Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Catalytic Reactivity of an Iridium Complex with a Proton Responsive N-Donor ligand in CO_2 Hydrogenation to Formate

Gunniya Hariyanandam Gunasekar,[a‡] Yeahsel Yoon,[a‡] Il-hyun Baek,[b] and Sungho Yoon*[a]

List of Figures

List of Tables

Figure S1. Crystal structure of **1** in a unit cell.

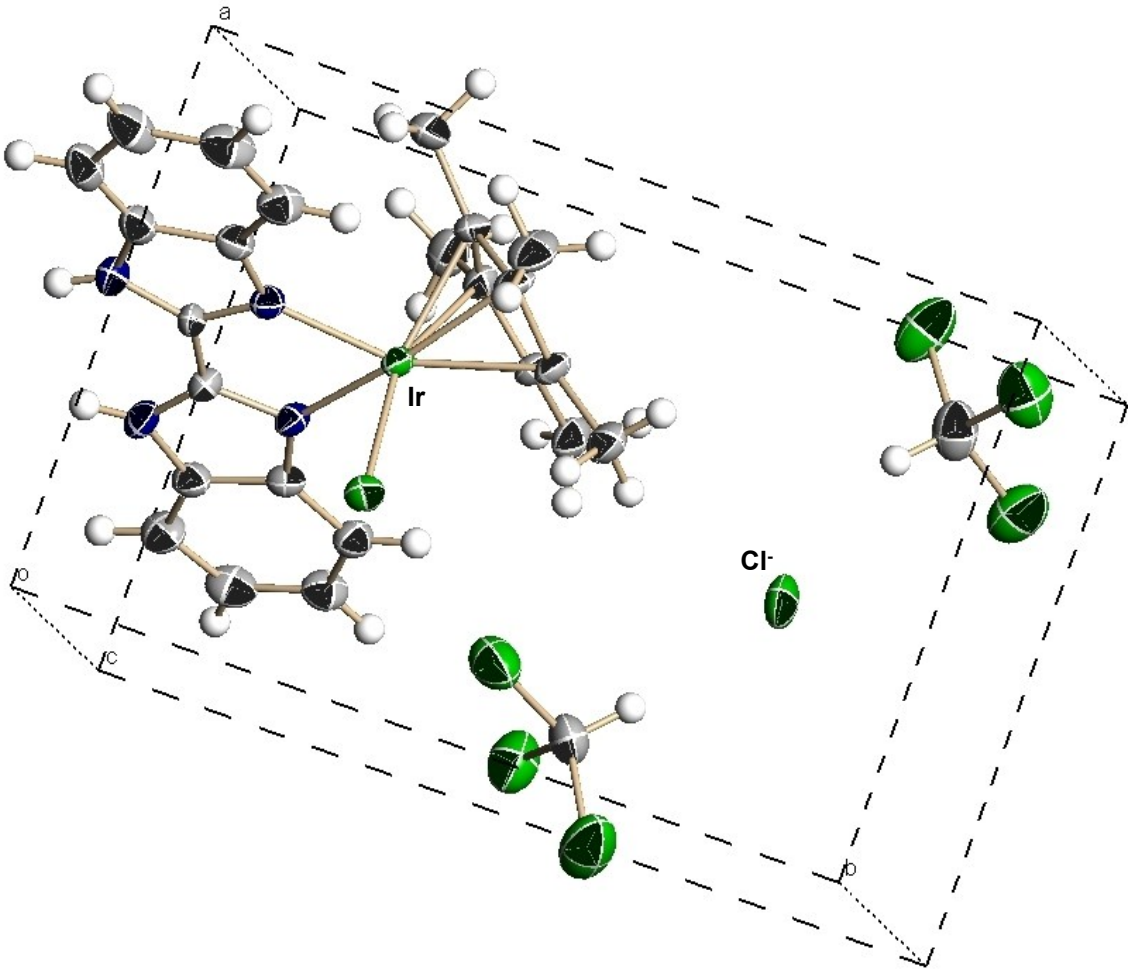
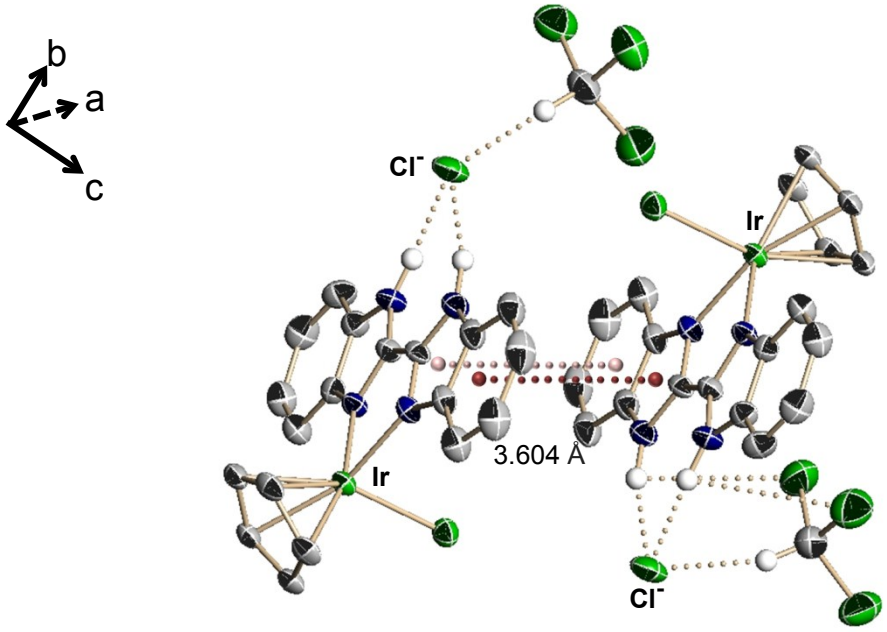


