Supporting Information

A Highly Active Cp*Ir Complex with an Anionic N,N-donor Chelate Ligand Catalyzes Robust Regeneration of NADH under Physiological Conditions

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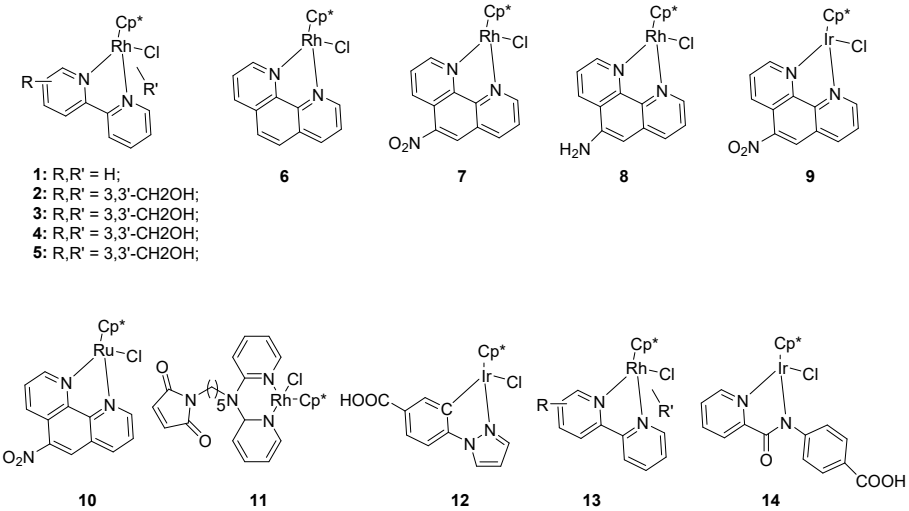
Table S1. Turnover frequency (TOF) comparison of various metal complexes for NADH regeneration.



Complexes	n_s/n_c	T [°C]	TOF [h^{-1}]	Ref.
1	1000	60	875	[S1]
2	1000	60	120	[S1]

3	1000	60	710	[S1]
4	1000	60	1110	[S1]
5	1000	60	100	[S1]
6	1000	38	560	[S2]
	1000	60	2000	[S2]
7	1000	38	400	[S2]
	1000	60	1740	[S2]
8	1000	38	400	[S2]
	1000	60	1500	[S2]
9	100	38	58	[S2]
10	100	38	10	[S2]
11	4000	45	71	[S3]
12	2000	37	7.2	This work
13	2000	37	345	This work
14	10000	37	7825	This work
14	10000	60	14450	This work

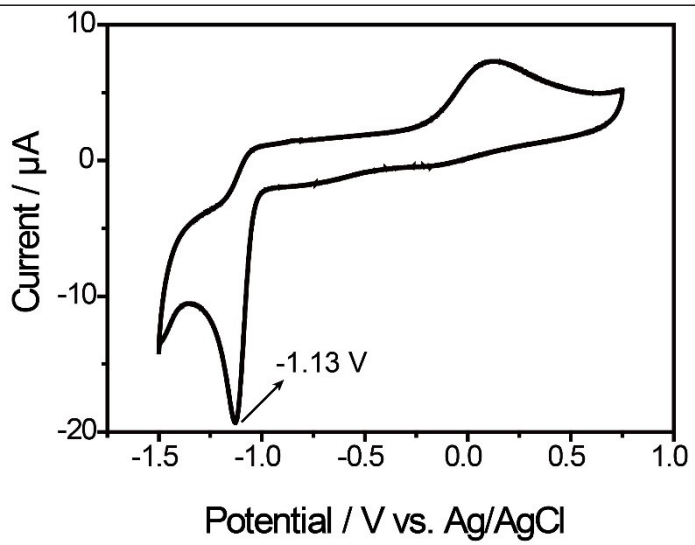


Figure S1. CVs of NAD^+ in (Tris)/HCl (0.100 M, pH 7.4).

