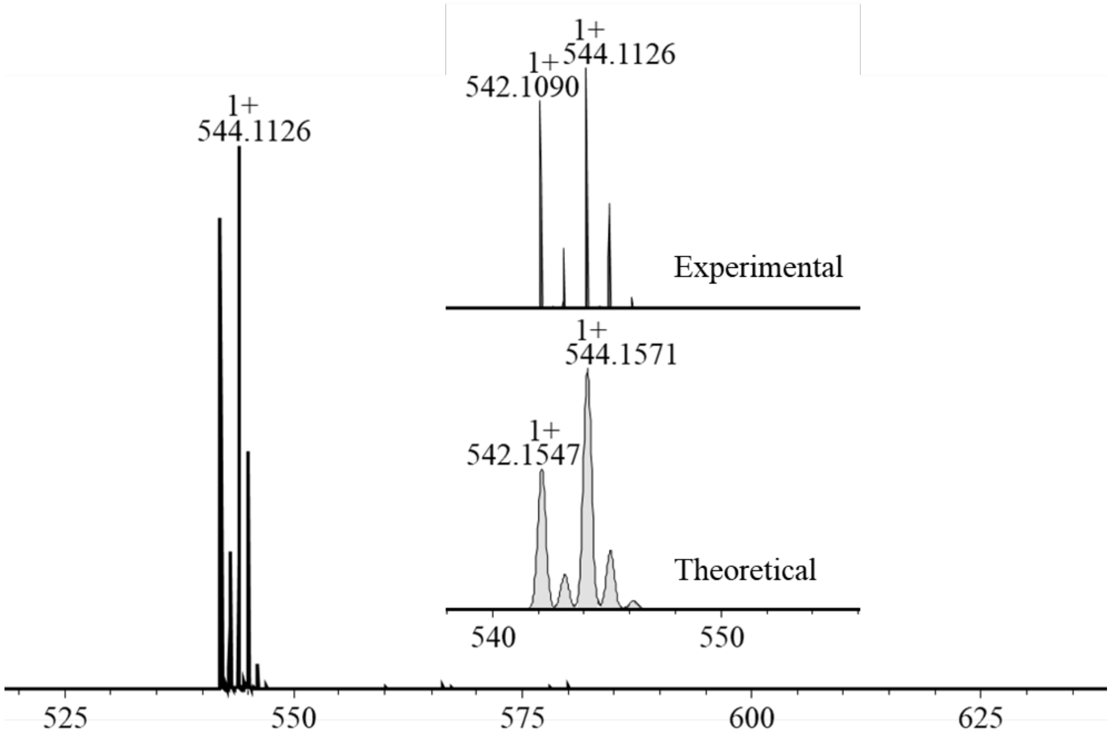


Figure S35. ESI-MS spectrum of complex **4-H_2O**

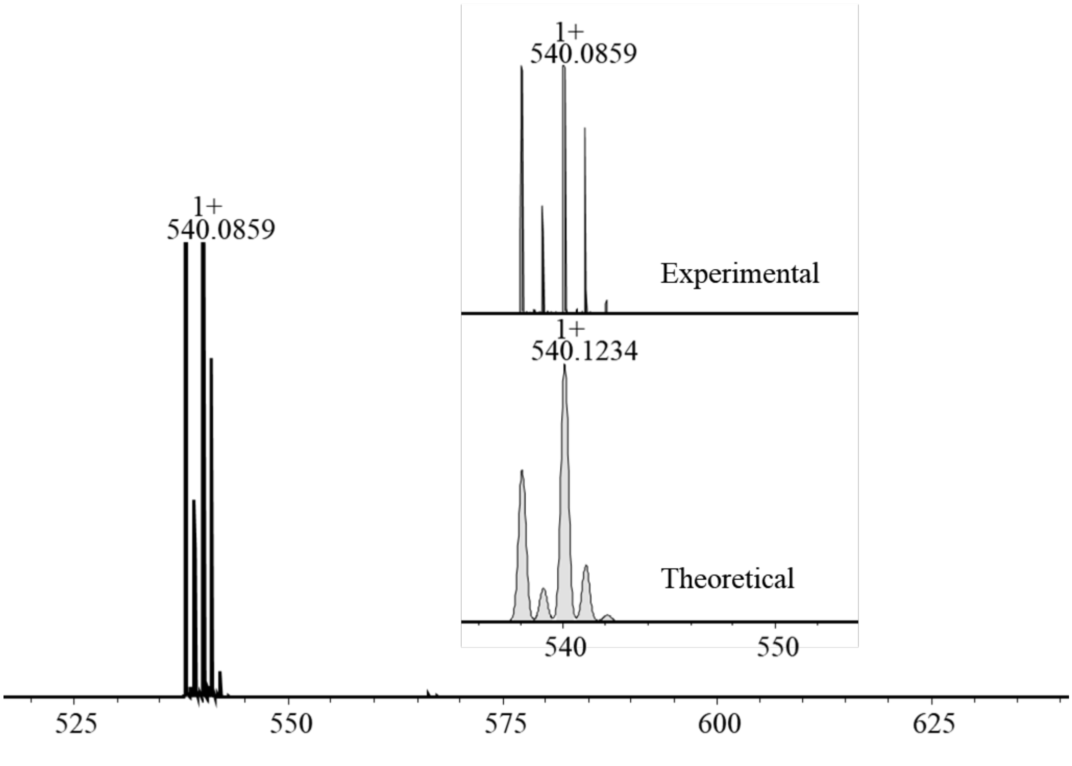


Figure S36. ESI-MS spectrum of complex **5-H_2O**

4.3. IR spectra

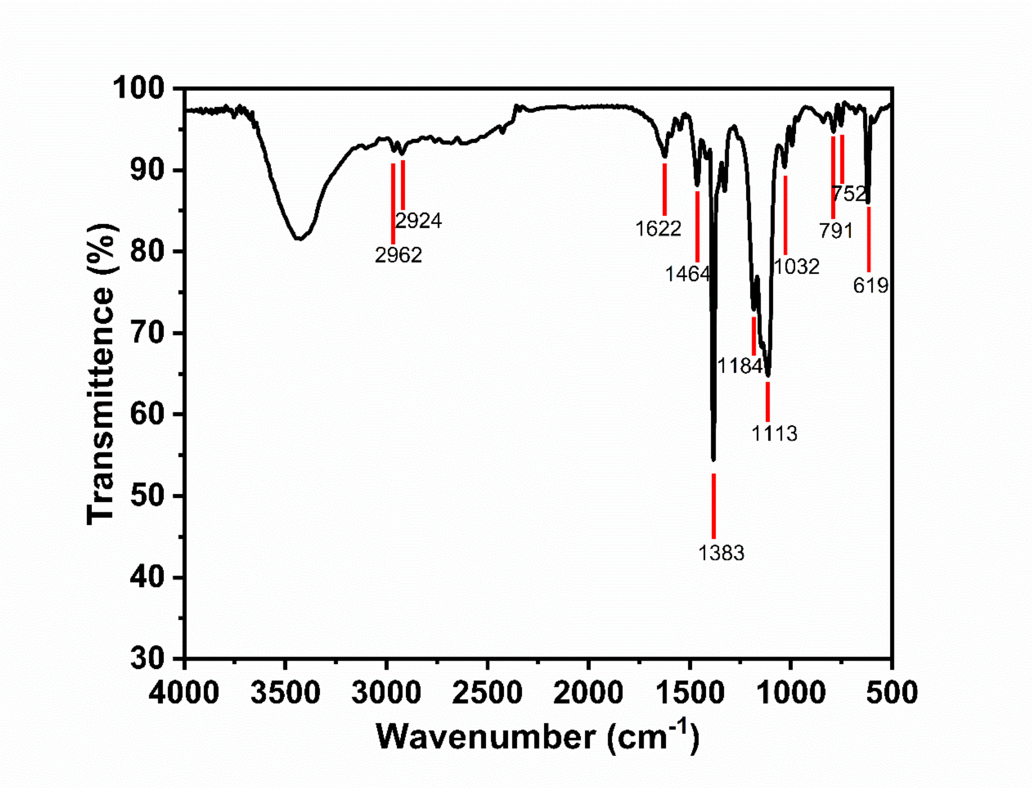


Figure S37. IR spectrum of complex **1-H_2O**

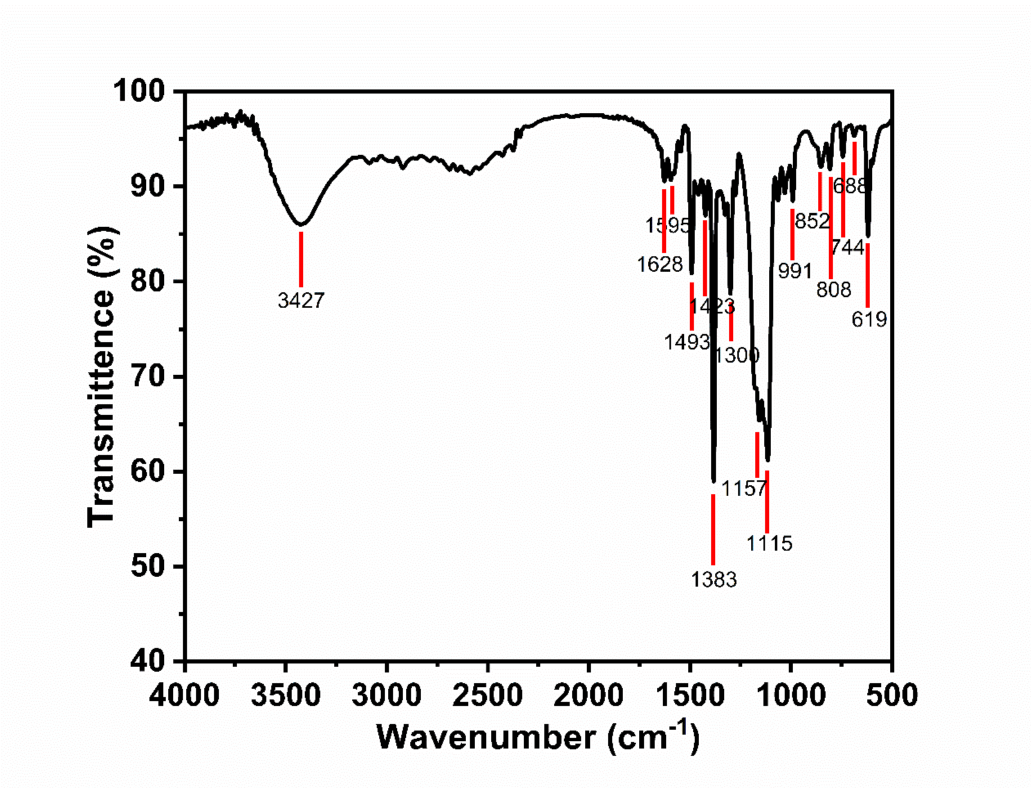


Figure S38. IR spectrum of complex **2-H_2O**

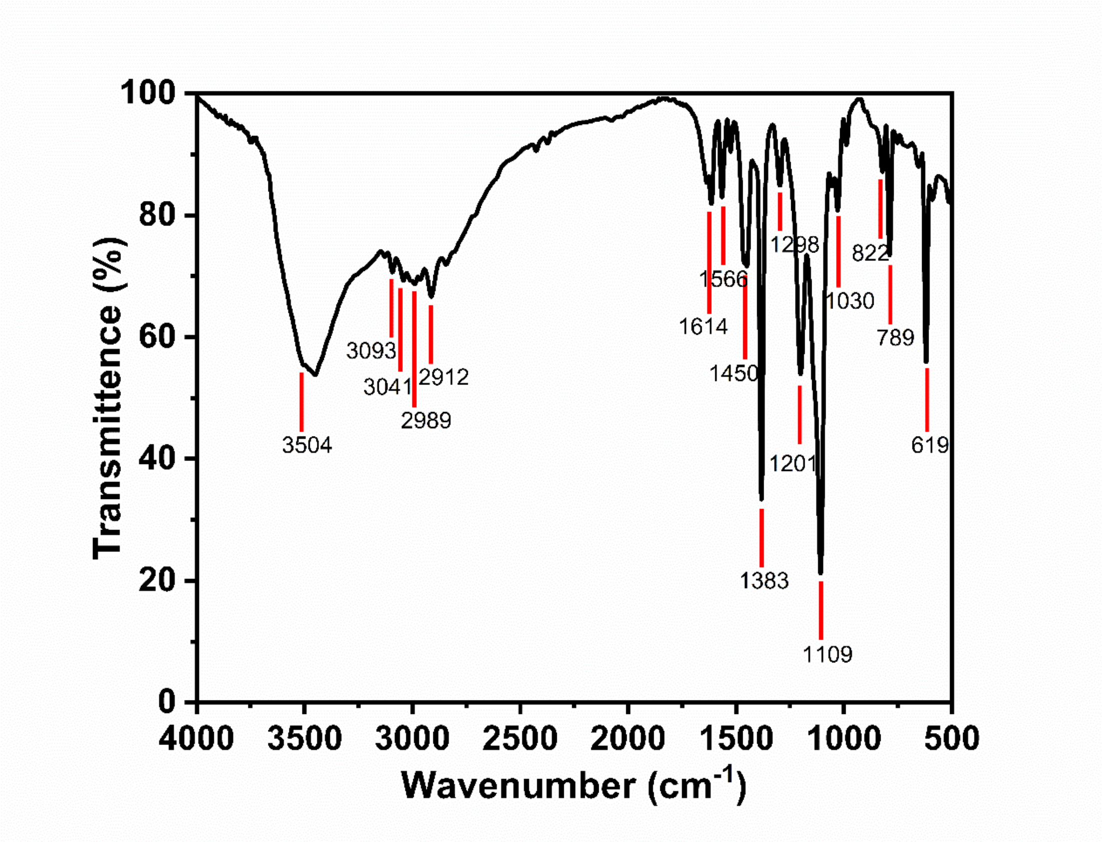


Figure S39. IR spectrum of complex **3-H_2O**

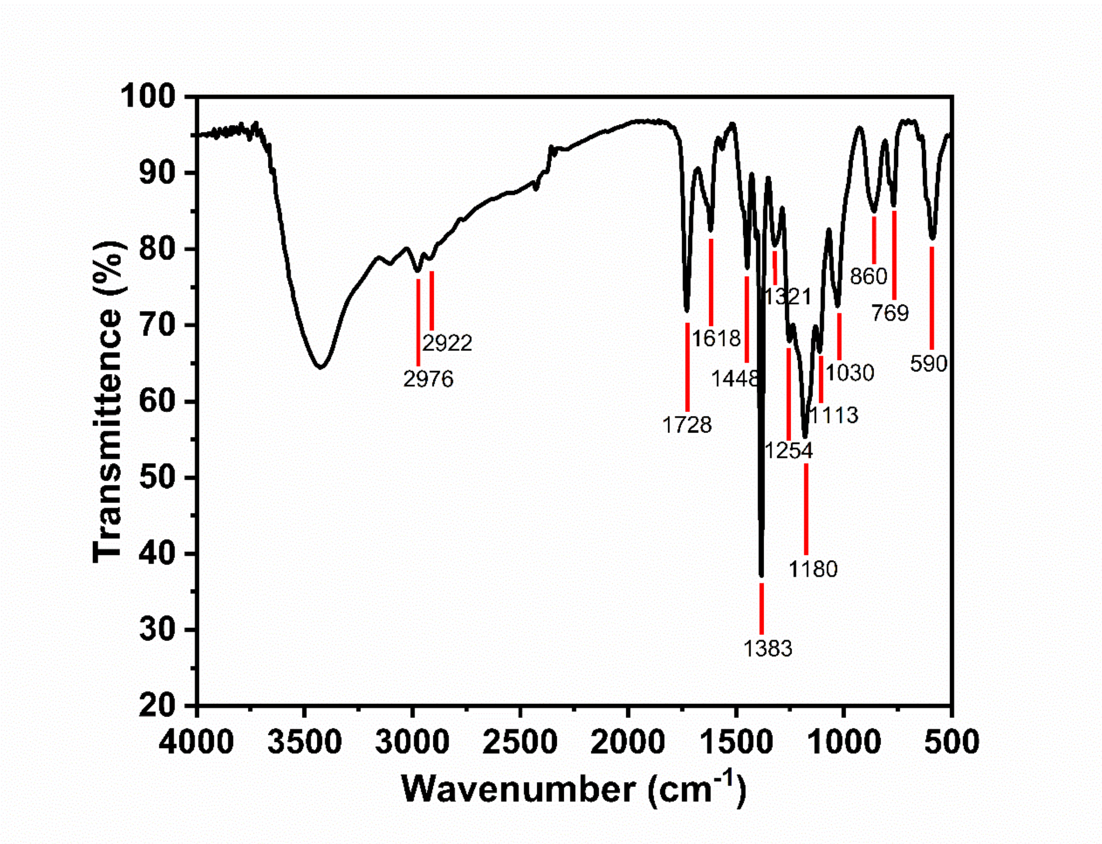


Figure S40. IR spectrum of complex **4-H_2O**

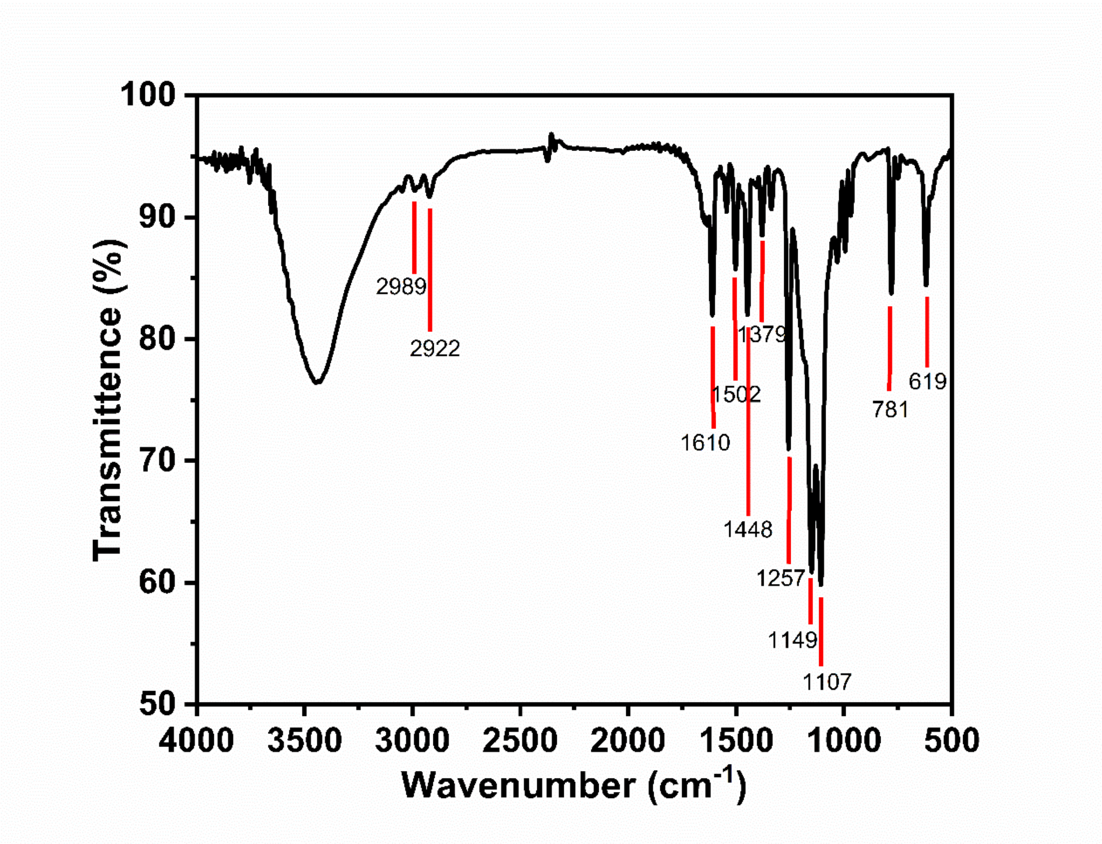


Figure S41. IR spectrum of complex **5-H$_2$O**

4.4. X-ray structure determination of **1-Cl**, **2-Cl**, **3-Cl**, **4-Cl**, **5-Cl**, **1-SO$_4$**, **2-H$_2$O, 4-H$_2$O** and **5-H$_2$O**

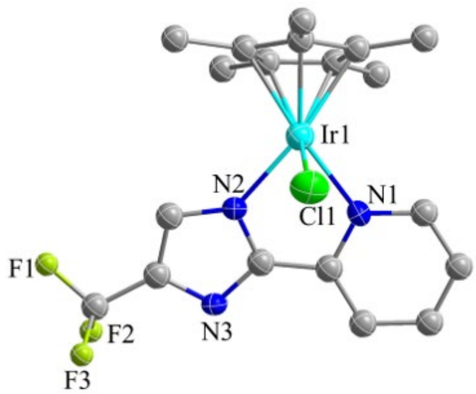


Figure S42. ORTEP structure of complex **1-Cl**

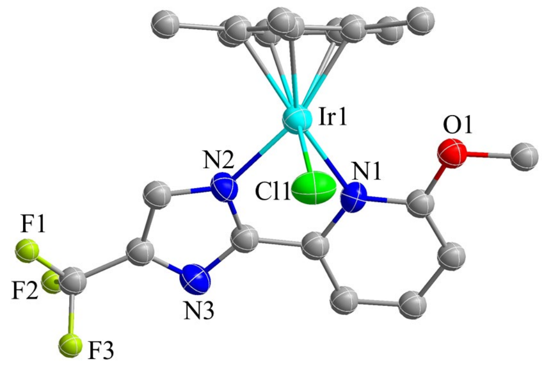


Figure S43. ORTEP structure of complex **2-Cl**

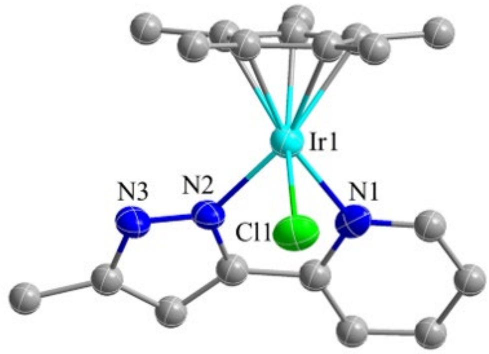


Figure S44. ORTEP structure of complex **3-Cl**

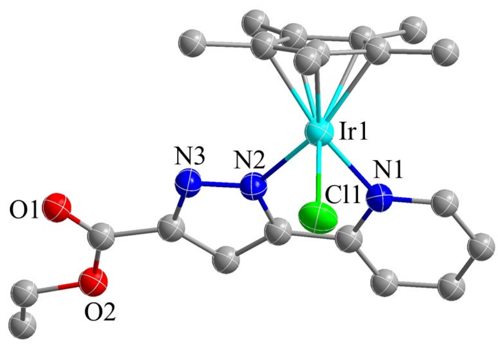


Figure S45. ORTEP structure of complex **4-Cl**

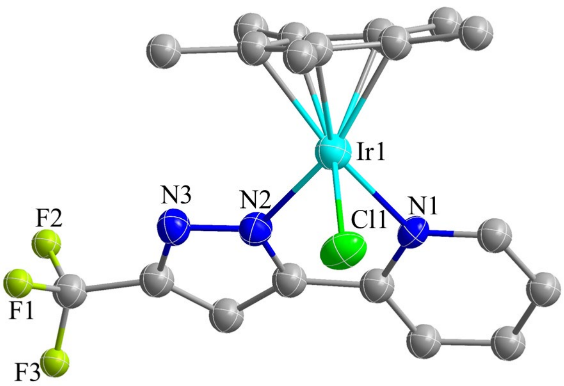


Figure S46. ORTEP structure of complex **5-Cl**

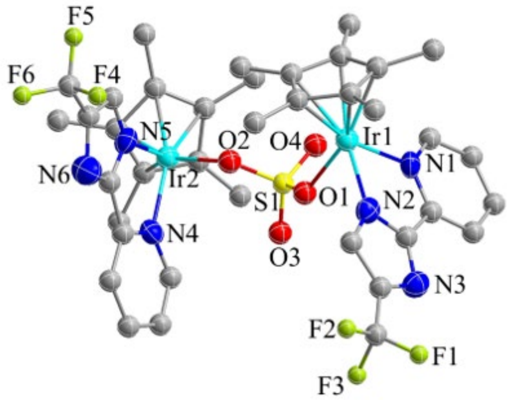


Figure S47. ORTEP structure of complex **1-SO_4**

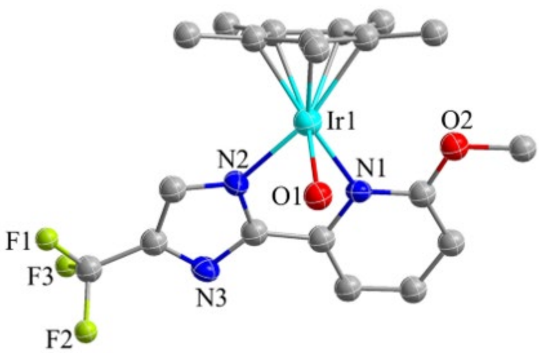


Figure S48. ORTEP structure of complex **2-H_2O**

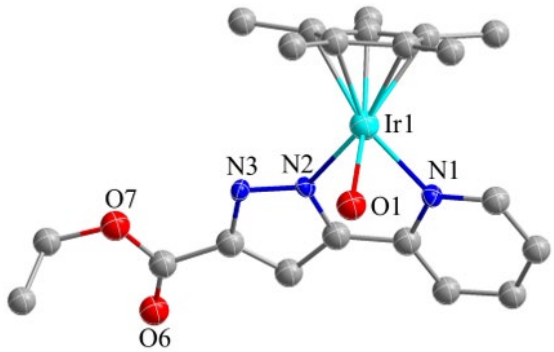


Figure S49. ORTEP structure of complex **4-H_2O**

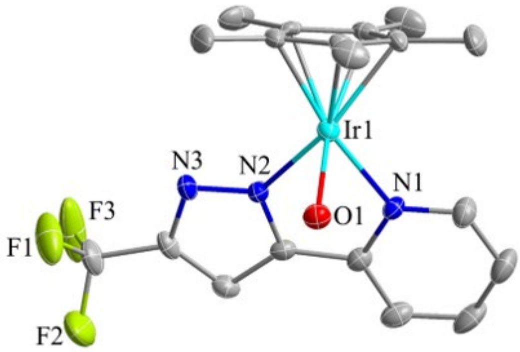


Figure S50. ORTEP structure of complex **5-H_2O**

Table S10. Crystallographic report of complexes **1-Cl, 1-SO_4, 2-Cl**

Complex	**1-Cl**	**1-SO_4**	**2-Cl**
CCDC	2270032	2270074	2270034
Formula	$C_{19}H_{23}Cl_2F_3IrN_3O$	$C_{39}H_{44}Cl_2F_6Ir_2N_6O_5S$	$C_{20}H_{22}ClF_3IrN_3O$