Figure S2. Stabilization structure of **1**. Protons on benzene ring and methyl groups on Cp* are omitted for clarity.



The crystal structure of **1** showed that the counter anion i.e. Cl^- formed a weak hydrogen bond with N-H unit of $BiBzImH_2$ and to C-H of chloroform. In addition, two molecules of **1** were stabilized through π-π interaction (of benzimidazole ring) with a distance of 3.604 Å.

Figure S3. UV-Visible spectrum of **1** in chloroform solution.

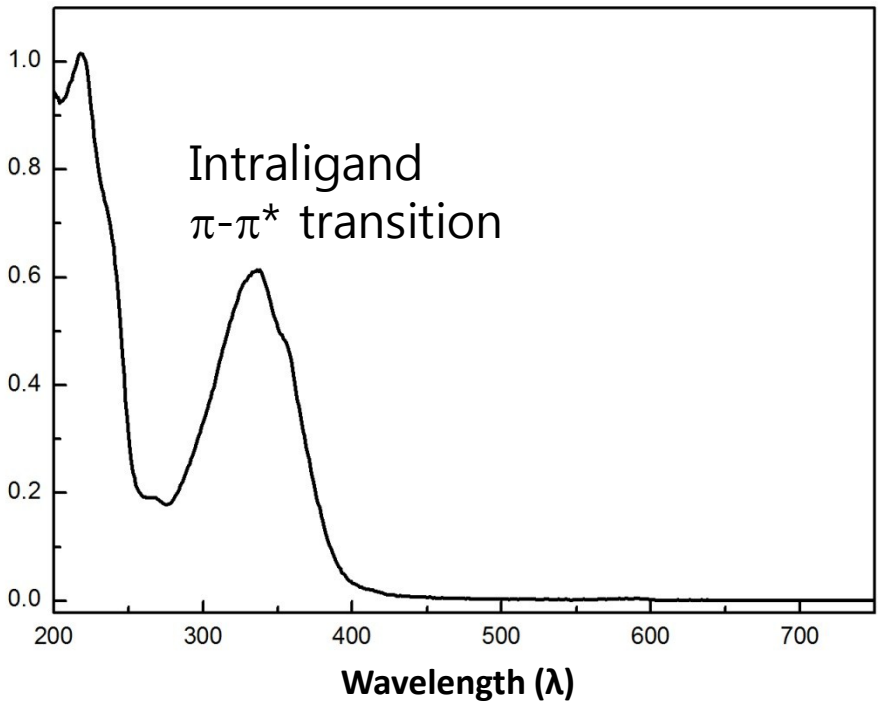


Figure S4. ESI-Mass spectra of **1**.