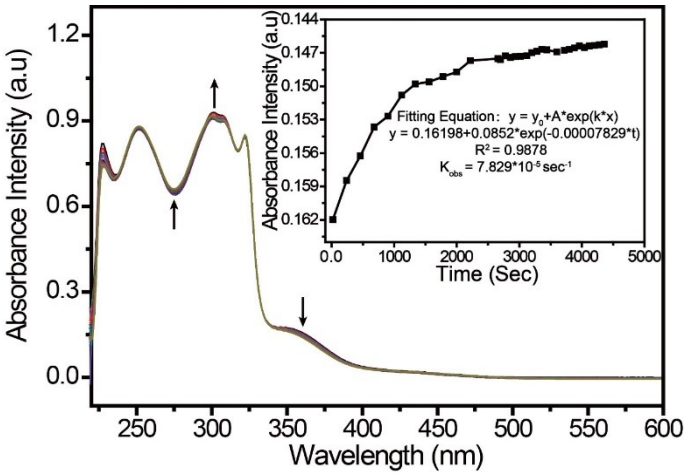


Figure S2. Kinetic traces of UV-Visible absorption spectrum during the reaction of complex **1** (50.0 μM, 2.50 mL) with 0.35 M HCO2Na in phosphate buffer solution (pH 7.4) at 300 K. (Inset) Plot of Ir-H species generation followed at 358 nm versus time and curve fitting for *kobs* calculation.

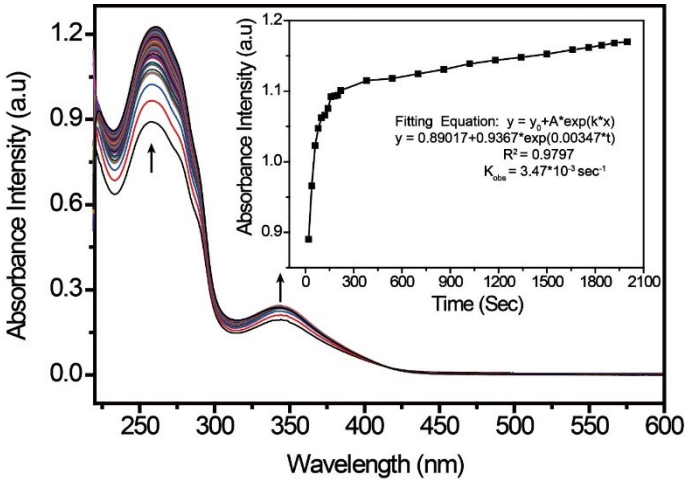


Figure S3. Kinetic traces of UV-Visible absorption spectrum during the reaction of complex 2 (50.0 μM, 2.50 mL) with 0.35 M HCO_2Na in phosphate buffer solution (pH 7.4) at 300 K. (Inset) Plot of Ir-H species generation followed at 259 nm versus time and curve fitting for *kobs* calculation.