Formula weight	629.50	1278.16	605.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$/c	$P2_1$/n	$P2_1$/c
a, Å	15.7727(14)	11.0027(16)	8.5972(4)
b, Å	15.9723(14)	13.9208(19)	20.5760(7)
c, Å	8.7172(7)	28.864(4)	12.0150(4)
α,°	90	90	90
β,°	90.068(4)	92.793(8)	90.950(3)
γ,°	90	90	90
V, $Å^3$	2196.1(3)	4415.7(11)	2125.11(14)
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.904	1.923	1.891
T, K	296.15	296.15	296.15
μ, mm^{-1}	6.363	6.264	6.450
No. of reflections	18598	52216	14811
No. of indep. refl.	6165	8215	4833
R_{int}	0.0420	0.0448	0.0506
Goodness-of-fit[a]	1.136	1.048	0.961
R_1[b], wR_2[c] [I>=2σ (I)]	0.0354, 0.0951	0.0344, 0.0753	0.0387, 0.0561
R_1, wR_2 [all data]	0.0399, 0.0967	0.0476, 0.0806	0.0772, 0.0646

[a]$GoF=[\Sigma_w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{½}$.

[b]$R_1=\Sigma||F_o||F_c||/\Sigma|F_o|$.

[c]wR_2 $[(\Sigma_w|F_o|- |F_c|)^2/\Sigma w^2|F_o|^2]^{½}$.

Table S11. Crystallographic report of complexes **2-H_2O, 3-Cl, 4-Cl**

Complex	**2-H_2O**	**3-Cl**	**4-Cl**
CCDC	2270076	2270035	2270042
Formula	$C_{20}H_{25}F_3IrN_3O_6S$	$C_{19}H_{26}Cl_2IrN_3O$	$C_{21}H_{25}ClIrN_3O_2$
Formula weight	684.69	575.53	579.09
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C*2/c	*P*na2$_1$	*P*2$_1$/n
a, Å	28.263(2)	8.3683(2)	12.7632(4)
b, Å	11.1731(10)	17.1524(6)	8.1428(2)
c, Å	18.2853(15)	14.5637(5)	21.1947(6)
α,°	90	90	90
β,°	127.296(3)	90	104.858(2)
γ,°	90	90	90
V, Å^3	4593.6(7)	2090.42(11)	2129.08(11)
Z	8	4	4
ρ_{calc}, g cm^{-3}	1.980	1.829	1.807
T, K	296.15	296.15	296.15
μ, mm^{-1}	5.971	6.656	6.418
No. of reflections	28595	15879	23510
No. of indep. refl.	5309	4459	4891
R_{int}	0.0410	0.0516	0.0347
Goodness-of-fit[a]	1.023	0.921	1.020
R_1[b], wR_2[c] [I>=2σ (I)]	0.0282, 0.0685	0.0295, 0.0461	0.0240, 0.0461
R_1, wR_2 [all data]	0.0390, 0.0740	0.0464, 0.0502	0.0342, 0.0491

[a]$GoF=[\Sigma_w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{½}$.