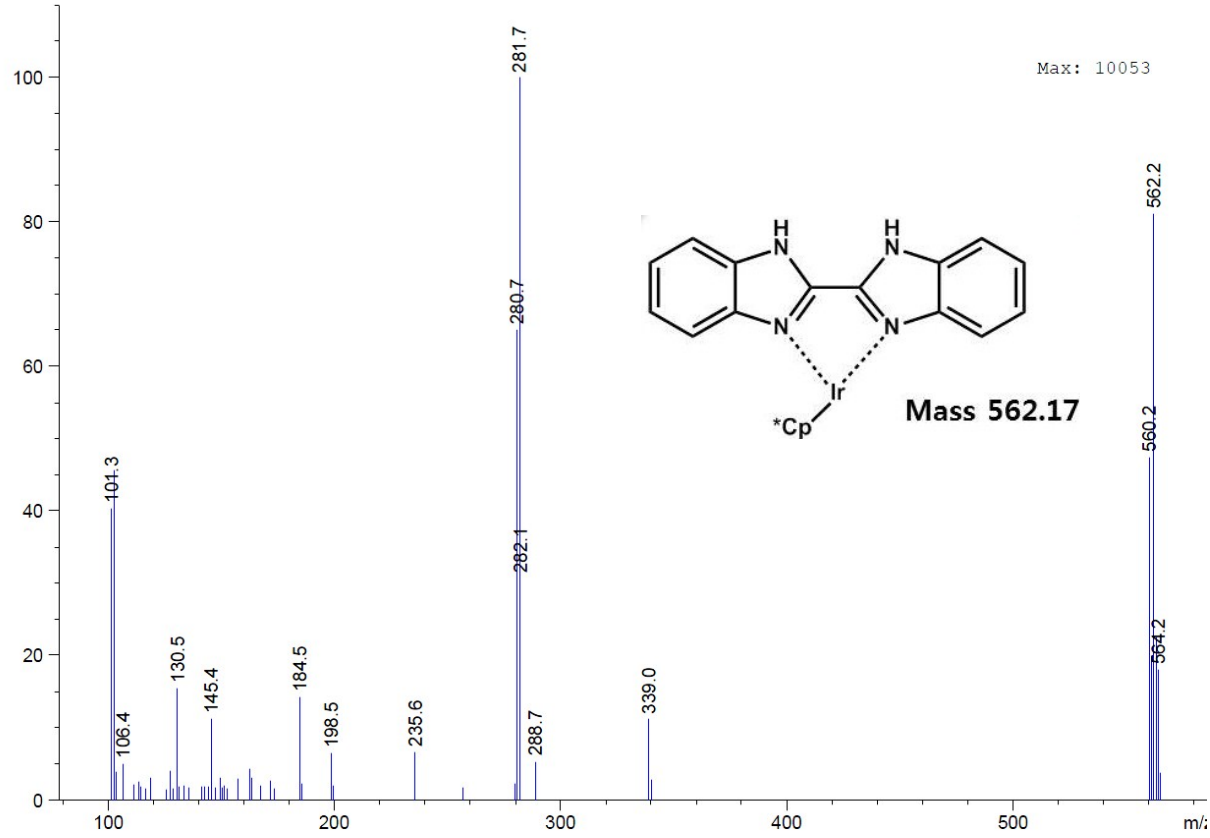


Figure S5. ^{1}H-NMR spectra of $BiBzImH_2$ ligand in DMSO-d^6 and **1** in $CDCl_3$