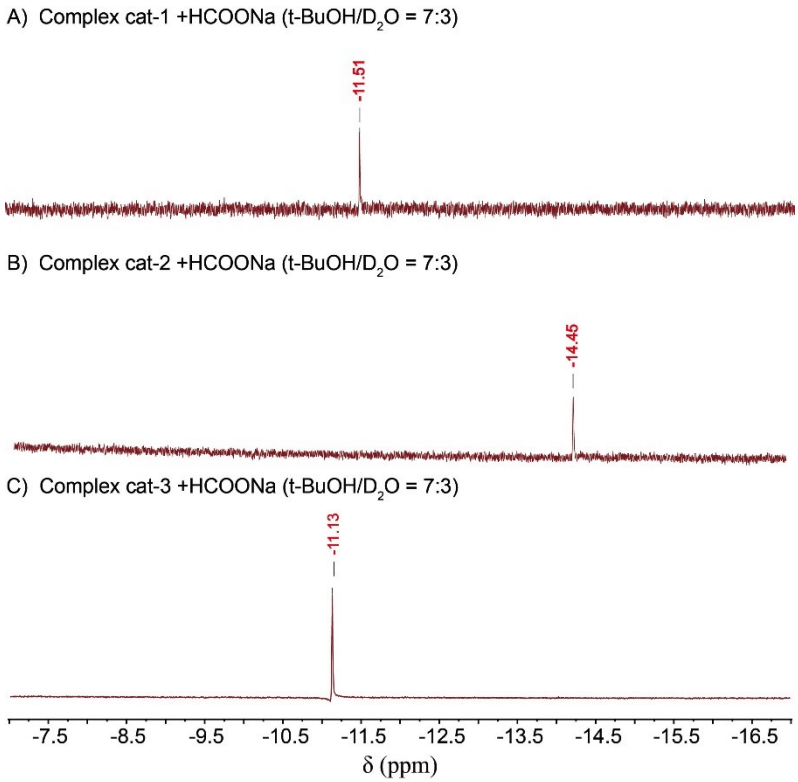


Figure S4. [1]H NMR spectra obtained from the reaction of the iridium complexes 1 (A), 2 (B), and 3 (C) with HCOONa (1:2) at 37 °C for 15 h. Only the NMR spectral regions where the hydride signals appear are shown. The signals at -11.51, -14.45, and -11.13 ppm match the hydride peaks for independently prepared samples of 1-H, 2-H, and 5-H, respectively.

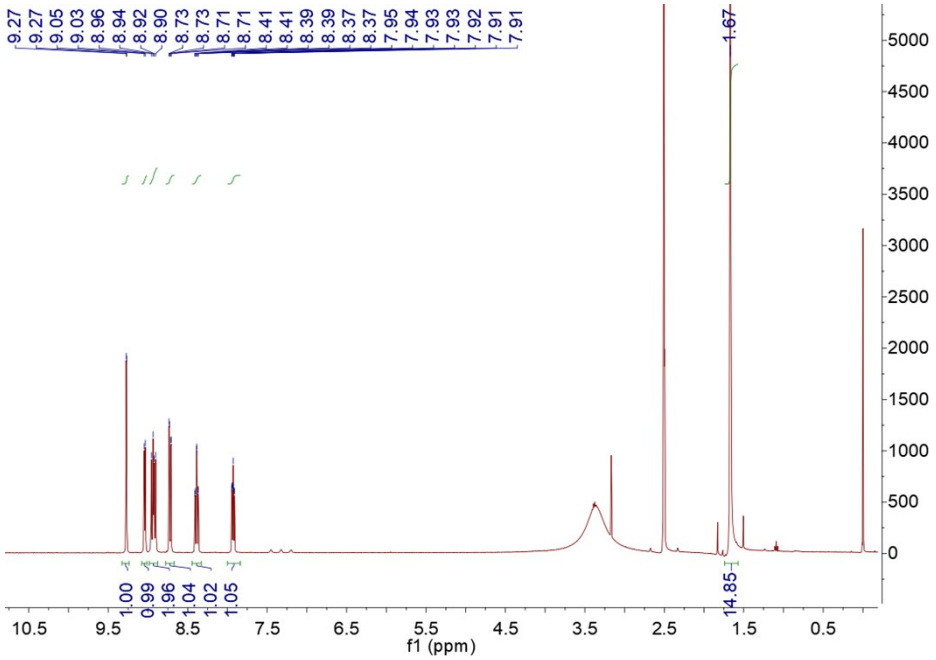


Figure S5. The [1]H NMR spectra of compound cat-1.