[b]$R_1=\Sigma||F_o||F_c||/\Sigma|F_o|$.

[c]wR_2 $[(\Sigma_w|F_o|- |F_c|)^2/\Sigma w^2|F_o|^2]^{½}$.

Table S12. Crystallographic report of complexes **4-H_2O, 5-Cl, 5-H_2O**

Complex	**4-H_2O**	**5-Cl**	**5-H_2O**
CCDC	2270077	2270073	2270078
Formula	$C_{21}H_{27}IrN_3O_7S$	$C_{19}H_{20}ClF_3IrN_3$	$C_{19}H_{23}F_3IrN_3O_5S$
Formula weight	657.71	575.03	654.66
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	Pbcn
a, Å	11.1655(3)	15.9215(16)	26.5371(11)
b, Å	15.1751(4)	7.5835(8)	8.5088(3)
c, Å	14.1532(3)	15.8947(15)	19.3466(7)
α,°	90	90	90
β,°	104.5240(10)	93.004(3)	90
γ,°	90	90	90
V, $Å^3$	2321.45(10)	1916.5(3)	4368.4(3)
Z	4	4	8
ρ_{calc}, g cm^{-3}	1.882	1.993	1.991
T, K	193	294.7	193
μ, mm^{-1}	5.889	7.143	6.271
No. of reflections	16286	33828	28207
No. of indep. refl.	4383	10266	3995
R_{int}	0.0336	0.0491	0.0444
Goodness-of-fit[a]	1.046	1.021	1.064
R_1[b], wR_2[c] [I>=2σ (I)]	0.0270, 0.0669	0.0389, 0.0841	0.0264, 0.0706
R_1, wR_2 [all data]	0.0315, 0.0692	0.0664, 0.0951	0.0293, 0.0728

[a]$GoF=[\Sigma_w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{½}$.

[b]$R_1=\Sigma||F_o||F_c||/\Sigma|F_o|$.

[c]$wR_2\ [(\Sigma_w|F_o|-|F_c|)^2/\Sigma w^2|F_o|^2]^{½}$.

Table S13. Bond lengths (Å) and angles (°) of **1-Cl**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-Cl1	2.3967(18)	Ir1-C2	2.159(6)
Ir1-N2	2.083(4)	Ir1-C5	2.148(6)
Ir1-C4	2.148(6)	F2-C19	1.312(8)
Ir1-N1	2.115(5)	F3-C19	1.335(7)
Ir1-C1	2.144(5)	F1-C19	1.340(7)
Ir1-C3	2.171(6)		
	Bond Angles (°)		Bond Angles (°)
N2-Ir1-Cl1	87.25(15)	N1-Ir1-C3	144.4(2)
N2-Ir1-C4	105.2(2)	N1-Ir1-C2	108.7(2)
N2-Ir1-N1	76.08(19)	N1-Ir1-C5	122.5(3)
N2-Ir1-C1	125.8(2)	C1-Ir1-Cl1	146.69(16)
N2-Ir1-C3	139.5(2)	C1-Ir1-C4	65.4(2)
N2-Ir1-C2	164.0(2)	C1-Ir1-C3	64.8(2)
N2-Ir1-C5	98.9(2)	C1-Ir1-C2	39.3(2)
C4-Ir1-Cl1	114.24(19)	C1-Ir1-C5	38.8(3)
C4-Ir1-C3	38.6(2)	C3-Ir1-Cl1	93.85(17)
C4-Ir1-C2	65.3(2)	C2-Ir1-Cl1	108.27(17)
C4-Ir1-C5	39.1(3)	C2-Ir1-C3	38.5(2)
N1-Ir1-Cl1	84.17(15)	C5-Ir1-Cl1	153.4(2)
N1-Ir1-C4	161.5(2)	C5-Ir1-C3	64.7(2)
N1-Ir1-C1	98.6(2)	C5-Ir1-C2	65.4(2)

Table S14. Bond lengths (Å) and angles (°) of **1-SO_4**

	Bond Distances(Å)		Bond Distances(Å)
Ir2-O2	2.123(4)	Ir1-O1	2.127(4)
Ir2-N4	2.120(5)	Ir1-N2	2.058(5)
Ir2-N5	2.079(5)	Ir1-N1	2.123(5)
Ir2-C23	2.171(6)	Ir1-C5	2.169(7)
Ir2-C22	2.138(6)	Ir1-C1	2.199(7)
Ir2-C24	2.197(6)	Ir1-C2	2.142(7)
Ir2-C21	2.129(6)	Ir1-C4	2.131(7)
Ir2-C20	2.163(6)	Ir1-C3	2.134(8)
S1-O1	1.498(4)	S1-O3	1.439(5)
S1-O2	1.500(4)	S1-O4	1.440(5)
	Bond Angles (°)		Bond Angles (°)
O2-Ir2-C23	110.3(2)	N5-Ir2-C21	101.7(2)
O2-Ir2-C22	146.0(2)	N5-Ir2-C20	102.6(2)
O2-Ir2-C24	100.1(2)	C23-Ir2-C24	38.6(2)
O2-Ir2-C21	161.4(2)	C22-Ir2-C23	38.6(2)
O2-Ir2-C20	121.5(3)	C22-Ir2-C24	64.2(3)
N4-Ir2-O2	80.74(17)	C22-Ir2-C20	65.2(3)
N4-Ir2-C23	113.1(2)	C21-Ir2-C23	65.1(3)
N4-Ir2-C22	98.7(2)	C21-Ir2-C22	38.6(3)
N4-Ir2-C24	150.5(2)	C21-Ir2-C24	64.6(3)
N4-Ir2-C21	117.9(3)	C21-Ir2-C20	39.8(3)
N4-Ir2-C20	157.5(3)	C20-Ir2-C23	64.8(3)
N5-Ir2-O2	80.80(17)	C20-Ir2-C24	37.7(3)
N5-Ir2-N4	76.04(19)	O1-Ir1-C5	120.8(3)
N5-Ir2-C23	166.2(2)	O1-Ir1-C1	100.8(2)
N5-Ir2-C22	132.4(2)	O1-Ir1-C2	111.8(3)

N5-Ir2-C24	133.4(2)	O1-Ir1-C4	159.9(3)
O1-Ir1-C3	148.5(3)	N1-Ir1-C4	101.0(3)
N2-Ir1-O1	78.56(17)	N1-Ir1-C3	127.8(3)
N2-Ir1-N1	76.47(19)	C5-Ir1-C1	37.4(3)
N2-Ir1-C5	160.5(3)	C2-Ir1-C5	64.4(3)
N2-Ir1-C1	144.4(3)	C2-Ir1-C1	38.3(3)
N2-Ir1-C2	108.3(3)	C4-Ir1-C5	39.1(3)
N2-Ir1-C4	121.6(3)	C4-Ir1-C1	63.7(3)
N2-Ir1-C3	97.9(3)	C4-Ir1-C2	64.8(3)
N1-Ir1-O1	82.28(18)	C4-Ir1-C3	38.2(3)
N1-Ir1-C5	106.5(3)	C3-Ir1-C5	64.7(3)
N1-Ir1-C1	139.1(3)	C3-Ir1-C1	64.0(3)
N1-Ir1-C2	165.6(3)	C3-Ir1-C2	39.0(3)

Table S15. Bond lengths (Å) and angles (°) of **2-Cl**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-Cl1	2.3974(15)	Ir1-C5	2.147(6)
Ir1-N2	2.071(4)	F3-C20	1.327(8)
Ir1-N1	2.165(4)	O1-C12	1.349(6)
Ir1-C3	2.138(6)	O1-C11	1.438(7)
Ir1-C7	2.167(5)	F2-C20	1.331(8)
Ir1-C9	2.167(6)	F1-C2O	1.290(8)
Ir1-C1	2.149(6)		
	Bond Angles (°)		Bond Angles (°)
N2-Ir1-Cl1	87.87(12)	C3-Ir1-C1	39.0(2)
N2-Ir1-N1	76.20(18)	C3-Ir1-C5	39.0(2)
N2-Ir1-C3	100.3(2)	C7-Ir1-Cl1	93.85(16)
N2-Ir1-C7	131.4(2)	C7-Ir1-C9	38.1(2)
N2-Ir1-C9	164.2(2)	C9-Ir1- Cl1	103.34(18)
N2-Ir1-C1	132.4(2)	C1-Ir1- Cl1	139.6(2)
N2-Ir1-C5	100.3(2)	C1-Ir1-N1	99.9(2)
N1-Ir1-Cl1	84.65(12)	C1-Ir1-C7	64.0(2)
N1-Ir1-C7	152.3(2)	C1-Ir1-C9	38.5(2)
N1-Ir1-C9	115.5(2)	C5-Ir1-Cl1	118.79(19)
C3-Ir1-Cl1	157.22(17)	C5-Ir1-N1	156.4(2)
C3-Ir1-N1	117.9(2)	C5-Ir1-C7	38.4(2)
C3-Ir1-C7	64.8(2)	C5-Ir1-C9	64.6(2)
C3-Ir1-C9	65.2(2)	C5-Ir1-C1	64.8(2)

Table S16. Bond lengths (Å) and angles (°) of **2-H_2O**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-O1	2.151(3)	Ir1-C2	2.147(4)
Ir1-N1	2.155(3)	O2-C12	1.334(5)
Ir1-N2	2.068(3)	O2-C11	1.431(5)
Ir1-C1	2.123(4)	F2-C20	1.341(6)
Ir1-C3	2.162(4)	F1-C20	1.317(6)
Ir1-C4	2.183(4)	F3-C20	1.341(5)
Ir1-C5	2.158(4)		
	Bond Angles (°)		Bond Angles (°)
O1-Ir1-N1	81.29(11)	C1-Ir1-O1	154.86(15)
O1-Ir1-C3	95.94(14)	C1-Ir1-N1	123.61(15)
O1-Ir1-C4	110.75(14)	C1-Ir1-C3	65.12(16)
O1-Ir1-C5	148.42(15)	C1-Ir1-C4	65.26(17)
N1-Ir1-C3	148.17(15)	C1-Ir1-C2	39.47(18)
N1-Ir1-C4	113.16(15)	C1-Ir1-C5	38.91(18)
N1-Ir1-C5	102.17(15)	C3-Ir1-C4	38.30(17)
N2-Ir1-O1	80.90(13)	C2-Ir1-O1	115.48(15)
N2-Ir1-N1	76.32(13)	C2-Ir1-N1	162.98(15)
N2-Ir1-C1	100.47(16)	C2-Ir1-C3	38.72(16)
N2-Ir1-C3	134.87(15)	C2-Ir1-C4	65.09(17)
N2-Ir1-C4	165.48(15)	C2-Ir1-C5	65.37(18)
N2-Ir1-C2	102.50(15)	C5-Ir1-C3	64.51(16)
N2-Ir1-C5	130.60(16)	C5-Ir1-C4	38.75(16)

Table S17. Bond lengths (Å) and angles (°) of **3-Cl**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-Cl1	2.391(2)	Ir1-N2	2.077(7)
Ir1-C9	2.164(7)	Ir1-C3	2.175(8)
Ir1-C7	2.163(8)	Ir1-C5	2.149(8)
Ir1-N1	2.129(7)	Ir1-C1	2.182(8)
	Bond Angles (°)		Bond Angles (°)
C9-Ir1-Cl1	159.9(3)	N2-Ir1-C9	112.6(3)
C9-Ir1-C3	64.7(4)	N2-Ir1-C7	98.7(3)
C9-Ir1-C1	39.3(3)	N2-Ir1-N1	75.0(3)
C7-Ir1-Cl1	134.1(3)	N2-Ir1-C3	157.4(3)
C7-Ir1-C9	38.7(3)	N2-Ir1-C5	118.3(3)
C7-Ir1-C3	64.7(3)	N2-Ir1-C1	150.5(3)
C7-Ir1-C1	64.8(3)	C3-Ir1-Cl1	95.2(2)
N1-Ir1-Cl1	84.14(18)	C3-Ir1-C1	37.6(3)
N1-Ir1-C9	107.7(3)	C5-Ir1-Cl1	100.2(2)
N1-Ir1-C7	141.3(3)	C5-Ir1-C9	64.6(4)
N1-Ir1-C3	127.6(3)	C5-Ir1-C7	38.1(3)
N1-Ir1-C5	166.1(3)	C5-Ir1-C3	39.3(3)
N1-Ir1-C1	102.1(3)	C5-Ir1-C1	64.4(3)
N2-Ir1-Cl1	85.73(19)	C1-Ir1-Cl1	123.5(3)

Table S18. Bond lengths (Å) and angles (°) of **4-Cl**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-Cl1	2.4025(9)	Ir1-C5	2.176(3)
Ir1-N2	2.057(3)	Ir1-C9	2.137(3)
Ir1-N1	2.108(3)	N2-N3	1.331(4)
Ir1-C1	2.157(3)	O2-C19	1.334(4)
Ir1-C7	2.149(3)	O2-C20	1.465(5)
Ir1-C3	2.169(3)	O1-C19	1.197(4)
	Bond Angles (°)		Bond Angles (°)
N2-Ir1-Cl1	88.36(8)	C1-Ir1-C3	38.50(13)
N2-Ir1-N1	76.07(10)	C1-Ir1-C5	64.18(13)
N2-Ir1-C1	125.74(13)	C7-Ir1- Cl1	114.32(10)
N2-Ir1-C7	103.68(12)	C7-Ir1- C1	64.95(14)
N2-Ir1-C3	162.56(13)	C7-Ir1- C3	64.81(14)
N2-Ir1-C5	137.84(13)	C7-Ir1- C5	38.34(13)
N2-Ir1-C9	97.92(12)	C3-Ir1- Cl1	108.12(11)
N1-Ir1-C11	83.81(8)	C3-Ir1- C5	38.37(14)
N1-Ir1-C1	100.11(13)	C5-Ir1- Cl1	93.70(9)
N1-Ir1-C7	161.87(13)	C9-Ir1- Cl1	153.63(11)
N1-Ir1-C3	110.57(13)	C9-Ir1- C1	38.50(14)
N1-Ir1-C5	146.04(13)	C9-Ir1- C7	39.31(14)
N1-Ir1-C9	122.57(13)	C9-Ir1- C3	64.78(14)
C1-Ir1-Cl1	145.75(11)	C9-Ir1- C5	64.61(13)