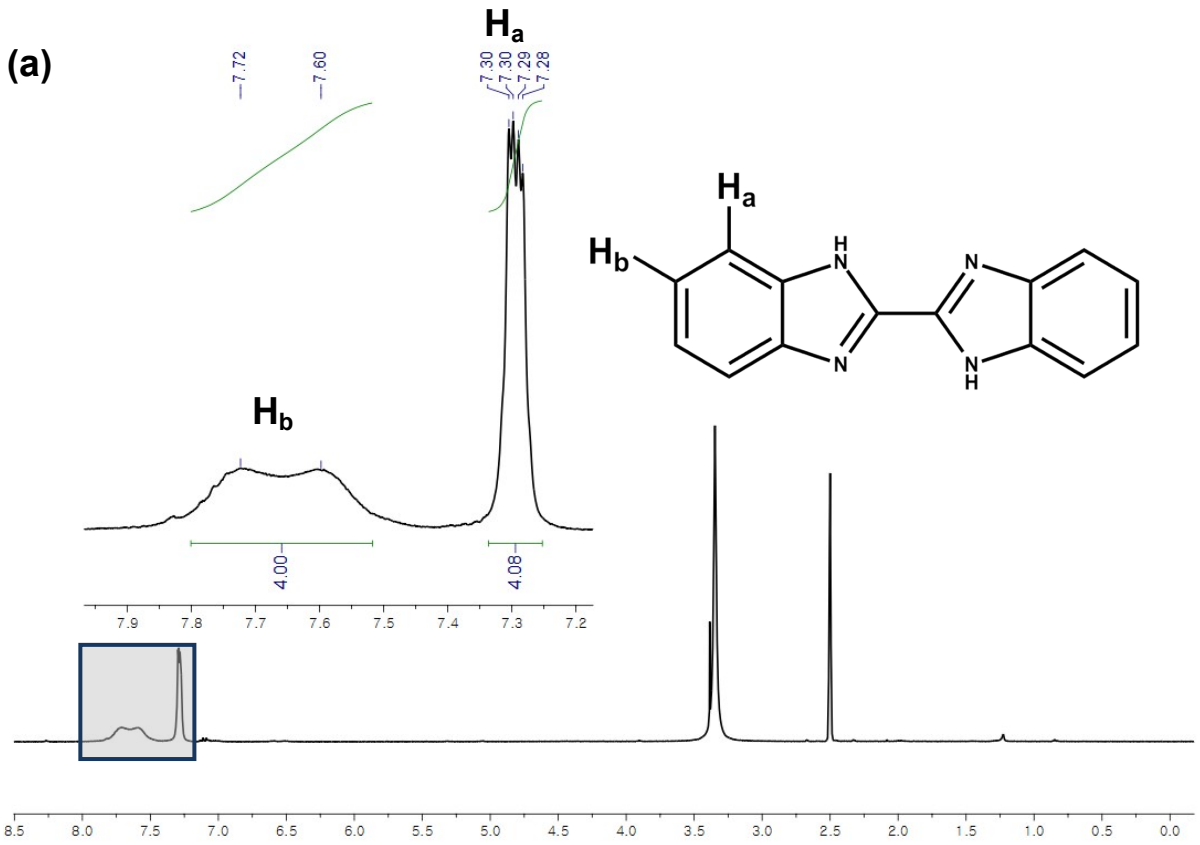
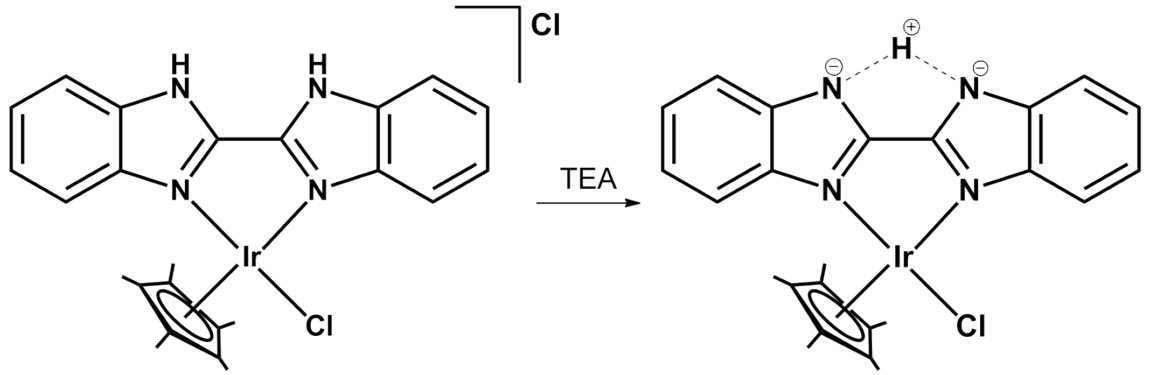
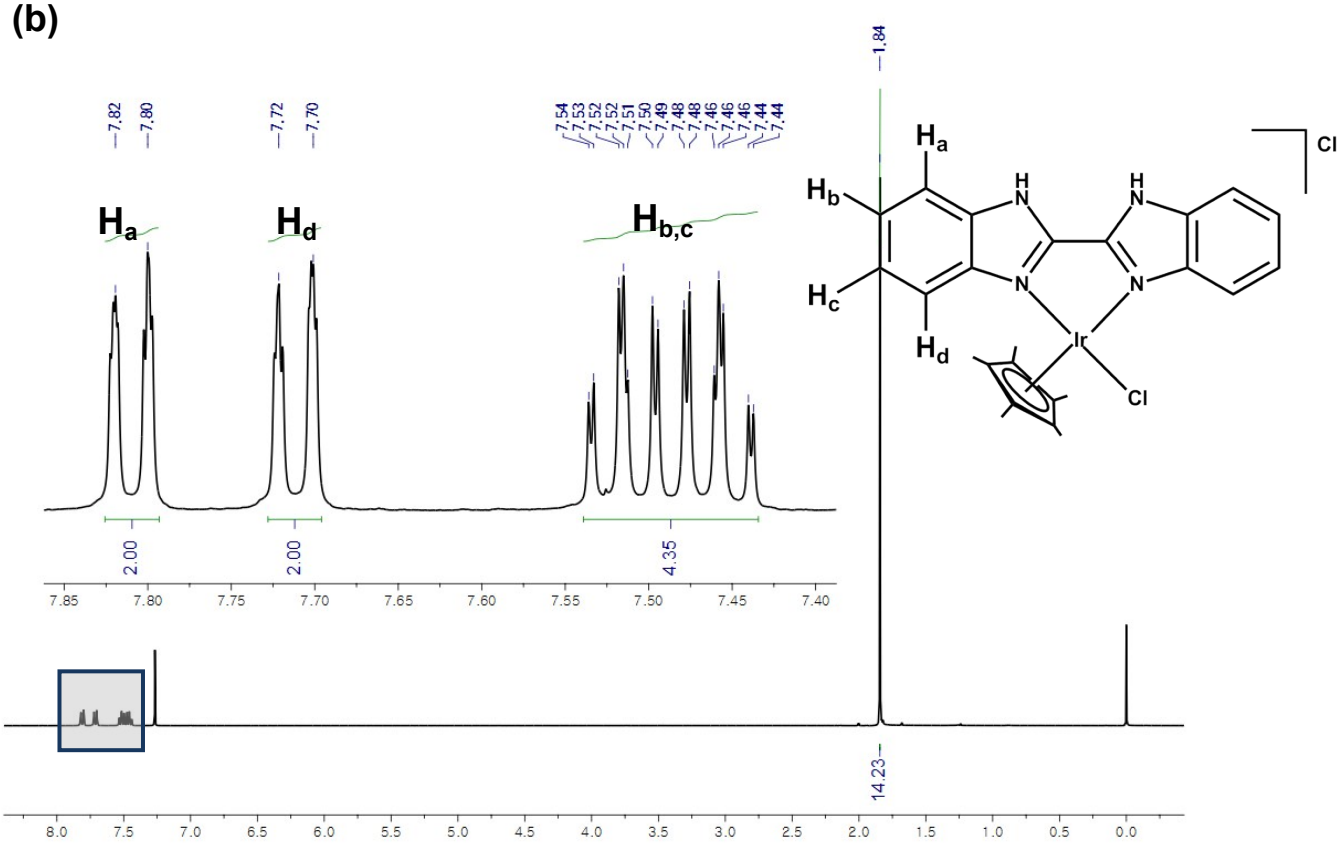


