Two Novel Metal-Organic Frameworks functionalised with pentamethylcyclopentadienyl iridium(III) chloride for catalytic conversion of carbon dioxide to formate

Maureen Gumbo,[1,2] Banothile E. C. Makhubela,*[2] and Gift Mehlana*[1]

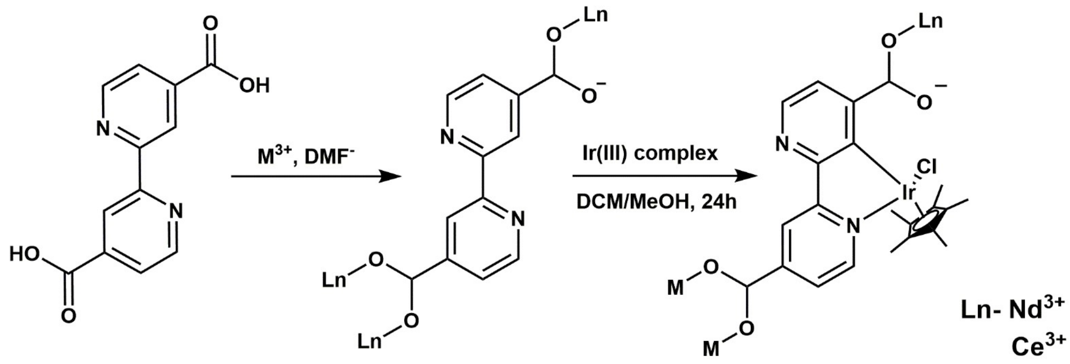
[1]Department of Chemical Sciences, Faculty of Science and Technology, Midlands State University, Private Bag 9055, Senga Road, Gweru, Zimbabwe

[2]Department of Chemical Sciences, Faculty of Science, University of Johannesburg, Kingsway Campus: C2 Lab 328, Auckland Park, 2006, South Africa

E-mail: mehlanag@staff.msu.ac.zw

Table S1: Iridium supported on different materials for CO2 hydrogenation.

	Product	Activity (TON)	Reference
Ir supported on mesoporous silica	formate	-	1
Ir supported on zeolite imidazolate framework	formate	30000	2
Ir on UiO-66 MOF	formate	6149	3
1,5-cyclooctadiene-iridium(I) chloride supported on polymerized cyclic (alkyl)(amino)carbenes	formate	195,600	4
Ir supported on Covalent Triazine Framework	formate	5000	5
Iridium supported on spinal cubic cobalt oxide	formate	3809	6
Ir supported on Covalent Triazine Framework	formate	-	7
Ir supported on Covalent organic Framework	formate	6400	8
Ir supported on mesoporous silica	formate	14200	9



Scheme S1: Synthesis and functionalization scheme of JMS-6a and JMS-7a. Due to steric hinderance some sites will remain unfunctionalized. This is in line with the observed catalyst load as determined by ICP-OES

Table S2: JMS-6 and JMS-7 crystallographic information.

	JMS-6	JMS-7
Empirical formula	C_{24} H_{26} N_5 Nd_1 O_{10}	C_{24} H_{26} N_5 Ce_1 O_{10}
Formula weight (gmol^{-1})	684.41	687.64
Temperature/K	100(2)	100(2)
Crystal system	Triclinic	Triclinic
Space group	*P-1*	P-1
a/Å	10.0085(4)	10.0554(4)
b/Å	11.2398(4)	11.1554(4)
c/Å	13.5602(6)	13.6202(5)
α/°	68.4370(12)	68.7124(12)
β/°	86.0626(14)	86.0229(14)
γ/°	74.5010(13)	74.3419(12)
Volume/Å^3	1366.33(15)	1370.04 (14)
Z	2	2
Calculated density (g/cm^3)	1.6763	1.6667
μ(Mo-Kα) /mm^{-1}	1.627	1.725
F(000)	686	692
Crystal size/mm^3	0.050 x 0.120 x 0.140	0.020 x 0.040x 0.090
Radiation	0.71073Å	0.71073Å
2θ range for data collection/°	55.11^o	56.57°
Index ranges	13,15,18	13,15,18
Reflections collected	6808	6850