Table S19. Bond lengths (Å) and angles (°) of **4-H_2O**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-O1	2.172(3)	Ir1-C1	2.155(4)
Ir1-N2	2.069(3)	Ir1-C5	2.160(4)
Ir1-N1	2.111(3)	O7-C19	1.326(5)
Ir1-C2	2.156(4)	O7-C20	1.465(6)
Ir1-C4	2.124(5)	N2-N3	1.336(5)
Ir1-C3	2.168(4)	O6-C19	1.197(5)
	Bond Angles (°)		Bond Angles (°)
N2-Ir1-O1	81.67(12)	C2-Ir1-C3	38.12(19)
N2-Ir1-N1	76.43(13)	C2-Ir1-C5	64.71(19)
N2-Ir1-C2	166.37(17)	C4-Ir1-O1	165.17(16)
N2-Ir1-C4	106.57(15)	C4-Ir1-C2	65.22(17)
N2-Ir1-C3	140.33(17)	C4-Ir1-C3	38.91(19)
N2-Ir1-C1	128.27(19)	C4-Ir1-C1	64.95(19)
N2-Ir1-C5	101.95(16)	C4-Ir1-C5	38.5(2)
N1-Ir1-O1	79.73(12)	C3-Ir1-O1	136.94(17)
N1-Ir1-C2	116.51(17)	C1-Ir1-O1	100.24(16)
N1-Ir1-C4	113.88(18)	C1-Ir1-C2	39.1(2)
N1-Ir1-C3	98.64(16)	C1-Ir1-C3	64.30(19)
N1-Ir1-C1	155.2(2)	C1-Ir1-C5	38.3(2)
N1-Ir1-C5	151.48(19)	C5-Ir1-O1	128.59(18)
C2-Ir1-O1	104.13(15)	C5-Ir1-C3	64.08(18)

Table S20. Bond lengths (Å) and angles (°) of **5-Cl**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-Cl1	2.4085(10)	Ir1-C5	2.157(4)
Ir1-N2	2.062(3)	Ir1-C1	2.145(3)
Ir1-N1	2.125(3)	N2-N3	1.342(4)
Ir1-C3	2.172(3)	F1-C19	1.260(6)
Ir1-C2	2.150(3)	C19- F2	1.234(6)
Ir1-C4	2.169(3)	C19- F3	1.263(6)
	Bond Angles (°)		Bond Angles (°)
N2-Ir1-Cl1	90.81(9)	C2-Ir1-Cl1	116.27(10)
N2-Ir1-N1	75.70(11)	C2-Ir1-C3	38.36(13)
N2-Ir1-C3	134.59(13)	C2-Ir1-C4	65.14(14)
N2-Ir1-C2	101.07(13)	C2-Ir1-C5	64.84(14)
N2-Ir1-C4	162.33(14)	C4-Ir1-Cl1	105.05(11)
N2-Ir1-C5	126.36(13)	C4-Ir1-C3	38.69(13)
N2-Ir1-C1	96.94(13)	C5-Ir1-Cl1	142.66(11)
N1-Ir1-Cl1	85.20(8)	C5-Ir1-C3	64.48(13)
N1-Ir1-C3	149.71(12)	C5-Ir1-C4	38.98(14)
N1-Ir1-C2	158.47(12)	C1-Ir1-Cl1	155.26(10)
N1-Ir1-C4	112.76(12)	C1-Ir1-C3	64.82(13)
N1-Ir1-C5	99.49(12)	C1-Ir1-C2	39.17(13)
N1-Ir1-C1	119.46(12)	C1-Ir1-C4	65.41(14)
C3-Ir1-Cl1	93.17(9)	C1-Ir1-C5	38.59(15)

Table S21. Bond lengths (Å) and angles (°) of **5-H_2O**

	Bond Distances(Å)		Bond Distances(Å)
Ir1-O1	2.154(3)	Ir1-C2	2.138(4)
Ir1-N1	2.118(3)	Ir1-C5	2.137(4)
Ir1-N2	2.040(3)	N2-N3	1.341(4)
Ir1-C3	2.191(4)	F1-C19	1.292(7)
Ir1-C4	2.178(4)	F2-C19	1.369(7)
Ir1-C1	2.138(4)	C19-F3	1.289(6)
	Bond Angles (°)		Bond Angles (°)
O1-Ir1-C3	119.37(13)	N2-Ir1-C5	109.41(13)
O1-Ir1-C4	97.75(12)	C4-Ir1-C3	38.09(14)
N1-Ir1-O1	79.16(11)	C1-Ir1-O1	146.87(13)
N1-Ir1-C3	106.49(13)	C1-Ir1-C3	65.58(14)
N1-Ir1-C4	136.84(13)	C1-Ir1-C4	65.56(15)
N1-Ir1-C1	132.95(14)	C2-Ir1-O1	158.78(14)
N1-Ir1-C2	104.15(13)	C2-Ir1-C3	39.43(15)
N1-Ir1-C5	169.96(13)	C2-Ir1-C4	65.22(14)
N2-Ir1-O1	80.59(11)	C2-Ir1-C1	39.12(15)
N2-Ir1-N1	76.48(12)	C5-Ir1-O1	109.50(13)
N2-Ir1-C3	160.03(13)	C5-Ir1-C3	65.13(14)
N2-Ir1-C4	146.11(13)	C5-Ir1-C4	39.00(14)
N2-Ir1-C1	97.59(13)	C5-Ir1-C1	39.66(15)
N2-Ir1-C2	120.63(14)	C5-Ir1-C2	65.92(14)

5. Stability testing of complexes 2-H_2O and 5-H_2O

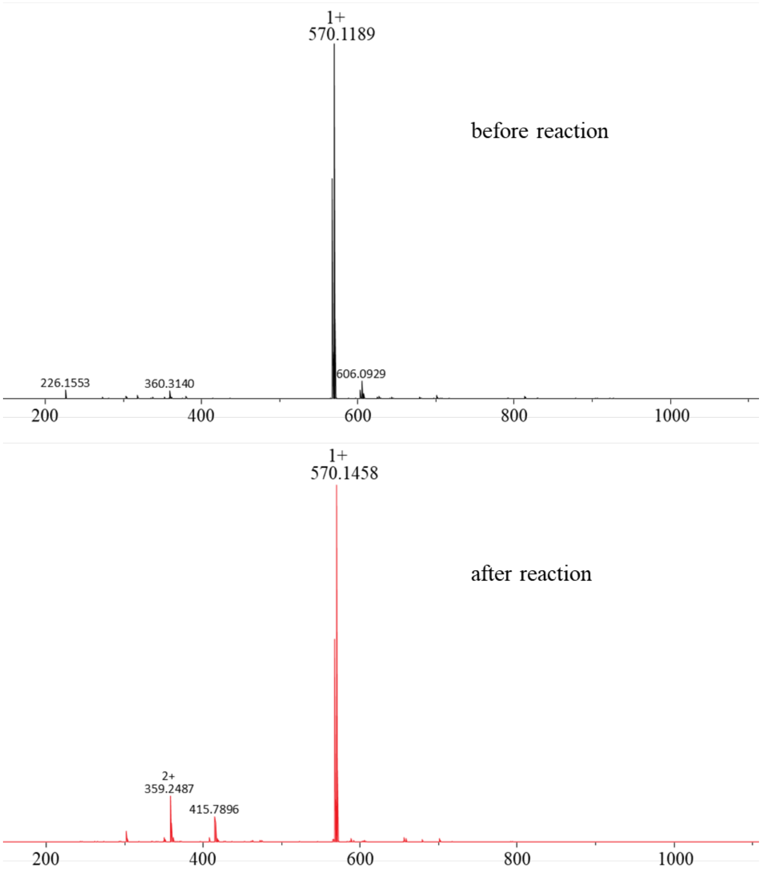


Figure S51. Mass spectra comparison of **2-H_2O** before and after reaction

Reaction condition: catalyst (**2-H_2O**), FA (4 mmol), H_2O (2 mL), T=90 ^oC.

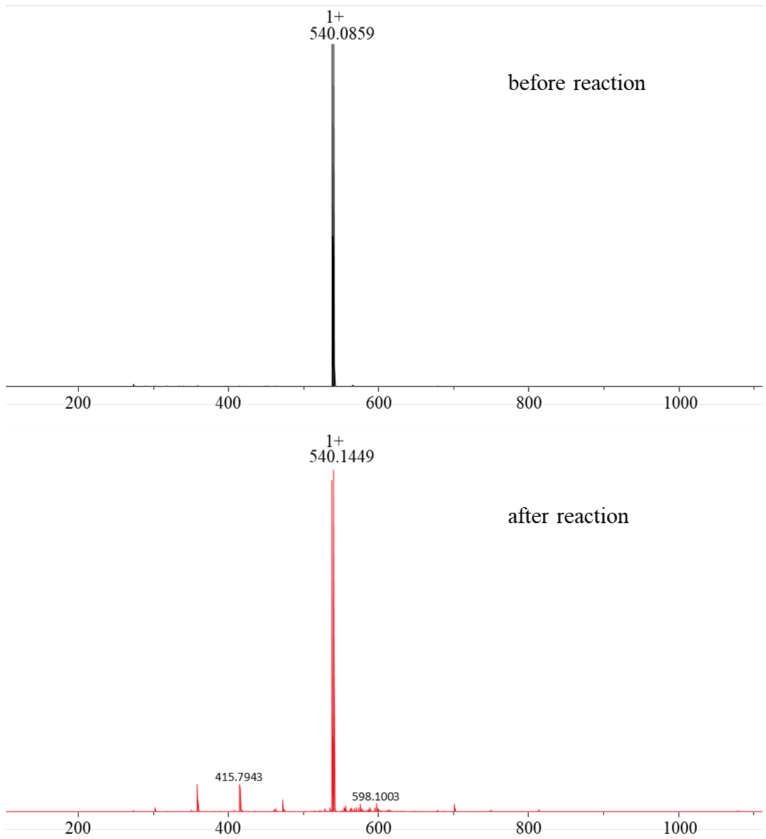


Figure S52. Mass spectra comparison of **5-H_2O** before and after reaction

Reaction condition: catalyst (**5-H_2O**), FA (4 mmol), H_2O (2 mL), T=90 ^oC.

6. Experimental detection of Ir-H intermediates in complexes 2-H_2O and 5-H_2O

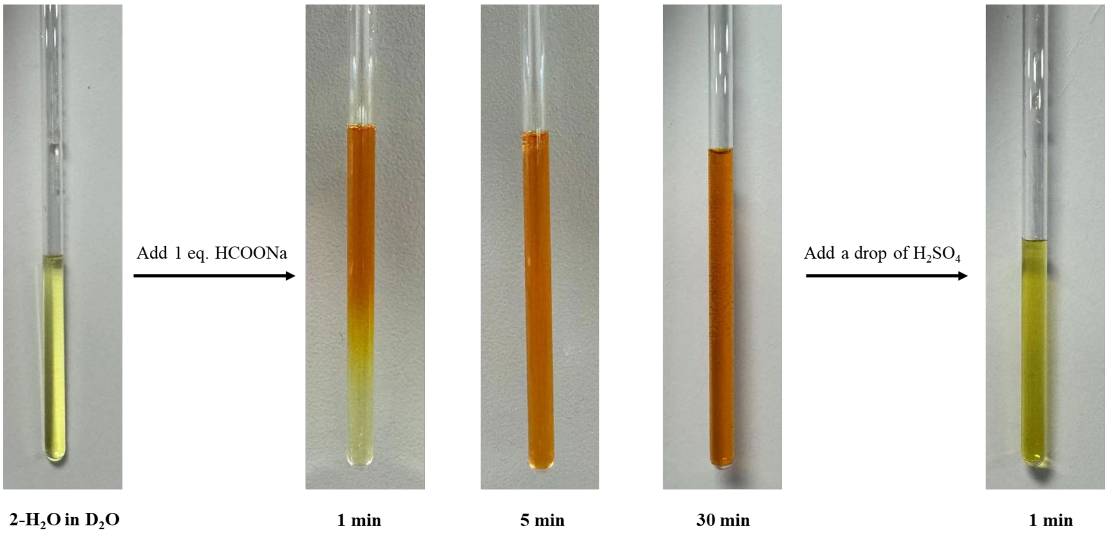


Figure S53. Color changes during the detection process of **2-H_2O** intermediate

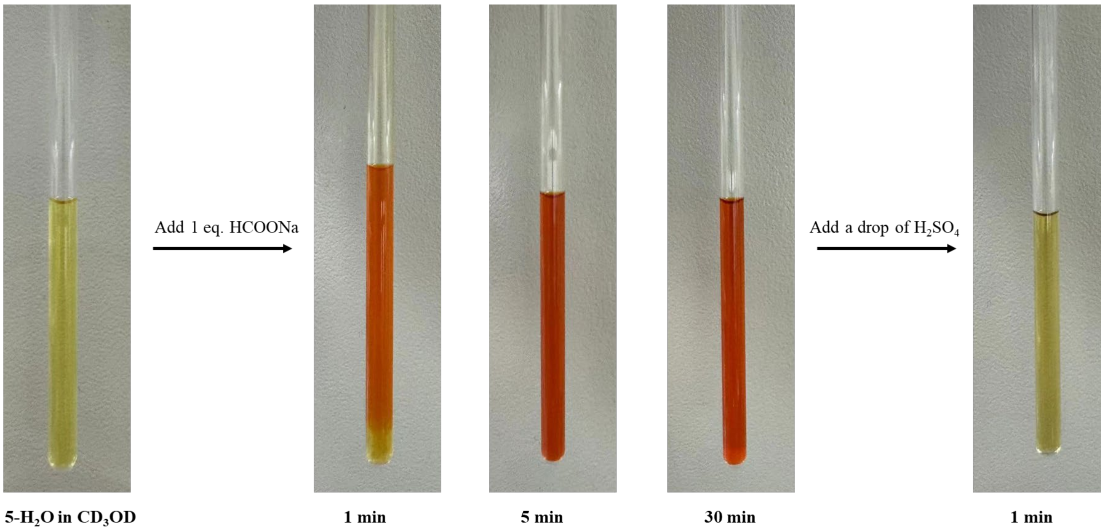


Figure S54. Color changes during the detection process of **5-H_2O** intermediate