Figure S6. Expected structure of **1** under basic condition

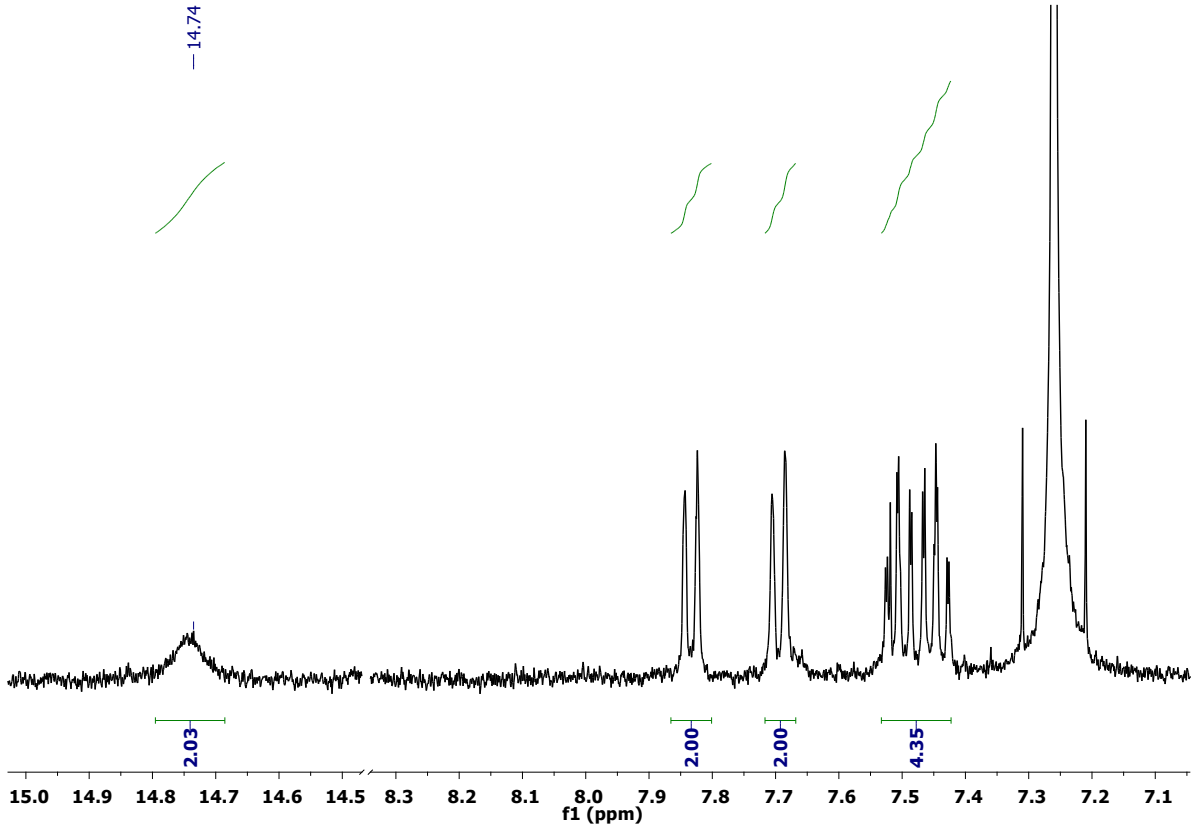


1 **[Cp*Ir(BiBzImH)⁻Cl] : 2**

(b)



(c)


14.74
2.03
2.00
2.00
4.35
15.0 14.9 14.8 14.7 14.6 14.5 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)

(d)