No. unique data	6452	6167
Goodness of fit on S	1.14	1.056
Final R indexes [I>=2σ (I)]	0.0265	0.0279
Final wR_2 indexes [all data]	0.0685	0.0581
Deepest hole/Highest peak	-0.99, 1.14	-0.96, 1

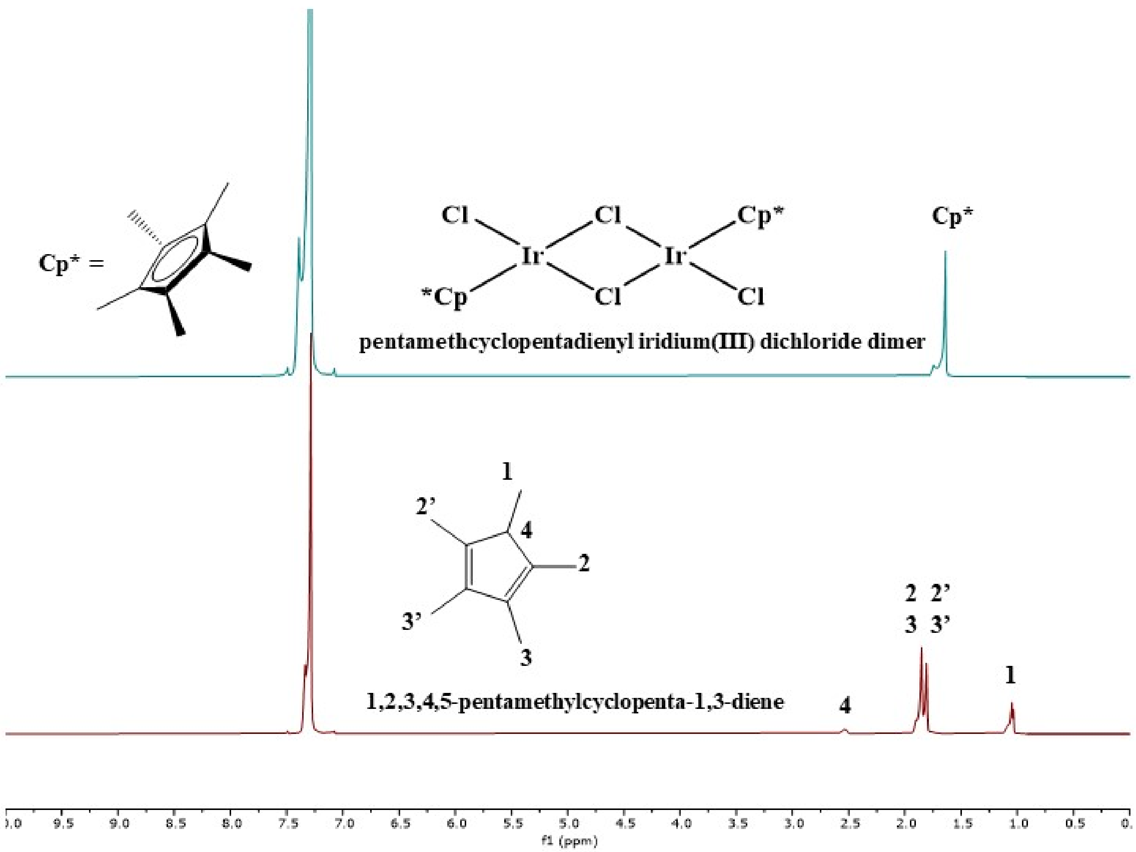


Fig S1: [1]H NMR (Bottom) Stacked NMR of precursor (1,2,3,4,5-pentamethylcyclopenta-1,3-diene) and (top) pentamethylcyclopentadienyl iridium(III) dichloride dimer.