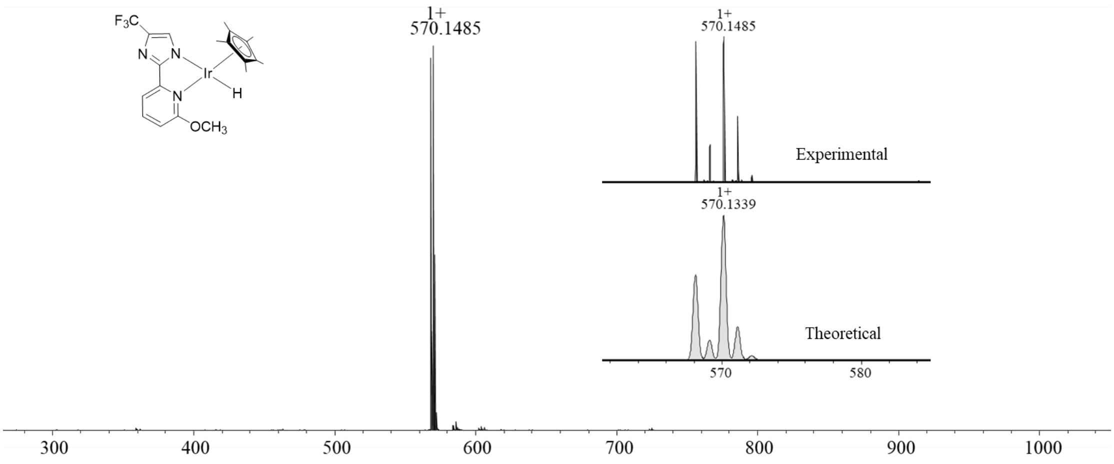


Figure S55. ESI-MS spectra after adding 1 eq HCOONa to **2-H_2O**

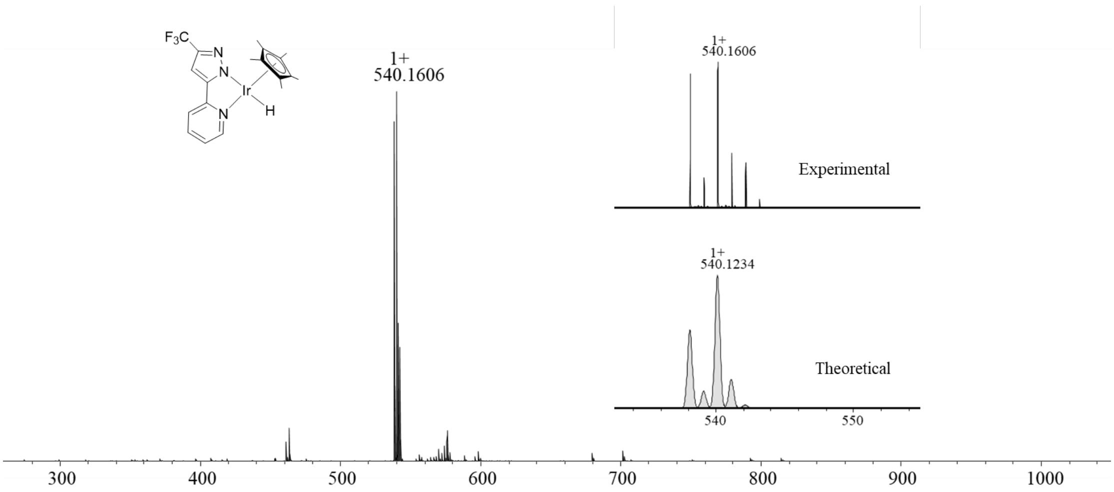


Figure S56. ESI-MS spectra after adding 1 eq HCOONa to **5-H_2O**

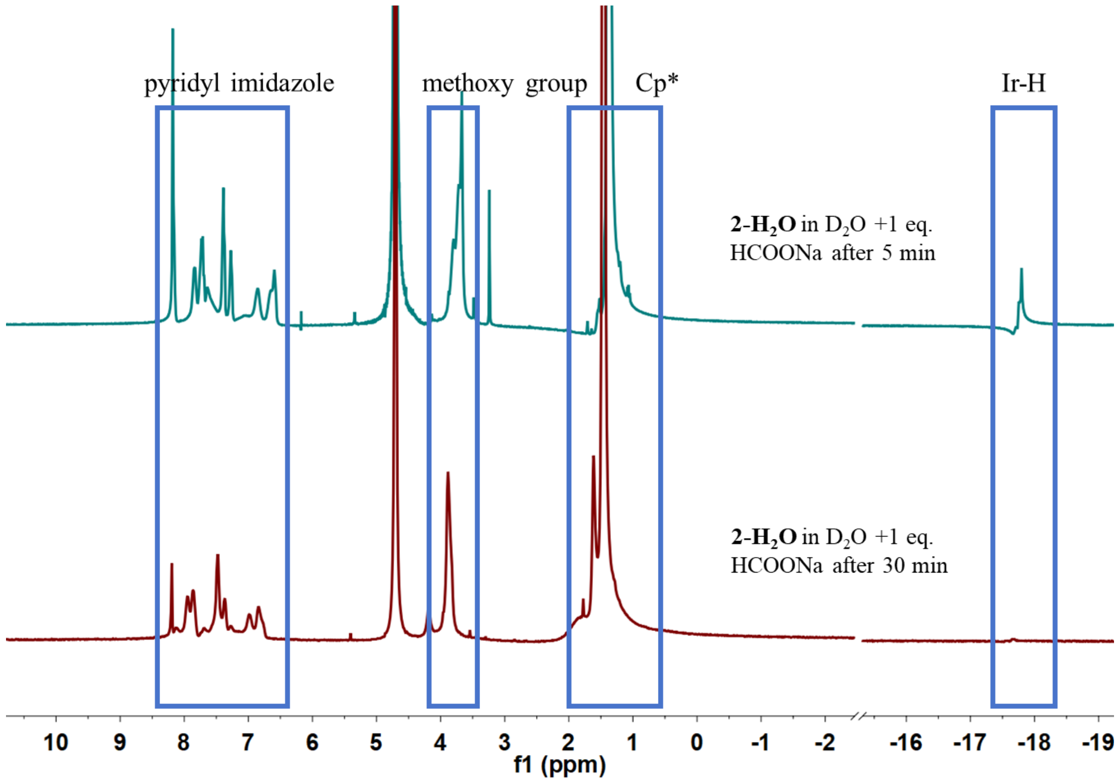


Figure S57. [1]H NMR changes of **2-H_2O** intermediate after 30 minutes

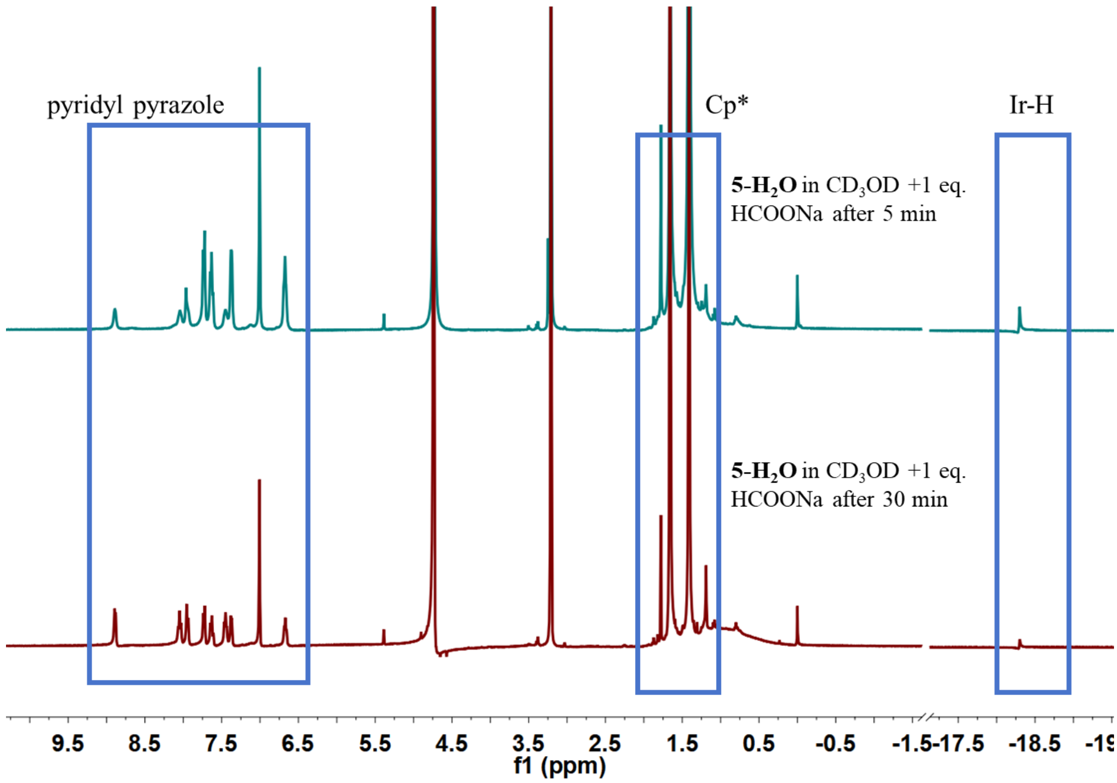


Figure S58. [1]H NMR changes of **5-H_2O** intermediate after 30 minutes

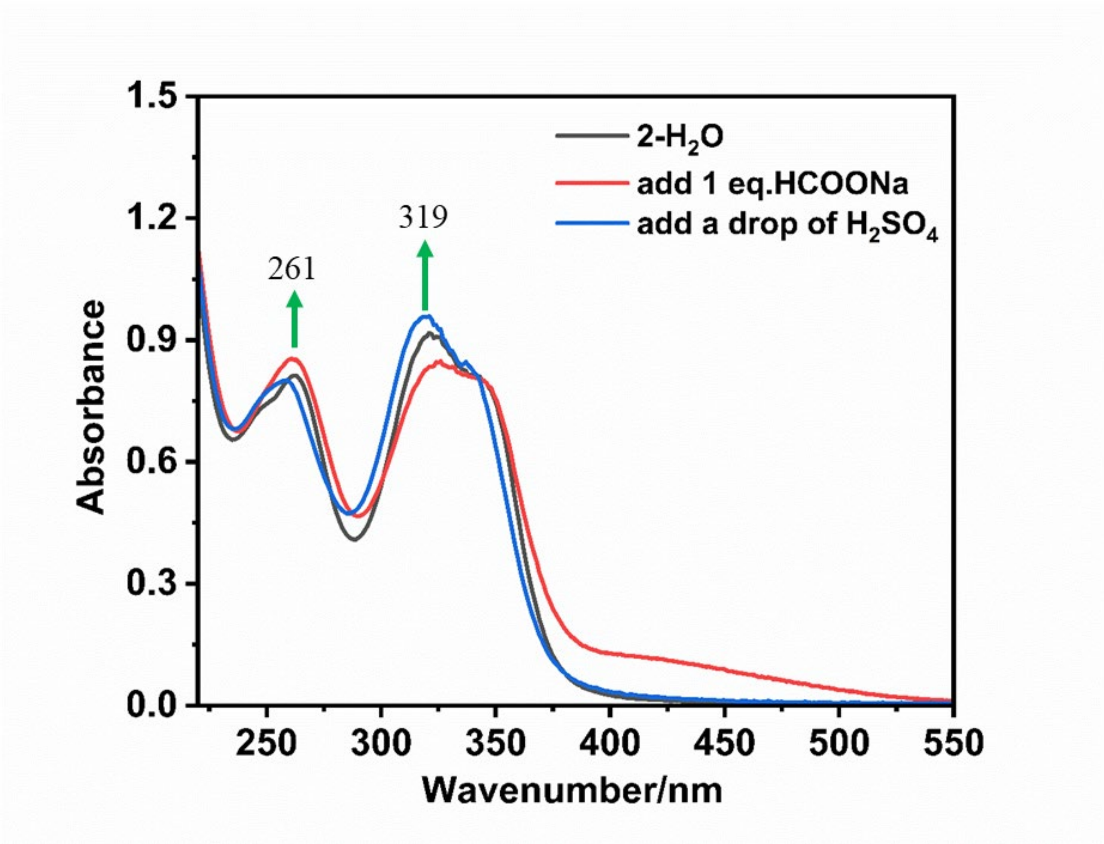


Figure S59. UV-vis spectra changes in the detection process of **2-H_2O** intermediate

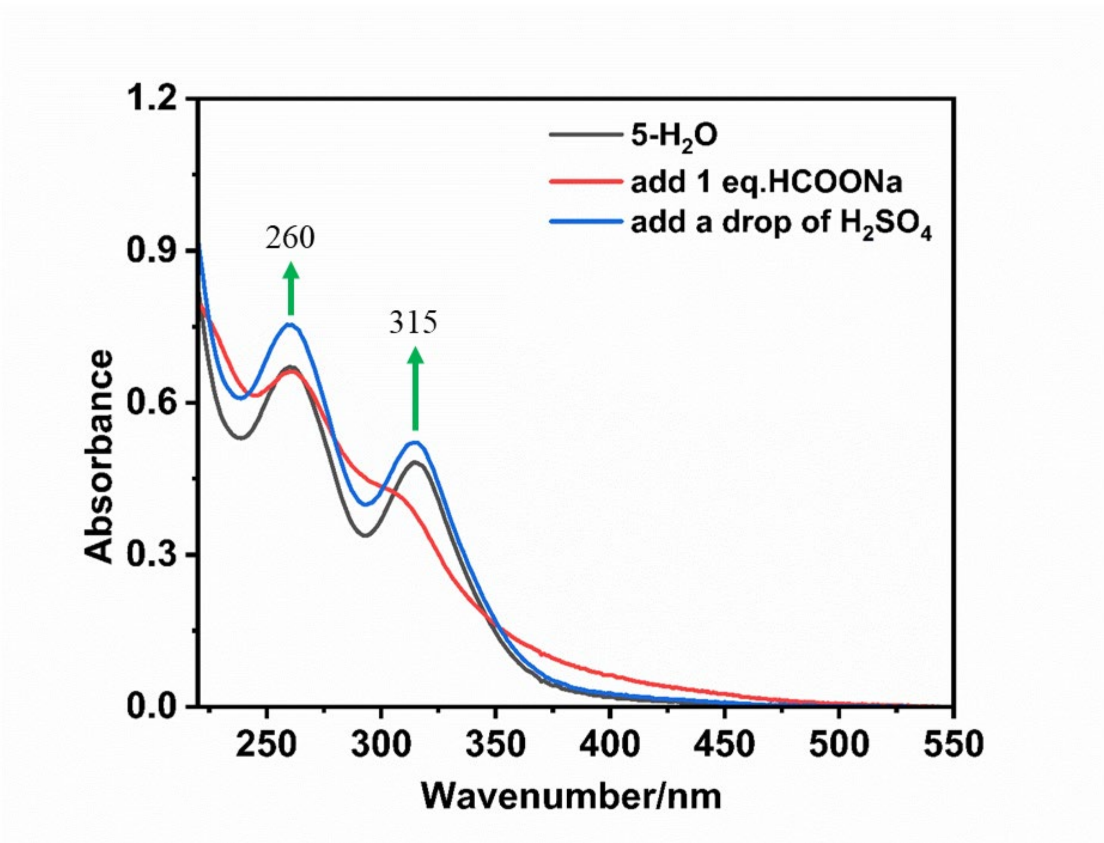


Figure S60. UV-vis spectra changes in the detection process of **5-H_2O** intermediate