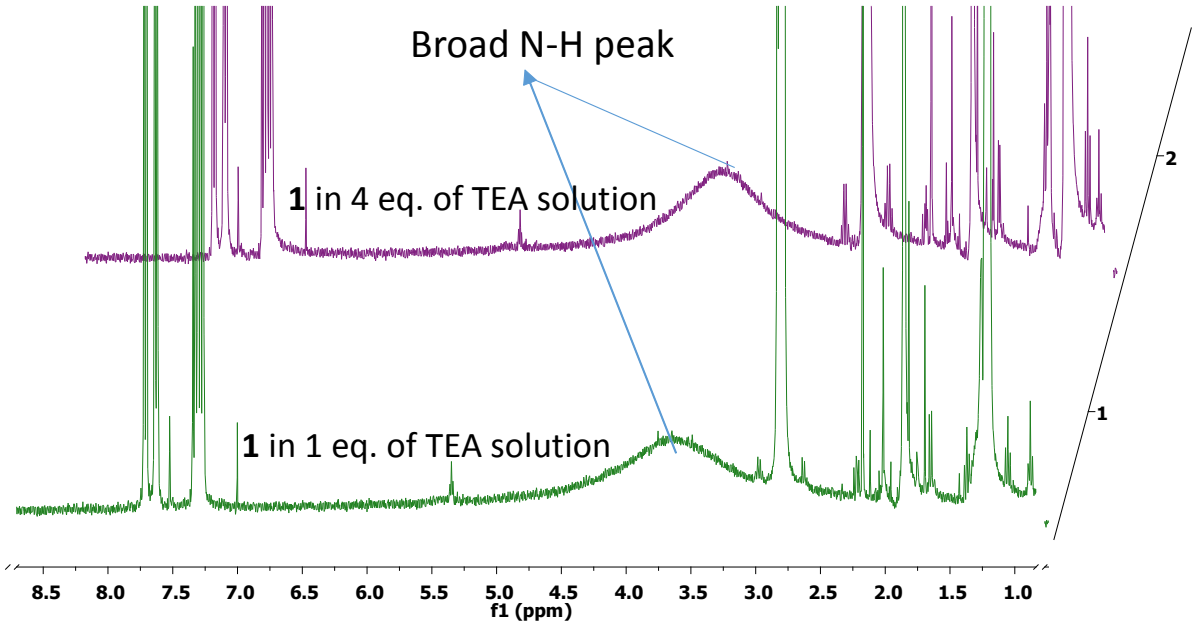

Broad N-H peak
1 in 4 eq. of TEA solution
1 in 1 eq. of TEA solution
2
1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