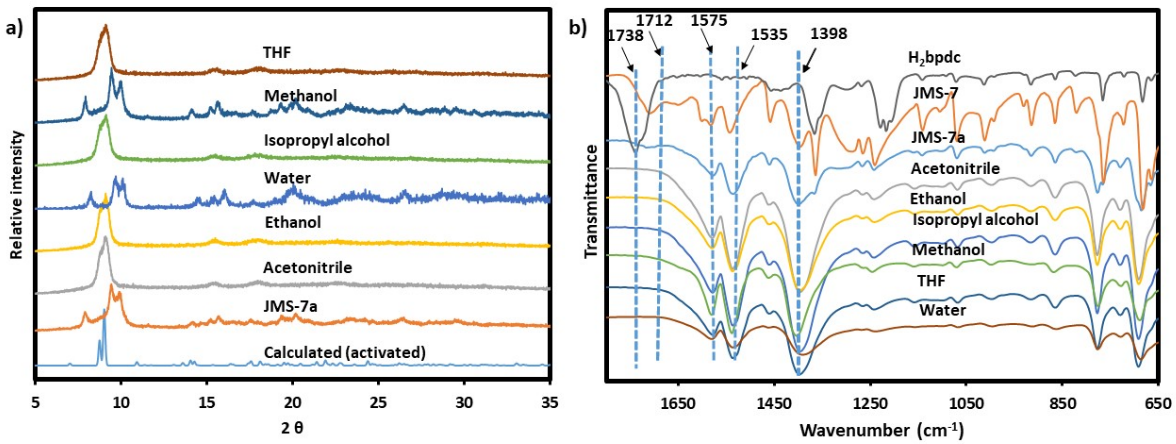


Fig S2: Solvent stability of JMS-7a, (a) PXRD **(b)** FTIR.