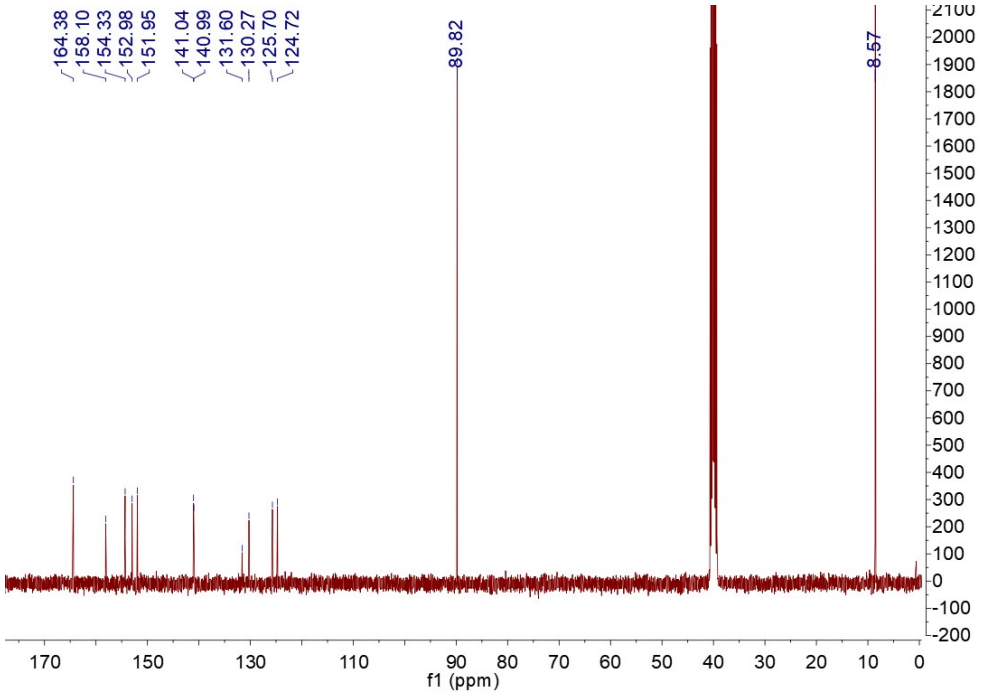


Figure S6. The ^{13}C NMR spectra of compound cat-1.

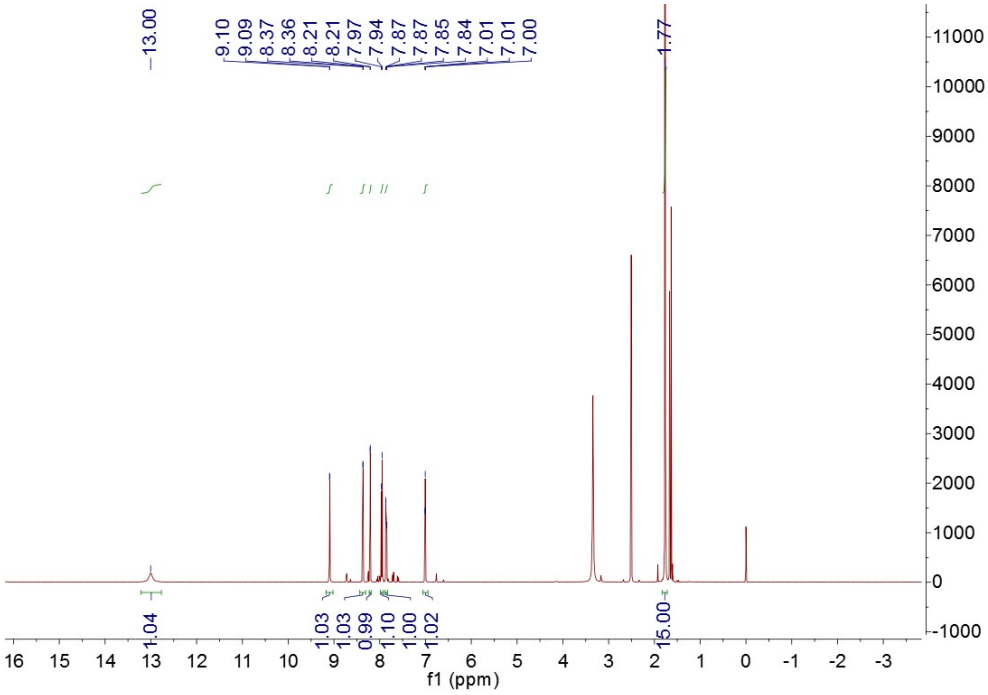


Figure S7. The ^{1}H NMR spectra of compound cat-2.