Figure S7. TOF between the time interval

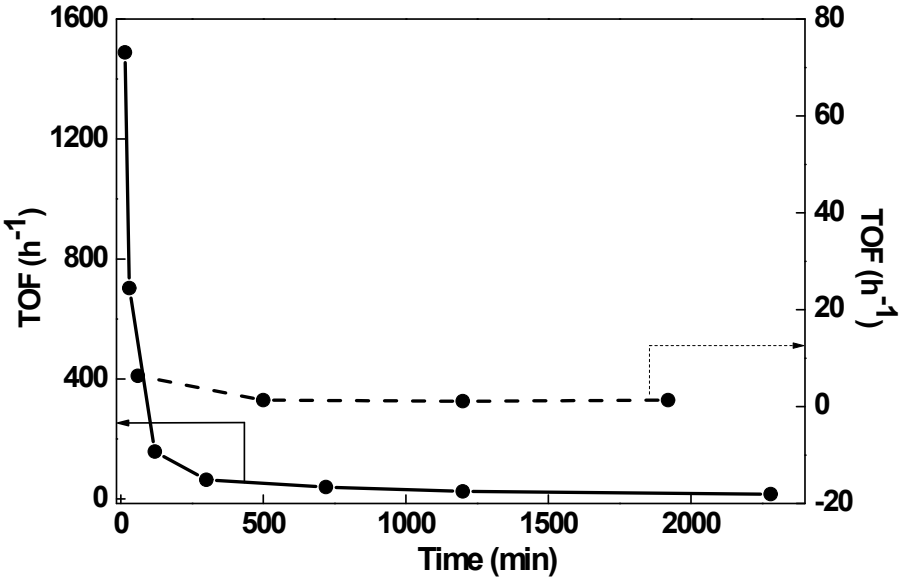


Figure S8. ^{1}H-NMR spectrum of **1** after hydrogenation

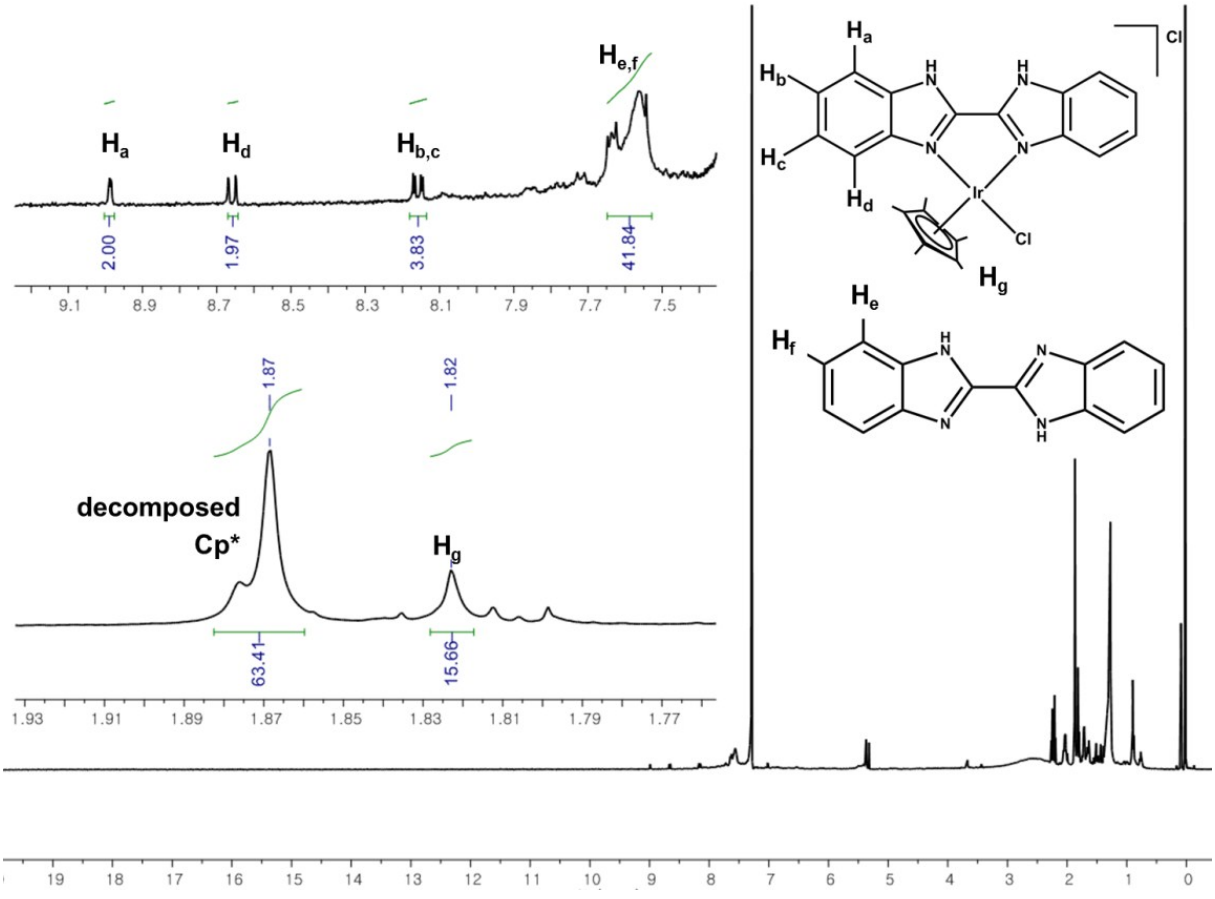


Figure S9. ESI-Mass spectrum of **1** after hydrogenation

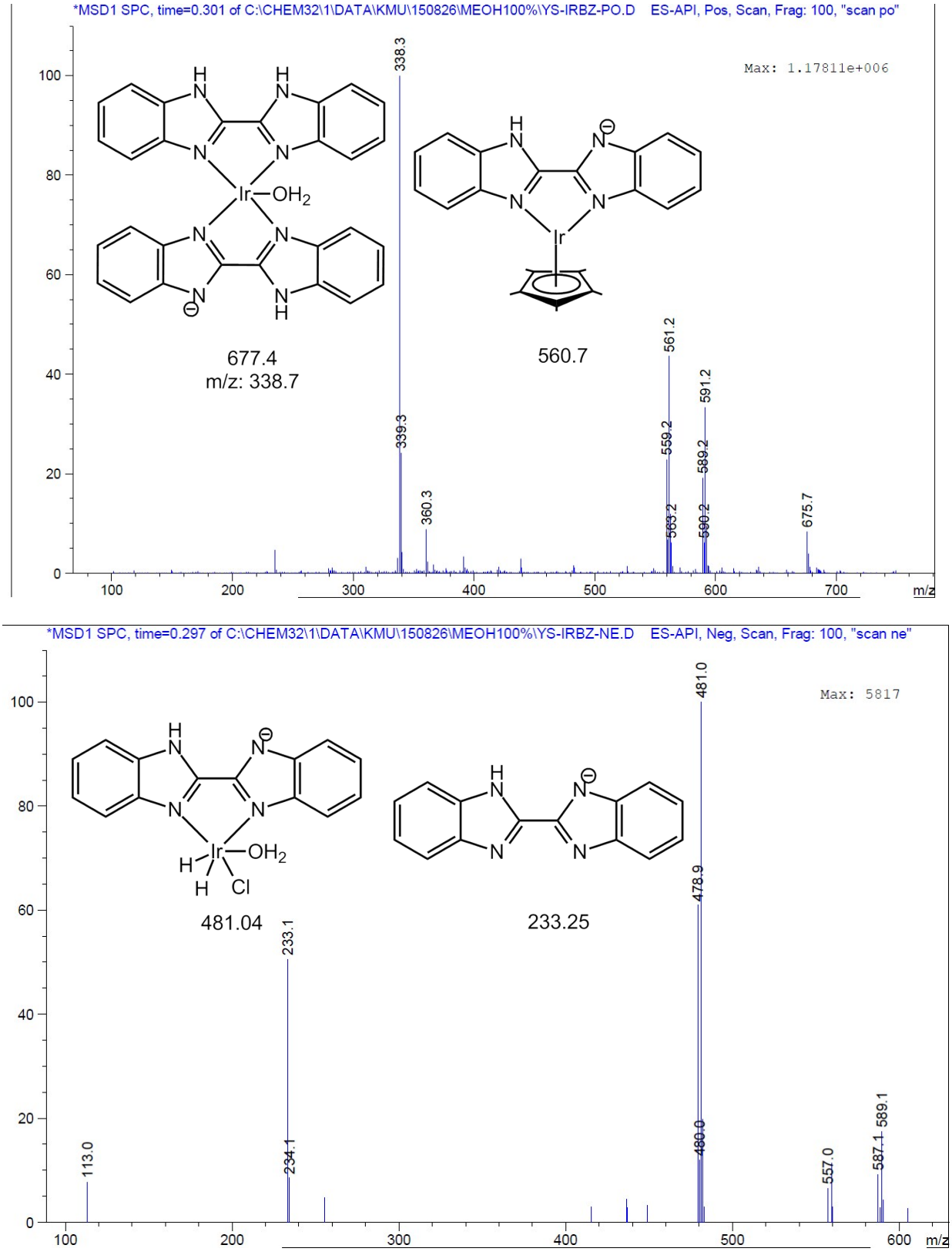


Table S1. TOF between the hours.

Time (min)	(TOF/h)
15	1500
30	700
120	158
300	65
720	40
1200	25
2280	16

Table S2. Comparison of bond lengths and angels of **1** with [Cp*Ir(Bpy)Cl]Cl

	[Cp*Ir(Bpy)Cl]$^+$	**1**
Ir-N (Å)	2.076 (8)	2.127(2)
	2.090 (9)	2.148(2)
Ir-Cl (Å)	2.404 (2)	2.3941(7)
Ir-Cp* Centroid(Å)*	1.785	1.789
N-Ir-Cl angle (°)	85.47	86.82