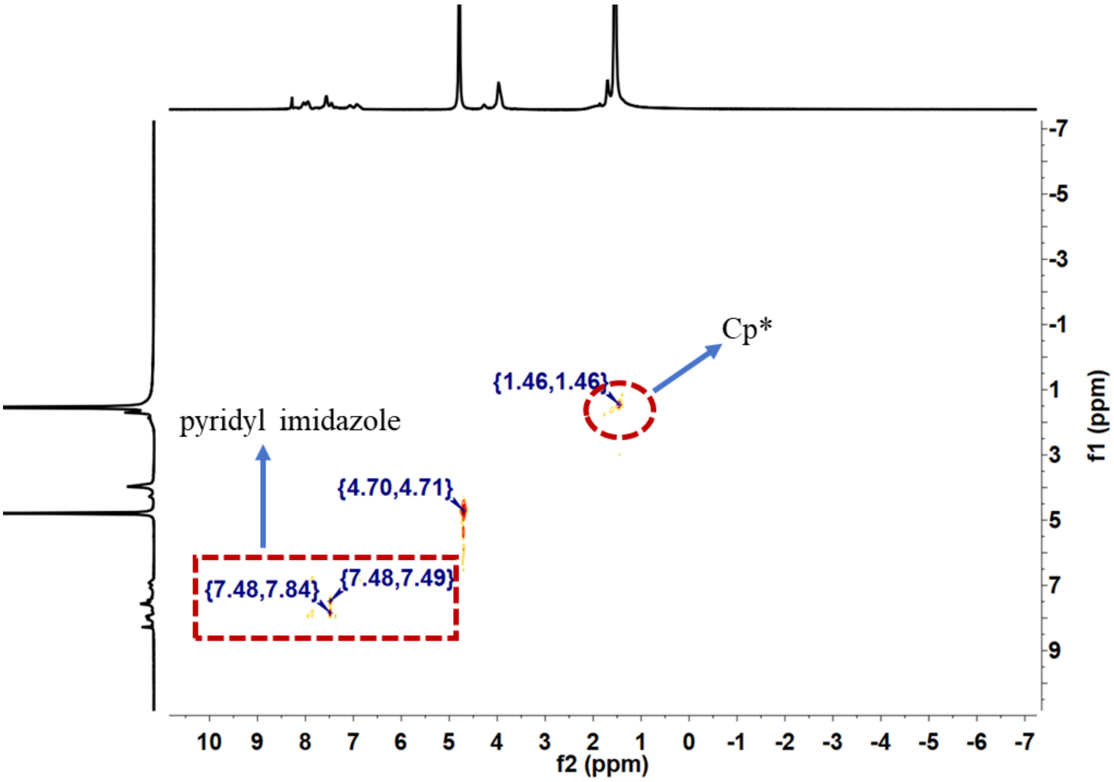


Figure S61. ^{1}H-COSY NMR of **Ir^{III}−H** intermediate of **2-H$_2$O**

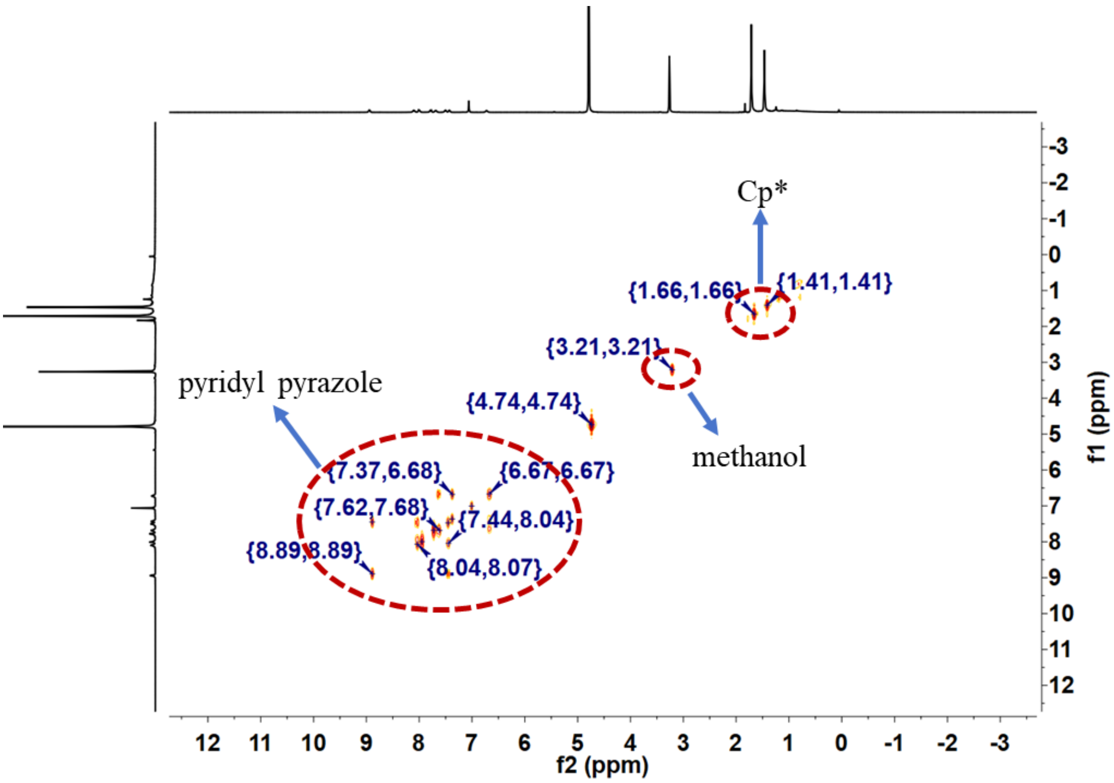


Figure S62. ^{1}H-COSY NMR of **Ir^{III}−H** intermediate of **2-H$_2$O**

7. Gas analysis

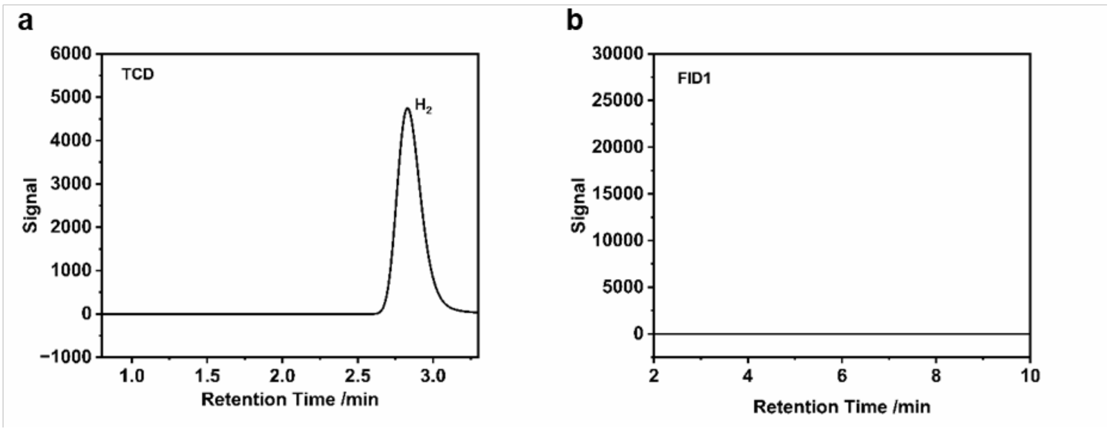


Figure S63. Gas chromatogram result of complex **5-H_2O**

8. DFT calculations

The structures of all species were optimized using the M06 exchange-correlation functional with the BSI basis set (the basis set combination of SDD for Ir atom and the all-electron 6-31G(d,p) for C, N, O, F and H atoms). All stationary points were minima or transition states by vibration frequency calculations. The solvation effects of water solvent were considered by solvation model density (SMD). Intrinsic reaction coordinate (IRC)analysis was carried out to confirm the right connections between a transition state and the respective minima on both sides. The energy was refined by a single-point calculation at the M06 level of theory coupled with an SMD solvent model, along with SDD for metal atom and the all-electron 6-311++G (2d, p) basis set for other atoms. All calculations were performed in the Gaussian 09 program package.

Table S22. Comparison of main bond lengths and bond angles of **2-H_2O** and **5-H_2O** from experimental and optimized results.

Bond Distances(Å)	**2-H_2O/** Exp.	**2-H_2O/**Cal.	Bond Distances(Å)	**5-H_2O/** Exp.	**5-H_2O/** Cal.
Ir1-O1	2.151(3)	2.33598	Ir1-O1	2.154(3)	2.34742
Ir1-N1	2.155(3)	2.23330	Ir1-N1	2.118(3)	2.17373
Ir1-N2	2.068(3)	2.14431	Ir1-N2	2.040(3)	2.10174
F2-C20	1.341(6)	1.33700	N2-N3	1.341(4)	1.32857
F1-C20	1.317(6)	1.33114	F1-C19	1.292(7)	1.34194
F3-C20	1.341(5)	1.33725	F2-C19	1.369(7)	1.33827
O2-C12	1.334(5)	1.33017	C19-F3	1.289(6)	1.34358
O2-C11	1.431(5)	1.42881	-	-	-
Bond Angles (°)	**2-H_2O/** experimental	**2-H_2O/** calculational	Bond Angles (°)	**5-H_2O/** experimental	**5-H_2O/** calculational
O1-Ir1-C3	95.94(14)	98.42184	N1-Ir1-O1	79.16(11)	80.48459
O1-Ir1-N1	81.29(11)	78.71232	O1-Ir1-C4	97.75(12)	97.63237
O1-Ir1-C4	110.75(14)	104.57116	N1-Ir1-C3	106.49(13)	106.98253
O1-Ir1-C5	148.42(15)	138.67391	N1-Ir1-C4	136.84(13)	138.45525
N1-Ir1-C3	148.17(15)	154.93968	N1-Ir1-C1	132.95(14)	130.69038
N1-Ir1-C4	113.16(15)	117.56006	N1-Ir1-C2	104.15(13)	102.48434
N1-Ir1-C5	102.17(15)	101.43559	N1-Ir1-C5	169.96(13)	167.98757
N2-Ir1-O1	80.90(13)	85.06067	N2-Ir1-O1	80.59(11)	80.57176
N2-Ir1-N1	76.32(13)	73.99703	N2-Ir1-N1	76.48(12)	75.14660

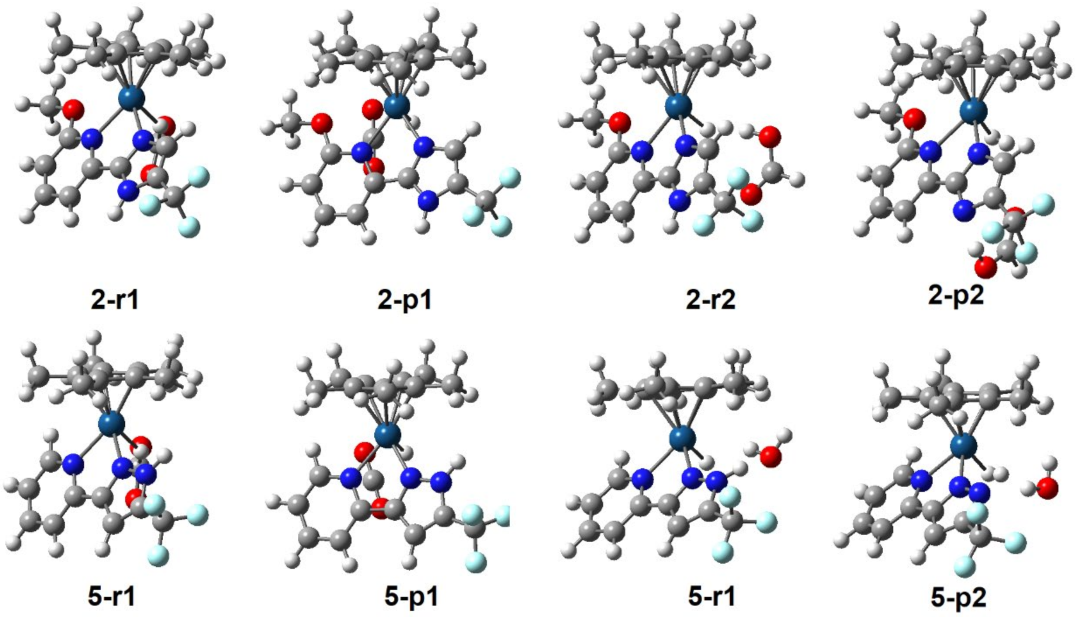


Figure S64. Optimized structures of intermediates 2-r1, 2-p1, 2-r2, 2-p2, 5-r1, 5-p1, 5-r2 and 5-p2

Table S23. Cartesian coordinates for the key structures involved in this study.

2-H_2O(IN1')

2 1

Ir	0.71704400	-0.50896600	-0.20955100
O	0.72182500	0.09510100	-2.46607400
H	0.77810400	-0.75473400	-2.92770500
H	1.59867900	0.49357200	-2.57969000
O	2.81363500	1.91841100	-0.35176700
F	-5.66267200	0.56806600	-1.06152000
F	-5.28846300	-1.37862700	-0.20060300
N	0.60227200	1.71678900	-0.06649200
N	-3.01133600	1.39698600	0.06192500
H	-3.51505200	2.26238600	0.24328500
F	-5.56885500	0.34749900	1.07126500
N	-1.36960600	-0.01925900	-0.27400700
C	-0.63567100	2.25206800	0.07095900
C	0.88224800	-1.61915200	1.60945300
C	1.74518600	-2.43788400	-0.39119000
C	-1.67925600	1.25418600	-0.03652800
C	1.66278400	2.53172400	-0.08958000
C	2.67266500	-1.44709200	0.11462800
C	0.65262900	-2.55549700	0.52063600
C	-0.85160200	3.60113900	0.27098100

H	-1.85735100	3.99463100	0.38482600
C	-3.56846600	0.15493400	-0.11413000
C	1.90375600	-3.18447700	-1.66237300
H	0.93589600	-3.40243000	-2.12601800
H	2.40201300	-4.14287500	-1.46647900
H	2.52145200	-2.63098600	-2.37699400
C	0.26644800	4.43232700	0.31838200
H	0.14421100	5.49812500	0.48792600
C	2.15261500	-0.96977500	1.36473700
C	1.53187300	3.91021400	0.13135700
H	2.40536700	4.55236300	0.14364300
C	-2.54014900	-0.72106300	-0.32079100
H	-2.57995600	-1.78591300	-0.50653400
C	-5.03089300	-0.07855600	-0.07647800
C	4.01814200	2.68595000	-0.31260900
H	4.00680200	3.46616800	-1.08098900
H	4.82471000	1.98086700	-0.51975100
H	4.16205600	3.13074400	0.67823900
C	-0.48179300	-3.50511100	0.39603700
H	-1.33191100	-3.20576900	1.01649100
H	-0.16366800	-4.50188700	0.72681000
H	-0.82152000	-3.59286900	-0.64167400
C	0.03760000	-1.46146400	2.82044600
H	0.13899200	-0.45899600	3.24848300
H	0.33913800	-2.18619700	3.58727800
H	-1.02108700	-1.63189400	2.59712800
C	2.78646700	0.02345400	2.26668700
H	3.49846200	0.66197400	1.73559700
H	3.32672000	-0.50615000	3.06178200
H	2.04040100	0.66432700	2.74833900
C	3.95902300	-1.08561700	-0.53826800
H	3.80649000	-0.80146600	-1.58660700
H	4.64267200	-1.94357700	-0.52659400
H	4.45128400	-0.25304300	-0.02902700

IN2’

1 1

Ir	0.74363300	-0.45998000	-0.06639000
O	2.82538200	1.94021100	-0.46457500
F	-5.64967300	0.63200200	-0.89376300
F	-5.28687800	-1.29688200	0.01441500
N	0.62349100	1.76250400	-0.07915200
N	-2.99428300	1.47635100	0.13593000
H	-3.49613300	2.35631000	0.22881100