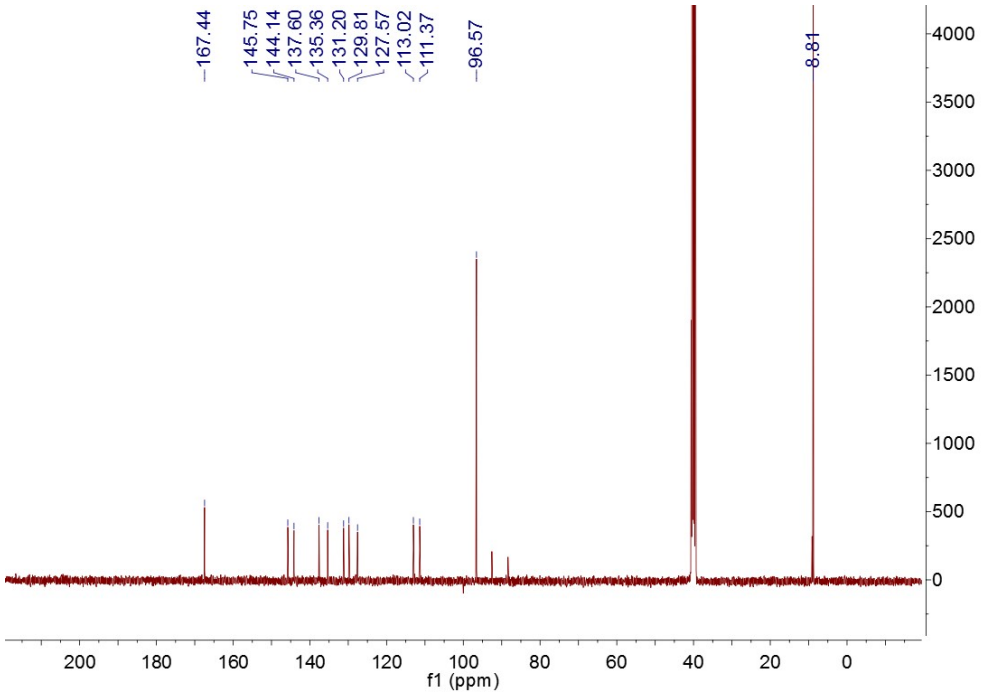


Figure S8. The ^{13}C NMR spectra of compound cat-2.

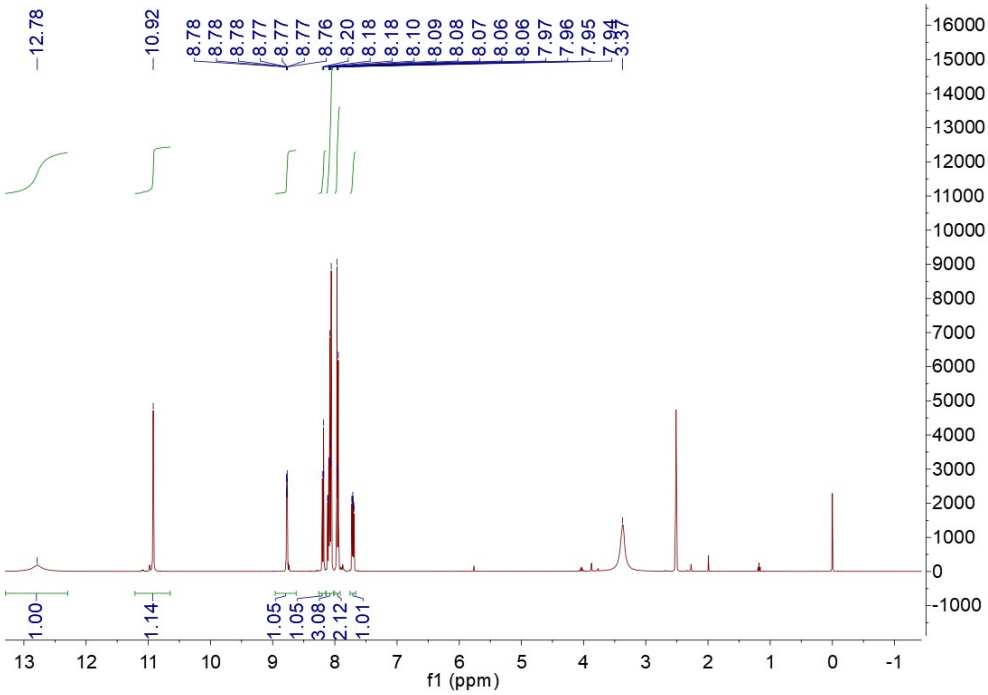


Figure S9. The ^{1}H NMR spectra of compound 3b.