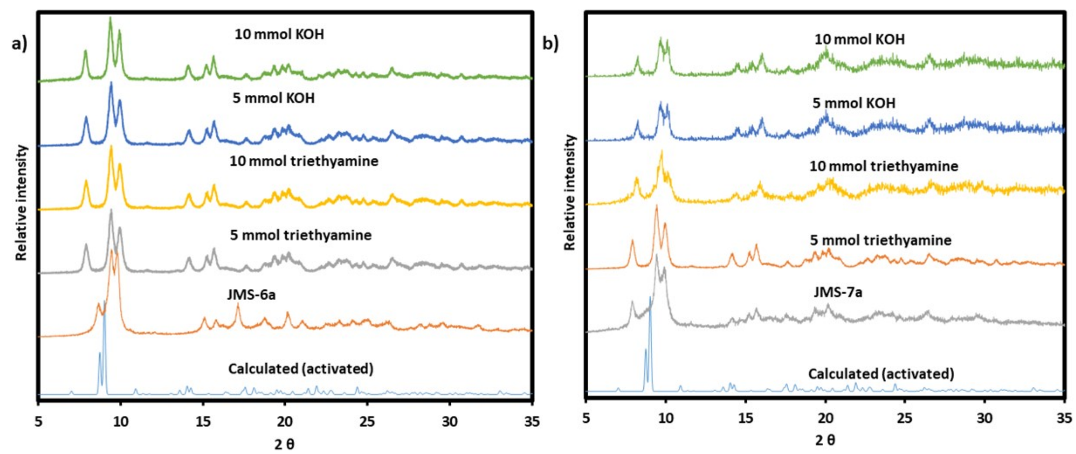


Fig S3: PXRD of base stability of **JMS-6a** and **JMS-7a.**

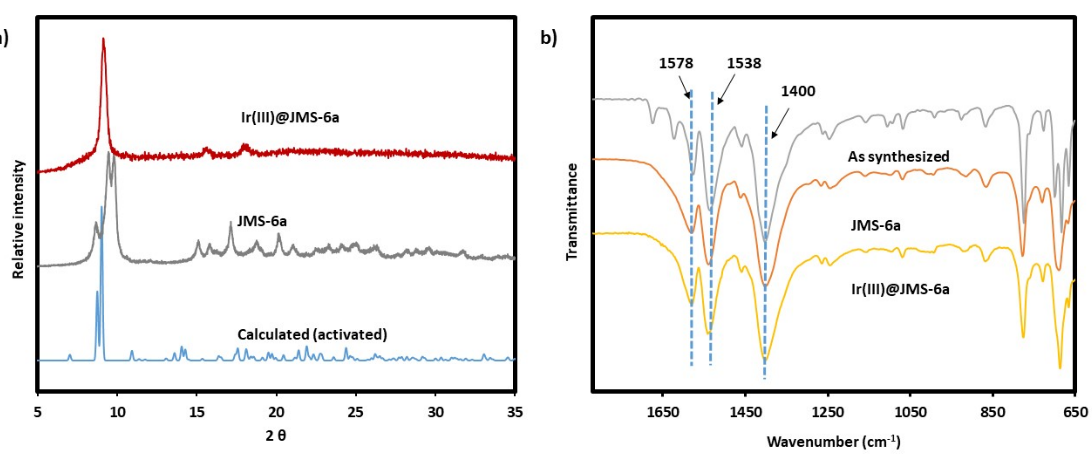


Fig S4: Functionalization of JMS-6a**, (a) PXRD a**nd **(b) FTIR.**

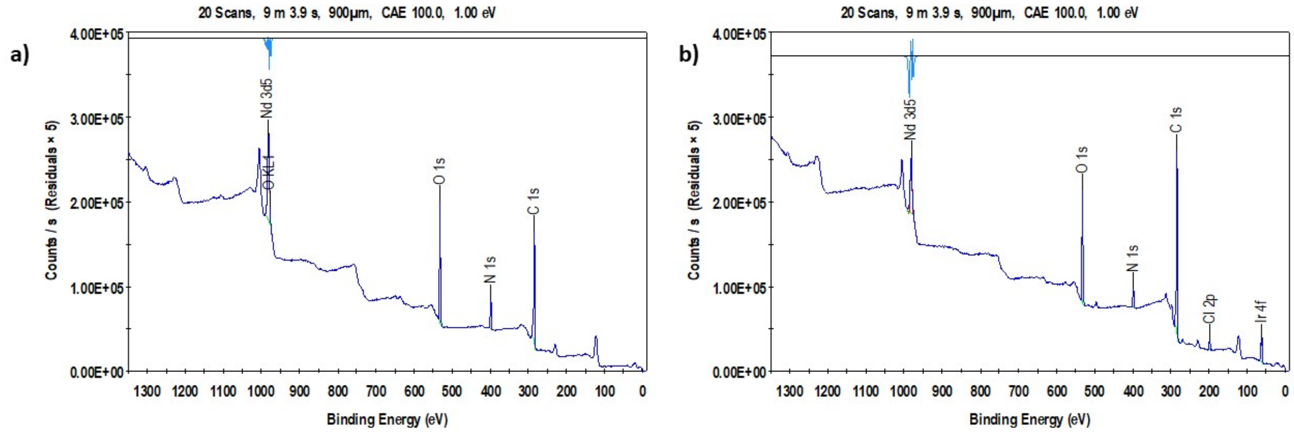


Fig S5: XPS spectra of JMS-6a and Ir(III)@JMS-6a.

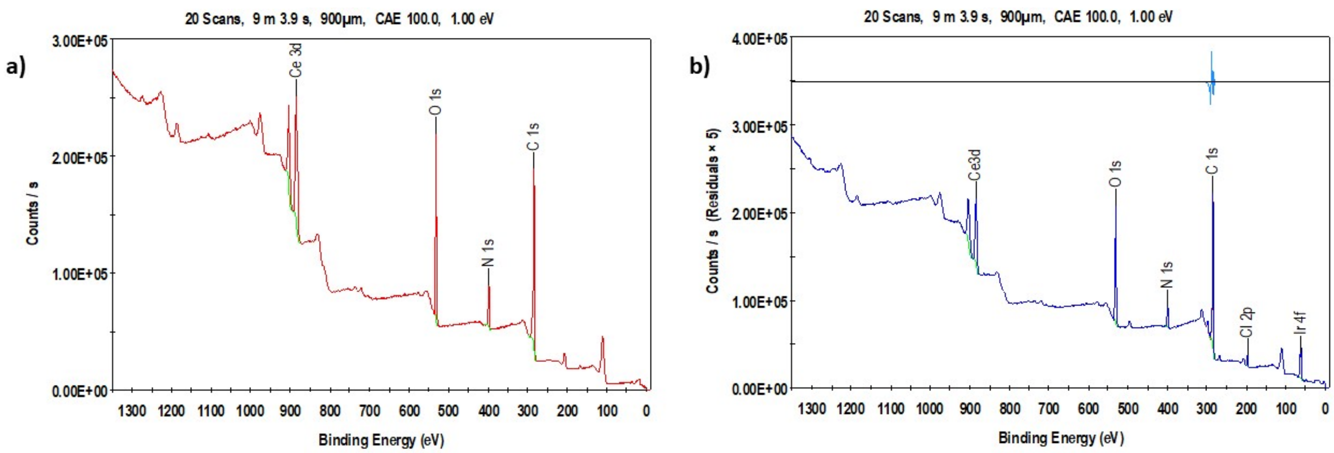


Fig S6: XPS spectra of JMS-7a and Ir(III)@JMS-7a.