F	-5.55422900	0.46040600	1.24331900
N	-1.35899300	0.02803400	-0.06995300
C	-0.60861000	2.31295900	0.05511500
C	0.91004400	-1.42941900	1.85892800
C	1.82716000	-2.37870700	-0.06249000
C	-1.66062800	1.31688200	0.05535900
C	1.68123300	2.57223900	-0.21007200
C	2.70358300	-1.31207000	0.36746900
C	0.72056900	-2.44874400	0.83849800
C	-0.81624200	3.67639500	0.14601900
H	-1.81649200	4.08420800	0.25804300
C	-3.55686600	0.22682800	0.05627200
C	2.07921900	-3.23489600	-1.24840300
H	1.21199300	-3.84836500	-1.50491000
H	2.92249300	-3.90510800	-1.03655600
H	2.35007300	-2.63080700	-2.12159000
C	0.30106400	4.50559100	0.08325800
H	0.18487000	5.58237300	0.16354400
C	2.14909700	-0.75805900	1.58106900
C	1.55871800	3.96436900	-0.10238500
H	2.43207700	4.60234100	-0.17622300
C	-2.53160000	-0.66849900	-0.07094700
H	-2.57604900	-1.74575900	-0.16394900
C	-5.01984800	0.00423800	0.10516500
C	4.02607200	2.71094500	-0.52498400
H	3.98103700	3.44320300	-1.33808700
H	4.82735500	1.99798900	-0.72477800
H	4.21069900	3.21520100	0.43020100
C	-0.39073400	-3.43340400	0.79299500
H	-1.29240200	-3.04772200	1.27959000
H	-0.09634200	-4.34734200	1.32449200
H	-0.64640600	-3.71183100	-0.23433000
C	0.02629500	-1.18315100	3.02861300
H	0.02515200	-0.12376900	3.30675300
H	0.36730900	-1.75871200	3.89834700
H	-1.00848400	-1.47495500	2.82063200
C	2.74439500	0.31430300	2.41719300
H	3.42478600	0.94953000	1.84362300
H	3.31594900	-0.14040800	3.23632100
H	1.97380600	0.94927700	2.86679000
C	4.02155400	-1.00787200	-0.25134900
H	3.93502500	-0.88347300	-1.33740100
H	4.72285700	-1.83236800	-0.06799500
H	4.46014500	-0.09620100	0.16273700

O	-0.61858700	-1.88071800	-2.66652300
O	0.64368300	-0.06056900	-2.21094400
C	0.00317300	-0.86331100	-2.98217000
H	0.04274000	-0.55416500	-4.04817800

TS1'

E= -1607.58719683 (a.u.) -532.35 *i* cm^{-1}

1 1

Ir	-0.64495500	-0.54453100	0.09349600
O	-2.74043200	1.85167300	-0.21878500
F	5.66434300	0.56328800	1.13424800
F	5.38027100	-1.40930500	0.30309900
N	-0.51753300	1.60932800	-0.38051200
N	3.09987200	1.31261400	-0.26892900
H	3.61051300	2.16280500	-0.49556200
F	5.72108300	0.29054300	-0.99381800
N	1.44344000	-0.08692600	0.08053900
C	0.72681700	2.13991000	-0.48025000
C	-0.94993400	-1.93978800	-1.62773400
C	-1.59508200	-2.45714200	0.55788400
C	1.76354800	1.16425200	-0.24143400
C	-1.56967400	2.43708900	-0.45547100
C	-2.59572000	-1.57342300	-0.00766900
C	-0.57980900	-2.66826200	-0.43014600
C	0.96356500	3.47847100	-0.72831000
H	1.97919600	3.85653500	-0.79532000
C	3.64781400	0.09578100	0.04855500
C	-1.65582600	-3.08108700	1.90567400
H	-0.65790300	-3.33434900	2.27725000
H	-2.24395700	-4.00733100	1.86548300
H	-2.13251000	-2.41701100	2.63395400
C	-0.14025600	4.31373600	-0.87130000
H	-0.00280900	5.37182200	-1.07411700
C	-2.19817400	-1.28986200	-1.36430900
C	-1.41656100	3.80156500	-0.73138800
H	-2.28437100	4.44591200	-0.81437500
C	2.61201200	-0.76940500	0.26646100
H	2.64707300	-1.81283900	0.54841800
C	5.11123400	-0.11790900	0.12462800
C	-3.93002200	2.63180700	-0.34125000
H	-3.93007600	3.45724600	0.37856500
H	-4.75493500	1.95351500	-0.11766400
H	-4.03706400	3.01650500	-1.36143500
C	0.59953600	-3.56083200	-0.29488600

H	1.41856400	-3.25018300	-0.95199800
H	0.32157300	-4.58464600	-0.57660200
H	0.97042900	-3.58984600	0.73510300
C	-0.20397000	-1.93142500	-2.91408000
H	0.87952800	-1.94493500	-2.74930000
H	-0.44418100	-1.04090300	-3.50462000
H	-0.45680100	-2.81174500	-3.51958900
C	-2.93814400	-0.46530100	-2.35553600
H	-3.76446200	0.08641000	-1.90096800
H	-3.35481600	-1.12013800	-3.13154400
H	-2.27451400	0.24917100	-2.85637100
C	-3.88374800	-1.21081300	0.64100000
H	-3.76578100	-1.09089900	1.72276300
H	-4.62740200	-2.00185800	0.47632600
H	-4.29625900	-0.27966700	0.24123800
H	-0.51678500	-0.00147900	1.71156500
C	-1.12380000	1.08012900	2.65422700
O	-2.09150400	0.56358100	3.12827400
O	-0.36247300	1.99799200	2.58077800

IN3'

1 1

Ir	0.73191900	-0.45058900	-0.32227000
O	2.78031800	2.05209100	-0.34582600
F	-5.69100000	0.43412800	-1.03511600
F	-5.25114700	-1.47392600	-0.11974400
N	0.56303100	1.76735100	-0.14883300
N	-3.04853400	1.36951500	0.01563400
H	-3.57392000	2.22868900	0.15690700
F	-5.56221000	0.28274900	1.10152000
N	-1.36811900	-0.02055900	-0.25379700
C	-0.68969600	2.27258600	-0.00593000
C	1.03840700	-1.94476300	1.45028500
C	1.92000200	-2.23496500	-0.70285100
C	-1.70965900	1.25252300	-0.07548900
C	1.59544100	2.62344200	-0.12923400
C	2.74384100	-1.29432800	0.00490300
C	0.81641400	-2.57134000	0.14935000
C	-0.94946100	3.61681000	0.19376300
H	-1.96864500	3.97395900	0.30824900
C	-3.57251300	0.10774000	-0.10489800
C	2.19708500	-2.79507300	-2.05367000
H	1.27371100	-3.05694200	-2.58035600
H	2.80226100	-3.70696000	-1.96563300

H	2.75339200	-2.08383700	-2.67311100
C	0.13573400	4.48378100	0.25394800
H	-0.01992600	5.54496500	0.42510600
C	2.20592700	-1.16417900	1.35407200
C	1.41875200	3.99438800	0.09097800
H	2.27290500	4.66044200	0.12908400
C	-2.52131700	-0.75039700	-0.27414600
H	-2.53505600	-1.82303000	-0.41306300
C	-5.02632800	-0.16377400	-0.04024300
C	3.94759000	2.87101800	-0.29805100
H	3.89910400	3.66726800	-1.04888700
H	4.78513800	2.21067000	-0.52717600
H	4.08051800	3.30133400	0.70095300
C	-0.24419100	-3.57265400	-0.14731100
H	-1.15058700	-3.38427200	0.43829100
H	0.10280000	-4.58332100	0.10597000
H	-0.51513000	-3.56905600	-1.20884500
C	0.15170300	-2.12328900	2.63102400
H	0.32793100	-1.35730000	3.39258300
H	0.31842800	-3.10355100	3.09724700
H	-0.90827700	-2.08166800	2.35194100
C	2.81160500	-0.31159700	2.41142400
H	3.12041000	0.66159500	2.00984100
H	3.71115300	-0.79127200	2.81893000
H	2.11869200	-0.13767600	3.24040200
C	4.08018200	-0.81103300	-0.44300400
H	4.06822900	-0.49579500	-1.49248800
H	4.82772000	-1.60993600	-0.34529200
H	4.41970700	0.03445200	0.16271500
H	0.60655600	-0.13019400	-1.90242000

TS2’

E= -1608.78435011 (a.u.) -48.45 *i* cm^{-1}

1 1

Ir	-0.89906800	-0.47592500	0.19351900
O	-2.86773500	2.10521200	0.11617200
F	5.48674800	0.08881200	0.32067700
F	4.97292200	-1.78138400	-0.62547500
N	-0.69599800	1.70427500	-0.28171300
N	2.85595700	1.11638000	-0.80033400
H	3.39164300	1.92691600	-1.10008300
F	5.31585600	-0.00697400	-1.81790700
N	1.17609600	-0.14471800	-0.15714000
C	0.55489600	2.13714700	-0.58639900

C	-2.43430900	-1.24403400	-1.32922000
C	-1.09407800	-2.62378500	-0.03257000
C	1.53784100	1.08065500	-0.52697800
C	-1.68852200	2.60535200	-0.25239100
C	-2.15925200	-2.15132300	0.80634900
C	-1.30264900	-2.08861500	-1.37564200
C	0.84811500	3.45279100	-0.89839700
H	1.86484800	3.75381900	-1.13266700
C	3.34655200	-0.14320900	-0.57730500
C	-0.08767600	-3.65450300	0.34018500
H	-0.51899200	-4.65936100	0.23806800
H	0.24325100	-3.53757500	1.37791200
H	0.79385800	-3.61215900	-0.30787400
C	-0.19858400	4.36796400	-0.89488700
H	-0.01510800	5.41050000	-1.13779300
C	-2.96008500	-1.24577100	0.03175300
C	-1.47644500	3.95278900	-0.56878200
H	-2.29798800	4.65939500	-0.55239200
C	2.29659200	-0.92280900	-0.17813500
H	2.29010900	-1.96906900	0.09816100
C	4.78706700	-0.46385000	-0.67792900
C	-4.00205100	2.97122600	0.11141300
H	-3.86928200	3.79563300	0.81987000
H	-4.84863600	2.36075700	0.42843900
H	-4.18683200	3.36366800	-0.89466200
C	-0.43121700	-2.37699900	-2.54575600
H	-0.66352100	-3.36135200	-2.97241000
H	0.62825200	-2.38960400	-2.26226800
H	-0.55953600	-1.62921500	-3.33498300
C	-3.00458300	-0.44642600	-2.44745900
H	-3.33946300	0.54037400	-2.10544900
H	-3.87840500	-0.95631800	-2.87339800
H	-2.27670800	-0.30092500	-3.25215200
C	-4.25890900	-0.65796000	0.46108500
H	-4.22379900	-0.31039900	1.49972600
H	-5.05521300	-1.41121800	0.39042200
H	-4.54627500	0.18787000	-0.17002300
C	-2.42315900	-2.57262800	2.20834800
H	-1.49823000	-2.83301900	2.73304100
H	-3.07183100	-3.45852000	2.21536700
H	-2.92817400	-1.78367200	2.77479800
H	-0.68427900	0.03862900	1.72804300
C	2.39199800	1.03218900	3.36479200
H	2.79385300	1.24795600	4.36659400

O	3.06519600	0.96140600	2.36131600
O	1.07506700	0.86412900	3.42035100
H	0.72309700	0.64229100	2.52824500

IN4'

2 1

Ir	0.75350600	-0.52326300	-0.37605700
O	2.83869200	1.89498500	-0.61427300
F	-5.62490400	0.62631200	-1.08494300
F	-5.29004800	-1.35953300	-0.30217800
N	0.63950400	1.68131100	-0.24097600
N	-2.96703800	1.36478900	0.06625500
H	-3.45908000	2.22795700	0.28706800
F	-5.53772300	0.32045300	1.03763300
N	-1.35143700	-0.05070400	-0.37003600
C	-0.58633800	2.20325000	0.01883700
C	0.82395700	-1.42920800	1.56605800
C	1.78921000	-2.49092300	-0.26680700
C	-1.63888100	1.21333800	-0.06681100
C	1.70156700	2.49538100	-0.27452600
C	2.69344500	-1.44569600	0.17047900
C	0.64402100	-2.48993300	0.58397600
C	-0.78516900	3.53948200	0.30211500
H	-1.78115800	3.92006300	0.50733000
C	-3.54122700	0.13849200	-0.15679600
C	2.02781400	-3.38559100	-1.42368900
H	1.09207800	-3.77880900	-1.83137500
H	2.64263500	-4.23703800	-1.10449700
H	2.56832100	-2.86732600	-2.22223400
C	0.33353500	4.37074000	0.31337900
H	0.22442500	5.42682300	0.54182100
C	2.11990500	-0.83615600	1.33661200
C	1.58356300	3.86037600	0.02011700
H	2.45781300	4.50150400	0.01016300
C	-2.52787700	-0.73946100	-0.42465100
H	-2.58091700	-1.79442600	-0.65809200
C	-5.00768500	-0.07122100	-0.12541600
C	4.04588300	2.66077600	-0.56901000
H	4.01511200	3.47578100	-1.29929500
H	4.84690600	1.96703100	-0.82704800
H	4.21175200	3.05985700	0.43792700
C	-0.49511400	-3.43948300	0.51557400
H	-1.39421200	-3.03407700	0.98917700
H	-0.23107800	-4.36463100	1.04308600

H	-0.73694900	-3.70349300	-0.51939300
C	-0.11404100	-1.08573400	2.66557400
H	-0.05435200	-0.02067500	2.91451700
H	0.12801400	-1.65918600	3.56887800
H	-1.14938700	-1.31061200	2.38868200
C	2.72962700	0.22491900	2.17163000
H	3.46719200	0.81222100	1.61826800
H	3.24123300	-0.25069000	3.01840100
H	1.97605500	0.90262300	2.58546000
C	4.03353400	-1.18119200	-0.41501800
H	3.98948800	-1.16383600	-1.50918800
H	4.73450200	-1.97281300	-0.12188700
H	4.43899200	-0.22438000	-0.07430500
H	1.02666400	-0.07495400	-2.27041400
H	0.44498500	-0.63135900	-2.29351900

5-H_2O(IN1)

1 1

Ir	0.87348000	-0.22877300	-0.19980900
O	0.45026000	0.27929100	-2.45217400
H	1.34404400	0.45601200	-2.78303400
H	0.23885500	-0.60302100	-2.79410000
N	0.65119500	1.92808200	-0.04603200
N	-1.20088900	0.09304800	-0.09626200
C	2.96139200	-0.70553500	0.36288500
C	2.49006000	-1.71233300	-0.53105100
C	1.08482100	-1.72786500	1.32555800
C	2.07752200	-0.69444200	1.51446700
N	-2.22034100	-0.75889500	-0.09556400
C	1.32135000	-2.34318600	0.03925000
C	1.67783000	2.79204800	-0.03903600
H	2.67488100	2.35911800	-0.08144000
C	-1.63853200	1.37728600	-0.03572700
C	-0.61975300	2.40232000	-0.01527700
F	-4.87644500	-1.45102800	-1.02261400
C	-3.32591700	0.00866100	-0.03402700
C	-3.02770900	1.36916000	0.00861300
H	-3.70782600	2.20846200	0.06532700
C	0.57634000	-3.48528700	-0.55474800
H	-0.41665800	-3.59275500	-0.10791000
H	1.11715300	-4.42662000	-0.39437200
H	0.44839500	-3.35647800	-1.63554600
C	-0.87869000	3.76903500	0.03754200
H	-1.90802000	4.11560400	0.06150100