Distortion angle (°) (ligand-Ir)	3.38	6.32 (19)
Internal angle of N-C-C	112.94	114.55(18)

- **N-C-C Internal angle**

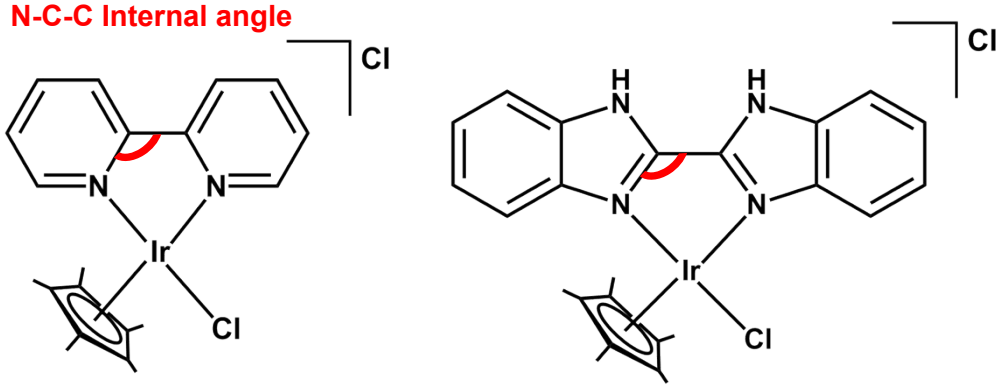


Table S3. X-ray Crystallographic information of **1**.

Formula	$C_{26}H_{27}Cl_8IrN_4$
M_r	874.34
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal color and shape	Yellow block
Crystal size	0.09 x 0.16 x 0.20
a (Å)	8.3668(4)
b (Å)	12.3575(5)
c (Å)	30.7228(13)
β (°)	90.5240(10)
V (Å^3)	3176.4(2)
Z	4
T (K)	223(2)
F(000)	1708
Scan range (°)	$2.52 < \theta < 28.49$
R_{int}	0.0269
Goodness-of-fit	0.925

$R1 = \Sigma||F_o|- |F_c||/ \Sigma|F_o|$; $wR2 = \{\Sigma[w(|F_o^2|- |F_c^2|)^2]/ \Sigma[w|F_o^2|^2]\}^{1/2}$