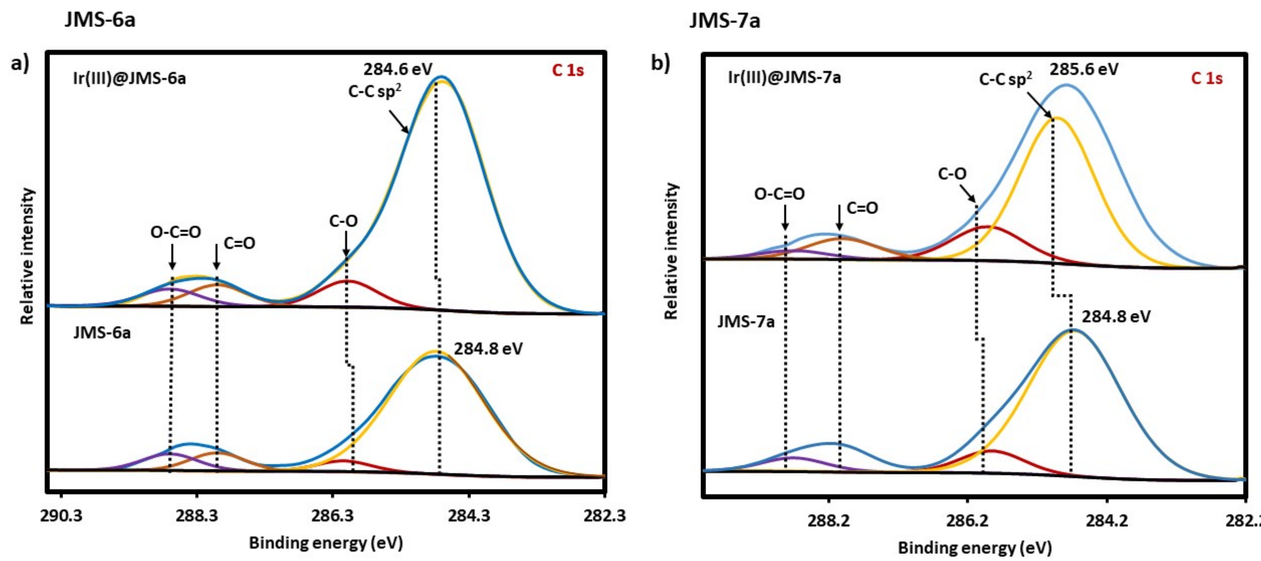


Fig S7: C Is XPS analysis of Ir(III)@JMS-6a and Ir(III)@JMS-7a.

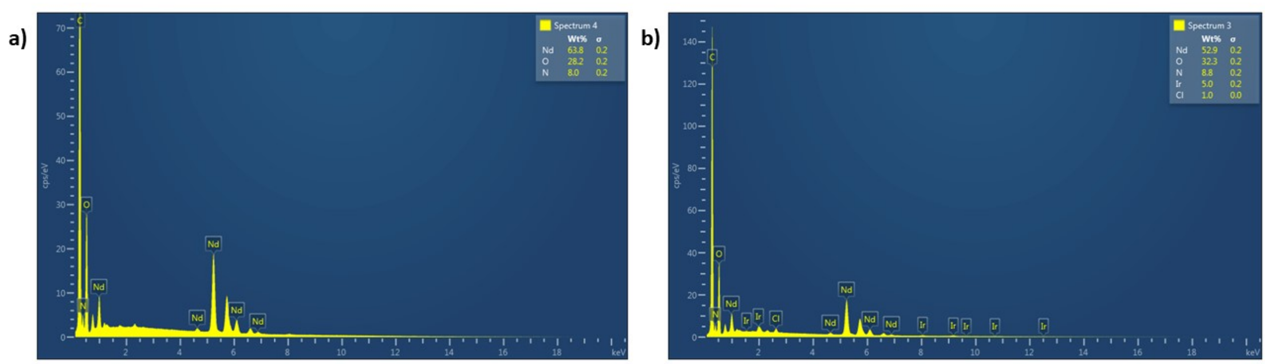


Fig S8: EDX spectra of JMS-6a and Ir(III)@JMS-6a.