C	0.18575900	4.65583400	0.05480000
H	0.00419400	5.72616900	0.09631400
F	-5.63626500	0.28182700	0.01886300
C	0.01334300	-2.10272200	2.28102100
H	-0.22774100	-1.27608300	2.95663600
H	0.33819400	-2.95487700	2.89085500
H	-0.90267900	-2.39288500	1.75620900
C	3.05914500	-2.01781000	-1.86611000
H	2.29293100	-2.39250500	-2.55310100
H	3.82850400	-2.79516000	-1.77288200
H	3.52968400	-1.13582600	-2.31313600
C	4.18340600	0.12037900	0.17526200
H	4.29452800	0.44778400	-0.86443100
H	5.07646500	-0.46204200	0.43540000
H	4.17794200	1.00913800	0.81396400
C	1.48732100	4.16209700	0.01358100
H	2.34706900	4.82394200	0.02085700
C	2.22277100	0.18435000	2.70274100
H	2.61111400	1.16949300	2.42238000
H	2.92420500	-0.25998500	3.41999400
H	1.26405100	0.32945700	3.21045200
C	-4.65933600	-0.63281700	0.01863500
F	-4.81682500	-1.38262400	1.12235900

IN2

1 1

Ir	-0.92700400	-0.19461400	0.09918400
N	-0.63216400	1.96847200	0.16593300
N	1.20749100	0.13886800	0.03616800
C	-3.00460400	-0.60640800	-0.39061300
C	-2.43931400	-1.81426300	0.15539800
C	-1.22847500	-1.26046400	-1.75657400
C	-2.27400000	-0.29273400	-1.60553800
C	-1.33119600	-2.20964100	-0.65732200
C	-1.64292500	2.84059900	0.27255100
H	-2.64240600	2.41838900	0.35077200
C	1.65260500	1.39969700	0.02213100
C	0.63700900	2.43570600	0.09993700
F	4.96666000	-1.39363100	0.78081100
C	3.40342100	0.08816400	-0.11389200
C	3.05287500	1.41743600	-0.07361600
H	3.71342200	2.27241900	-0.11043200
C	-0.49319000	-3.42792100	-0.50746400
H	0.56282800	-3.21882600	-0.71380000

H	-0.81938700	-4.19177100	-1.22522300
H	-0.57100100	-3.85588500	0.49562300
C	0.91975400	3.79422800	0.11076100
H	1.95135200	4.12935800	0.05200500
C	-0.13324500	4.69466400	0.19830500
H	0.06079100	5.76322500	0.20238000
F	5.69806500	0.36951100	-0.23353200
C	-0.23698600	-1.34724300	-2.85852200
H	-0.07552000	-0.37420900	-3.33285300
H	-0.58891300	-2.04731000	-3.62687300
H	0.72751000	-1.71486000	-2.49107200
C	-2.90749400	-2.48342500	1.39486500
H	-2.09482500	-3.00200500	1.91292200
H	-3.67667300	-3.22378600	1.14093700
H	-3.35717700	-1.76573200	2.08878300
C	-4.21084800	0.08998300	0.12970900
H	-4.17517300	0.18647000	1.22073000
H	-5.11709300	-0.47400800	-0.12528200
H	-4.31508500	1.09206000	-0.29822300
C	-1.43313900	4.21157100	0.28817900
H	-2.28252300	4.88191600	0.36784400
C	-2.57398400	0.82923000	-2.52940300
H	-2.97552000	1.69770800	-1.99722000
H	-3.32882300	0.51140800	-3.25945400
H	-1.68326100	1.14511000	-3.08165700
C	4.74046200	-0.55254100	-0.23189200
F	4.83991200	-1.26175100	-1.36023500
O	0.42981100	-1.87512100	2.48454500
O	-0.68680700	0.07502600	2.24814600
C	-0.07784900	-0.83722200	2.91712100
H	-0.03243500	-0.61236800	4.00329300
N	2.27221000	-0.65178600	-0.04798700
H	2.16741900	-1.66378400	-0.01883200

TS1

E= -1493.08822538 (a.u.)   -437.28 *i* cm^{-1}

1 1

Ir	-0.82531300	-0.31207300	0.06231600
N	-0.57280800	1.76624800	-0.48488500
N	1.27790300	0.02527600	-0.02415600
C	-2.89166800	-0.99138800	-0.09807500
C	-2.14736700	-1.95815900	0.68009500
C	-1.22855900	-1.89162200	-1.46646800
C	-2.33703300	-0.99321600	-1.43511700

C	-1.10006700	-2.48048000	-0.14223200
C	-1.60306400	2.61246600	-0.63170100
H	-2.59867600	2.18612100	-0.52806300
C	1.71855000	1.25544600	-0.31864300
C	0.69092000	2.24892100	-0.56321300
F	4.91637500	-1.35624200	1.26591300
C	3.47995100	-0.00447800	0.02380500
C	3.12170900	1.28281900	-0.29945700
H	3.78029200	2.11780300	-0.49429800
C	-0.11174100	-3.52449100	0.23751200
H	0.81393100	-3.42798200	-0.34070600
H	-0.52027400	-4.52363100	0.03873300
H	0.14279300	-3.47315700	1.30107700
C	0.95004400	3.58856400	-0.81926700
H	1.97738900	3.93710000	-0.87493100
C	-0.11993100	4.45590700	-0.98383600
H	0.05591200	5.50957800	-1.17999600
F	5.76662000	0.31655600	0.18813300
C	-0.37342500	-2.22146500	-2.63621800
H	0.67884500	-2.32388800	-2.34814200
H	-0.44134300	-1.45390100	-3.41334500
H	-0.68595700	-3.17653100	-3.07813100
C	-2.43292000	-2.32958300	2.08997800
H	-1.54149800	-2.71427700	2.59466400
H	-3.20165300	-3.11245100	2.11785500
H	-2.80779100	-1.47371200	2.65992400
C	-4.12679200	-0.28652200	0.33580600
H	-4.11876700	-0.09315200	1.41298900
H	-5.01216000	-0.89587800	0.11185200
H	-4.24886500	0.67148300	-0.18124800
C	-1.41623500	3.96150500	-0.88428200
H	-2.27964400	4.60908300	-0.99487000
C	-2.84304600	-0.18335800	-2.57097500
H	-3.30804200	0.74682600	-2.22823300
H	-3.61006100	-0.74854900	-3.11577300
H	-2.04614000	0.06755300	-3.27821100
C	4.82632900	-0.62266700	0.15333600
F	5.09178000	-1.43447600	-0.87484000
N	2.35008400	-0.73429600	0.18131700
H	2.25166100	-1.71456400	0.43650700
H	-0.65034700	0.28553400	1.67055800
C	-1.06837100	1.47578600	2.49381200
O	-2.17403900	1.23165000	2.88718400
O	-0.12139000	2.20999500	2.48850200

IN3

1 1

Ir	0.89623600	-0.17203700	-0.30994300
N	0.57625100	1.96418000	-0.12183200
N	-1.20372700	0.09817500	-0.14697300
C	3.00884500	-0.66877000	-0.08042600
C	2.34530500	-1.72980000	-0.79245000
C	1.49978100	-1.65434100	1.39214800
C	2.50449000	-0.67329000	1.28962500
C	1.34322700	-2.27402000	0.07798100
C	1.56922200	2.86691400	-0.10265200
H	2.58060400	2.47285000	-0.17148600
C	-1.69298500	1.34326100	-0.06640000
C	-0.70593600	2.40356800	-0.05436100
F	-4.89493500	-1.54208700	-1.02678900
C	-3.40352100	-0.02951800	-0.05940800
C	-3.09573200	1.30814400	-0.00817100
H	-3.78615900	2.13682300	0.06388800
C	0.44157900	-3.42124200	-0.21726400
H	-0.47652700	-3.36930900	0.37978500
H	0.93186800	-4.37390300	0.02393200
H	0.15946000	-3.44827300	-1.27509900
C	-1.01765900	3.75517400	0.02132500
H	-2.05880100	4.06261000	0.06447200
C	0.01467100	4.68091700	0.04110700
H	-0.20293500	5.74324900	0.10071200
F	-5.70619000	0.18085300	-0.00240600
C	0.68815400	-2.01035400	2.58651100
H	0.77792300	-1.25839300	3.37664700
H	1.01422200	-2.97356800	3.00067000
H	-0.37419600	-2.11455000	2.33383600
C	2.66603300	-2.19606900	-2.16891500
H	1.78350600	-2.60126700	-2.67395500
H	3.42199800	-2.99089500	-2.12584100
H	3.06921200	-1.38572800	-2.78467200
C	4.18793800	0.10801600	-0.55327300
H	4.13971600	0.29903000	-1.63062100
H	5.11898800	-0.43838900	-0.35109200
H	4.26226300	1.07353200	-0.04043500
C	1.32885900	4.22839800	-0.01785000
H	2.16659900	4.91796000	-0.00338800
C	2.97295200	0.25939500	2.34777000
H	3.05790100	1.28326300	1.96203500
H	3.96846600	-0.03217300	2.70681900

H	2.29477200	0.27430300	3.20634600
C	-4.72107300	-0.71274100	0.00630800
F	-4.83368200	-1.44548400	1.11889400
N	-2.24509000	-0.73018700	-0.14045000
H	-2.10704600	-1.73569500	-0.21200300
H	0.66429800	0.13879400	-1.87706200

TS2

E= -1380.98157013 (a.u.)   -1361.71 *i* cm^{-1}

1 1

Ir	0.87866200	-0.21506700	-0.23646100
N	0.70663300	1.95179000	-0.29997100
N	-1.15752200	0.19490100	0.11392200
C	3.02079700	-0.64728700	0.13113500
C	2.42458700	-1.79138800	-0.48542500
C	1.35384100	-1.43606700	1.55665400
C	2.35788900	-0.43584900	1.40984500
N	-2.19965200	-0.63427500	0.13811800
C	1.35896400	-2.26238400	0.36602300
C	1.74081600	2.78369200	-0.49912500
H	2.70171200	2.31798800	-0.70299000
C	-1.56503800	1.48446600	0.10138900
C	-0.52366600	2.47406400	-0.05858800
F	-4.80388400	-1.22698200	-0.95035200
C	-3.28984000	0.16085800	0.16421500
C	-2.95790700	1.51107500	0.14931100
H	-3.61725400	2.36865500	0.14903400
C	0.52926600	-3.48399100	0.17740700
H	-0.51821100	-3.30351000	0.44443700
H	0.89674900	-4.29639200	0.81765100
H	0.56339200	-3.84029400	-0.85706300
C	-0.73256300	3.84904400	-0.01162000
H	-1.73227800	4.22842400	0.18141900
C	0.34165200	4.70065900	-0.21146400
H	0.20024500	5.77709300	-0.17572400
F	-5.59849300	0.46434500	0.13445300
C	0.43946400	-1.62539600	2.71119400
H	-0.52986700	-2.01931600	2.38783200
H	0.26926200	-0.69005400	3.25395300
H	0.86965900	-2.34966600	3.41465300
C	2.82527800	-2.37453100	-1.79170300
H	1.97496500	-2.82618600	-2.31337500
H	3.57614600	-3.15944300	-1.63502900
H	3.26616300	-1.61641000	-2.44674600

C	4.21829700	0.08526000	-0.36031800
H	4.19962900	0.21185000	-1.44795200
H	5.13017100	-0.47054100	-0.10580400
H	4.30553800	1.07471500	0.09997100
C	1.60036400	4.16024700	-0.46041100
H	2.46689700	4.79146100	-0.62707800
C	2.70866300	0.61867200	2.39606300
H	3.00331800	1.55123200	1.90212600
H	3.55546400	0.29535400	3.01470600
H	1.87027200	0.83780800	3.06473200
C	-4.63400800	-0.46121700	0.14047100
F	-4.84920400	-1.26024200	1.19621300
O	-1.16205600	-1.67732500	-2.27961100
H	-0.22404900	-0.84852200	-1.92804800
H	0.40716800	-0.07135200	-1.90316200
H	-0.75158500	-2.55715300	-2.30935500
H	-1.72709800	-1.66753800	-1.47145500

IN4

1 1

Ir	0.89688000	-0.22078300	-0.36939900
N	0.66294400	1.93904900	-0.22355000
N	-1.18310900	0.10448700	-0.23360300
C	2.95983100	-0.70129200	0.32235300
C	2.50317600	-1.78665800	-0.48680800
C	1.05207500	-1.61337100	1.32197400
C	2.05606100	-0.59390300	1.45215100
N	-2.19430000	-0.75367600	-0.22528900
C	1.29946000	-2.33242500	0.09458200
C	1.69221600	2.80037700	-0.23227500
H	2.68452000	2.36805700	-0.33827400
C	-1.62170500	1.38426200	-0.11830100
C	-0.60493300	2.40918200	-0.11229000
F	-4.85689300	-1.47480200	-1.04982100
C	-3.30135400	0.00536300	-0.10205900
C	-3.00903200	1.36527400	-0.02747100
H	-3.69160900	2.19791100	0.07659000
C	0.54976300	-3.52007800	-0.39246400
H	-0.51201200	-3.45665400	-0.13476800
H	0.94959800	-4.43571500	0.06134900
H	0.62804600	-3.62309800	-1.47913600
C	-0.85791600	3.77378500	-0.00283000
H	-1.88459000	4.11885800	0.08158400
C	0.20747900	4.65890300	-0.00531800

H	0.02955300	5.72718100	0.08041900
F	-5.61169000	0.26202300	-0.01028700
C	-0.03633200	-1.89417000	2.28892600
H	-0.34267200	-0.99175700	2.82695000
H	0.31819900	-2.62267600	3.02901400
H	-0.91566700	-2.31838200	1.79592800
C	3.13065900	-2.24892500	-1.74802800
H	2.38501700	-2.62499600	-2.45535400
H	3.82428000	-3.07046300	-1.52784600
H	3.69978300	-1.45029700	-2.23284600
C	4.20384200	0.08561000	0.11257800
H	4.36722200	0.30748800	-0.94725000
H	5.07386800	-0.47796700	0.47256800
H	4.17833700	1.03241500	0.66118400
C	1.50540800	4.16679800	-0.12167200
H	2.36553000	4.82799900	-0.13033000
C	2.18751500	0.36321100	2.57895000
H	2.60772300	1.31924800	2.24988500
H	2.86016300	-0.05051100	3.34080200
H	1.21981900	0.55723800	3.05213700
C	-4.62887600	-0.64602300	-0.01997200
F	-4.76188200	-1.38640300	1.09329300
H	1.01218900	0.28029100	-2.18188000
H	0.43433800	-0.30576600	-2.19074300