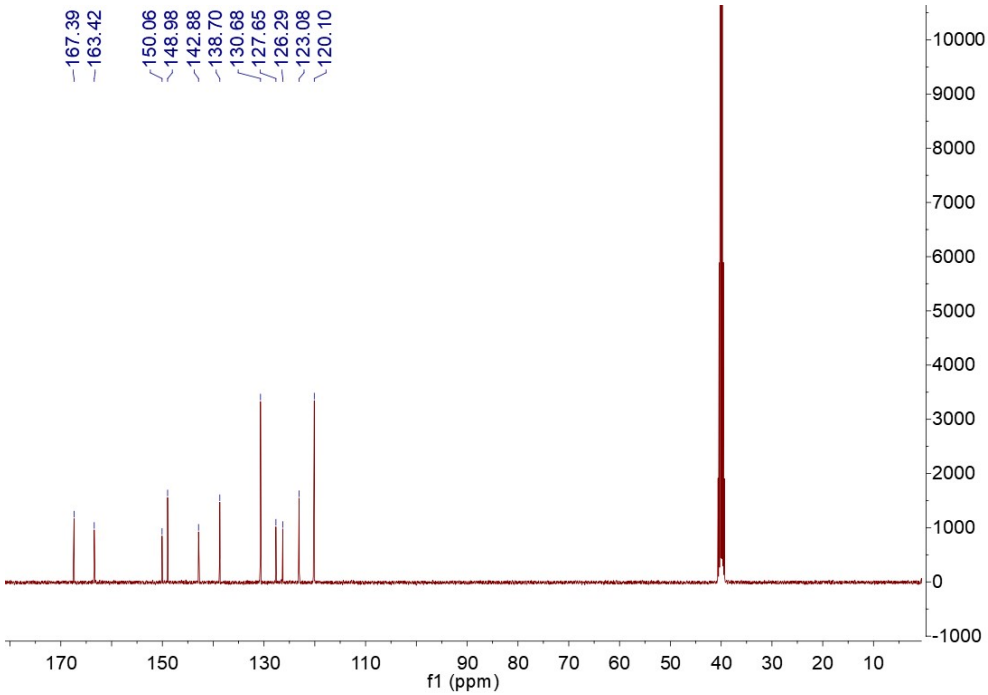


Figure S10. The ^{13}C NMR spectra of compound 3b.