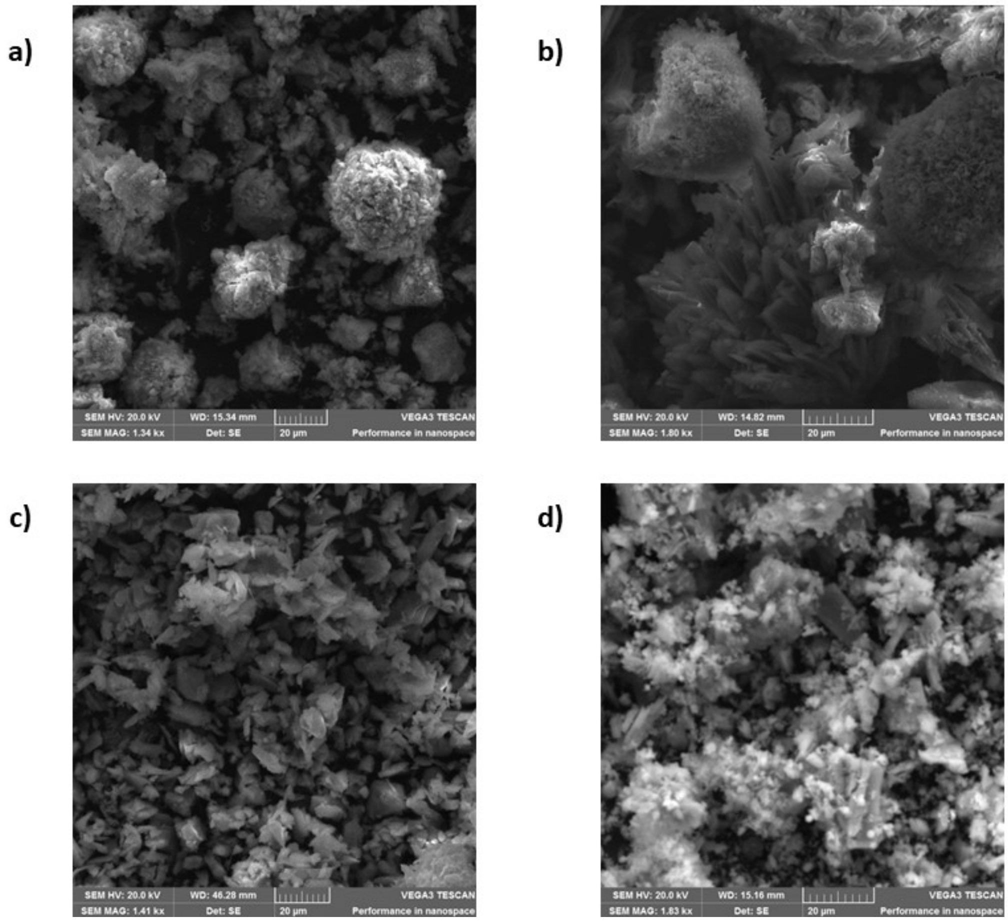


Fig S9: SEM images of, **(a)** JMS-6a, **(b)** JMS-7a, **(c)** Ir(III)@JMS-6a, **(d)** Ir(III)@JMS-7a.

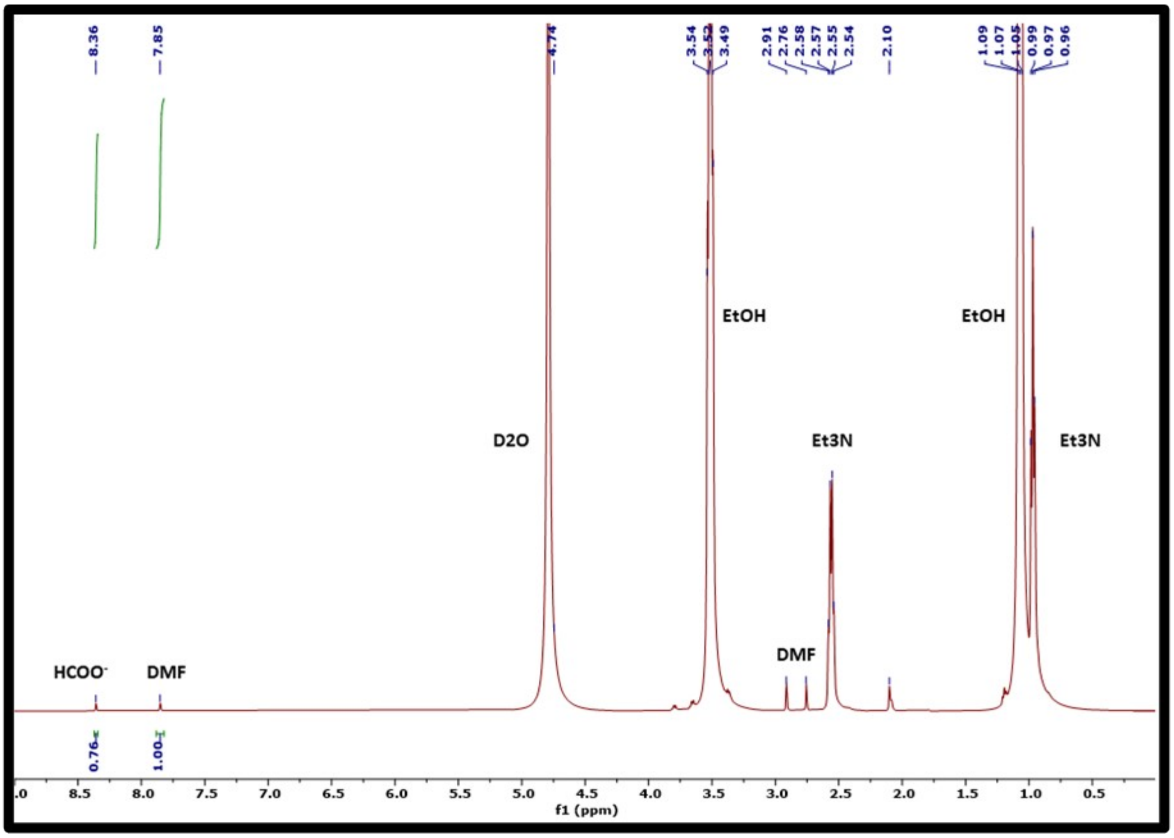


Fig S10: ^{1}H NMR post catalysis (Ir(III)@JMS-7a, used to detect and quantify formate.

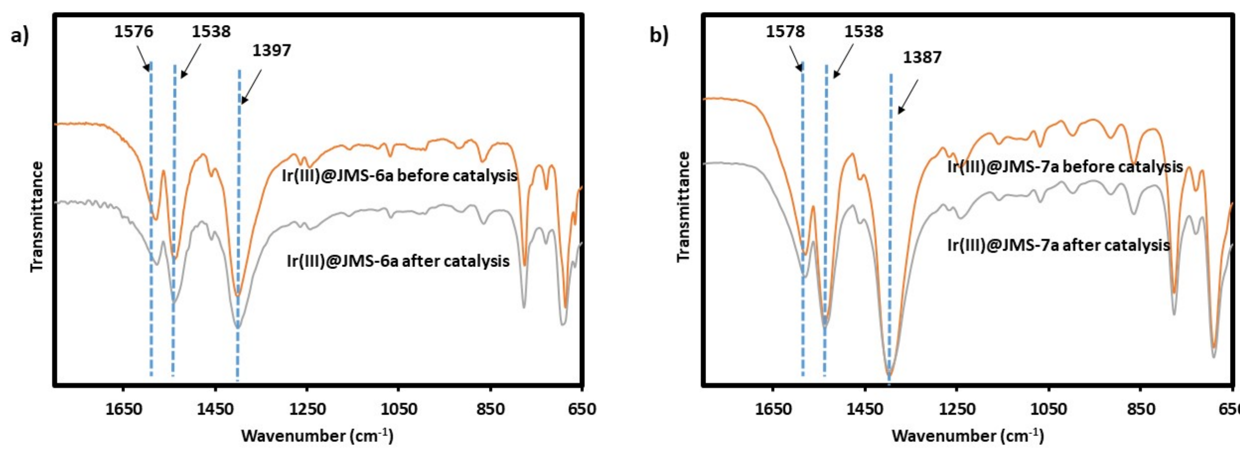


Fig S11: FTIR analysis of Ir(III)@JMS-6a and Ir(III)@JMS-7a before and after catalysis.