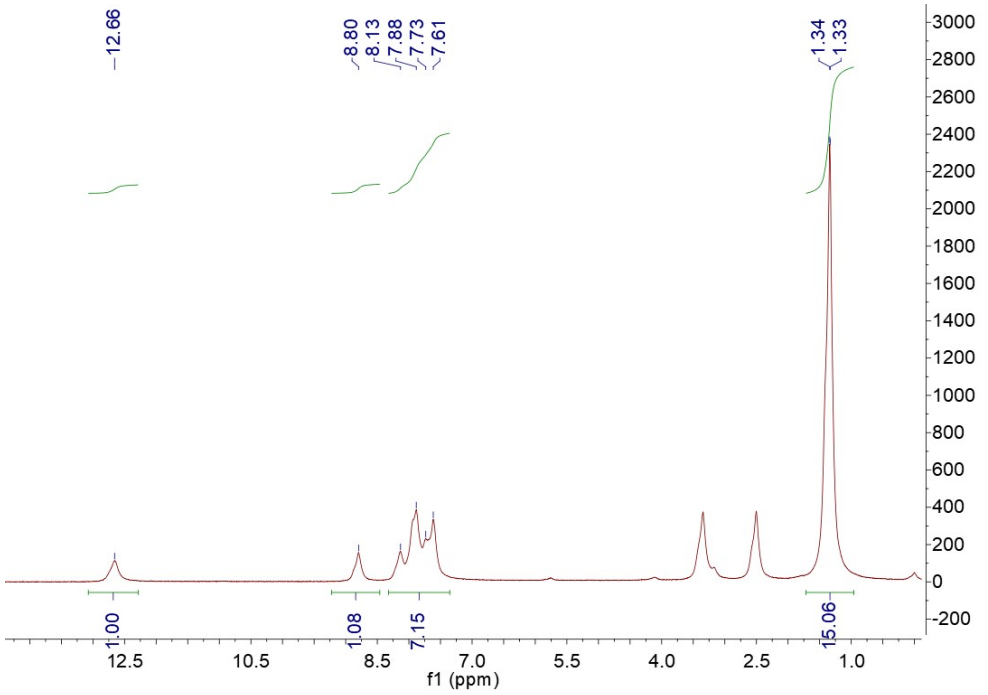


Figure S11. The ^{1}H NMR spectra of compound cat-3.

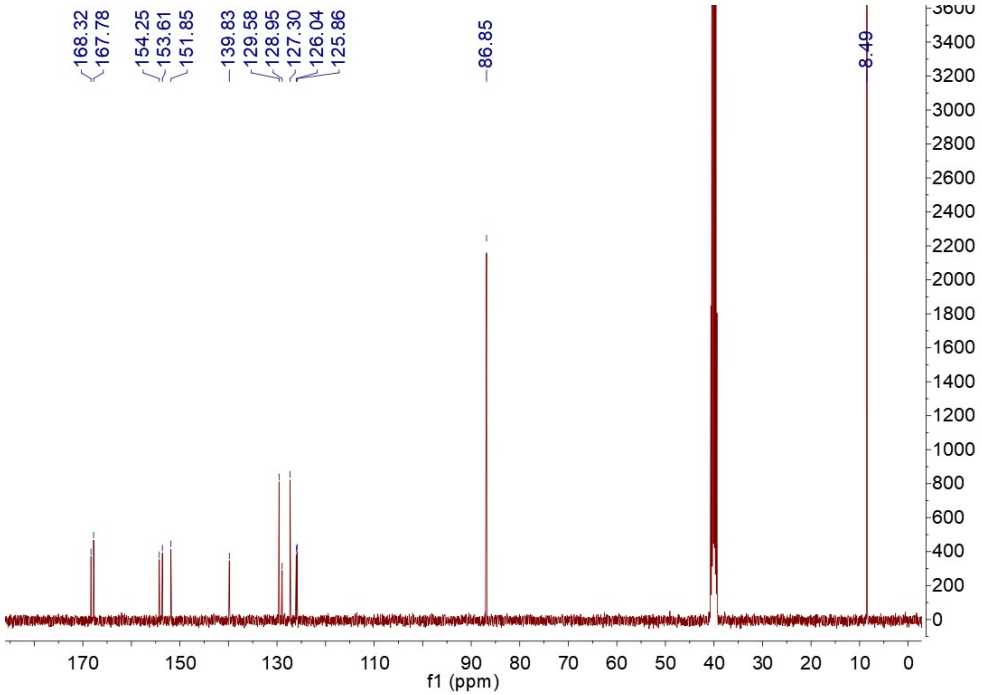


Figure S12. The ^{13}C NMR spectra of compound cat-3.

[S1] G. Vinothkumar, S. Dharmalingam and Y. Sungho, *Inorg. Chem.*, 2017, **56**, 1366-1374.
[S2] J. Canivet, G. Suss-Fink, P. Stepnicka, *Eur. J. Inorg. Chem*., 2007, **30**, 4736-4742.
[S3] P. Haquette, B. Talbi, L. Barilleau, N. Madern, C. Fossec, M.Salmain, *Org. Biomol. Chem*., 2011, 9, 5720-5727.