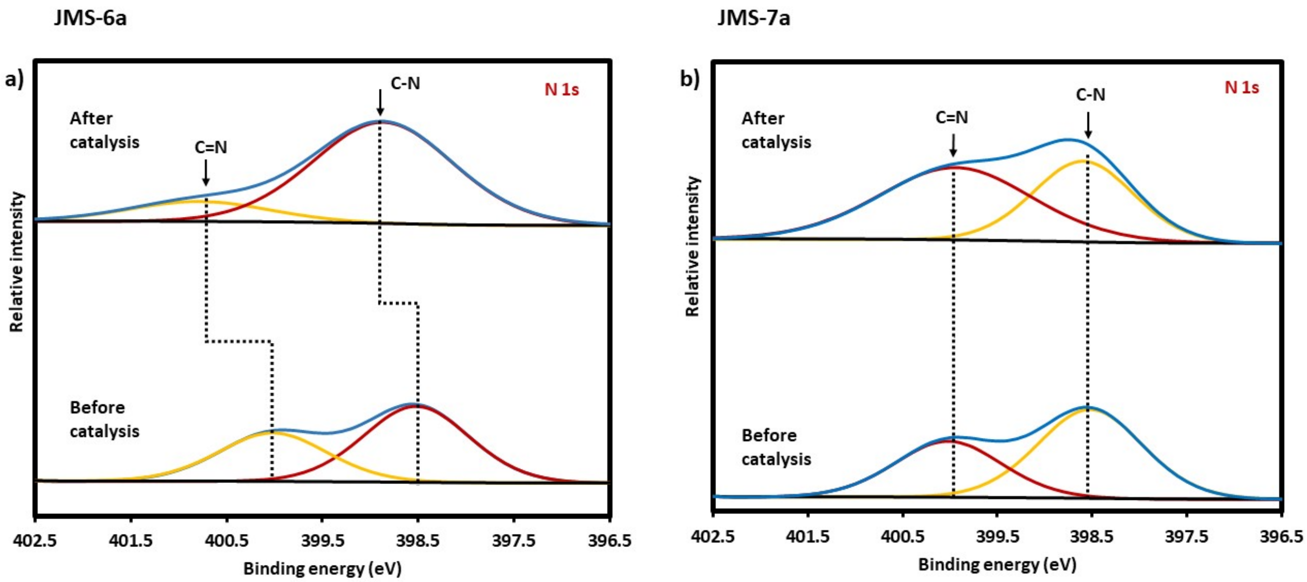


Fig S12: N Is XPS analysis of Ir(III)@JMS-6a and Ir(III)@JMS-7a before and after catalysis.

References

1 S. Yamaguchi and S. Hashimoto, *Asian J. Org. Chem.*, 2020, **9**, 99–104.

2 K. R. Oh, G. N. Yun, K. D. Kim, Y. J. Cheong, C. Yoo, F. Prihatno, H. Y. Jang, A. H. Valekar, G. Y. Cha, M. Lee, J. Jung, Y. U. Kwon and Y. K. Hwang, *Chem. Mater.*, 2022, **34**, 8153–8162.

3 B. An, L. Zeng, M. Jia, Z. Li, Z. Lin, Y. Song, Y. Zhou, J. Cheng, C. Wang and W. Lin, *J. Am. Chem. Soc.*, 2017, **139**, 17747–17750.

4 L. Zhou, C. Yao, W. Ma, J. Hu, Y. Wu, Z. Zhang and X. Hu, *J. CO_2 Util.*, 2021, **54**, 101769.

5 K. Park, G. H. Gunasekar, N. Prakash, K. D. Jung and S. Yoon, *ChemSusChem*, 2015, **8**, 3410–3413.

6 B. D. Bankar, K. Ravi, R. J. Tayade and A. V Biradar, *J. CO_2 Util.*, 2023, **67**, 102315.

7 J. J. Corral-Pérez, A. Billings, D. Stoian and A. Urakawa, *ChemCatChem*, 2019, **11**, 4725–4730.

8 G. Gunniya Hariyanandam, D. Hyun, P. Natarajan, K. D. Jung and S. Yoon, *Catal. Today*, 2016, **265**, 52–55.

9 H. K. Lo, I. Thiel and C. Copéret, *Chem. - A Eur. J.*, 2019, **25**, 9443–9446.