

Aldehydic Carbon-Hydrogen Bond Activation with Iridium(III) Porphyrin β -Hydroxyethyl

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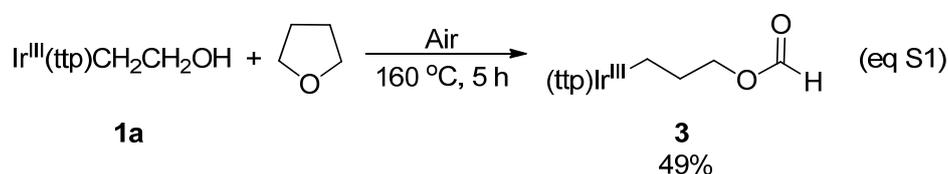
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Supplementary Experimental Results

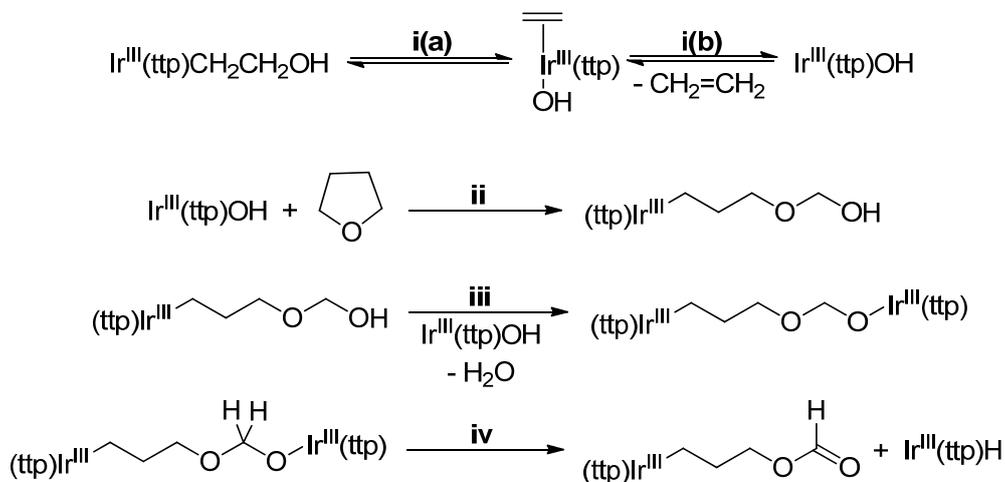
(1) CCA of THF with Ir^{III}(ttp)CH₂CH₂OH

To confirm that the origin of Ir^{III}(ttp)(CH₂)₃OCHO **3** from the CCA of THF with Ir^{III}(ttp)CH₂CH₂OH **1a**, an independent experiment for the CCA of THF was performed. Ir^{III}(ttp)CH₂CH₂OH **1a** reacted with THF at 160 °C to give Ir^{III}(ttp)(CH₂)₃OCHO **3** in 49% yield in 5 hours (eq S1).



Scheme S1 illustrates the proposed mechanism of the CCA of THF with Ir^{III}(ttp)CH₂CH₂OH **1a**.^{1,2} Ir^{III}(ttp)CH₂CH₂OH **1a** initially undergoes β -hydroxyl elimination to yield Ir^{III}(ttp)OH (pathway i(a) and i(b)).¹ Ir^{III}(ttp)OH then cleaves the C(α)-C(β) bond of THF *via* σ -bond metathesis to give Ir^{III}(ttp)(CH₂)₃OCH₂OH (pathway ii).² Condensation of Ir^{III}(ttp)(CH₂)₃OCH₂OH with Ir^{III}(ttp)OH yields the metalloether, Ir^{III}(ttp)(CH₂)₃OCH₂OIr^{III}(ttp) (pathway iii),² which then undergoes β -hydride elimination to give Ir^{III}(ttp)(CH₂)₃OCHO **3** (pathway iv).²

Scheme S1. Proposed Mechanism for the CCA of THF by Ir^{III}(ttp)CH₂CH₂OH **1a**



(2) HRMS Analysis of PPh₃-Coordinated Iridium porphyrin Complex

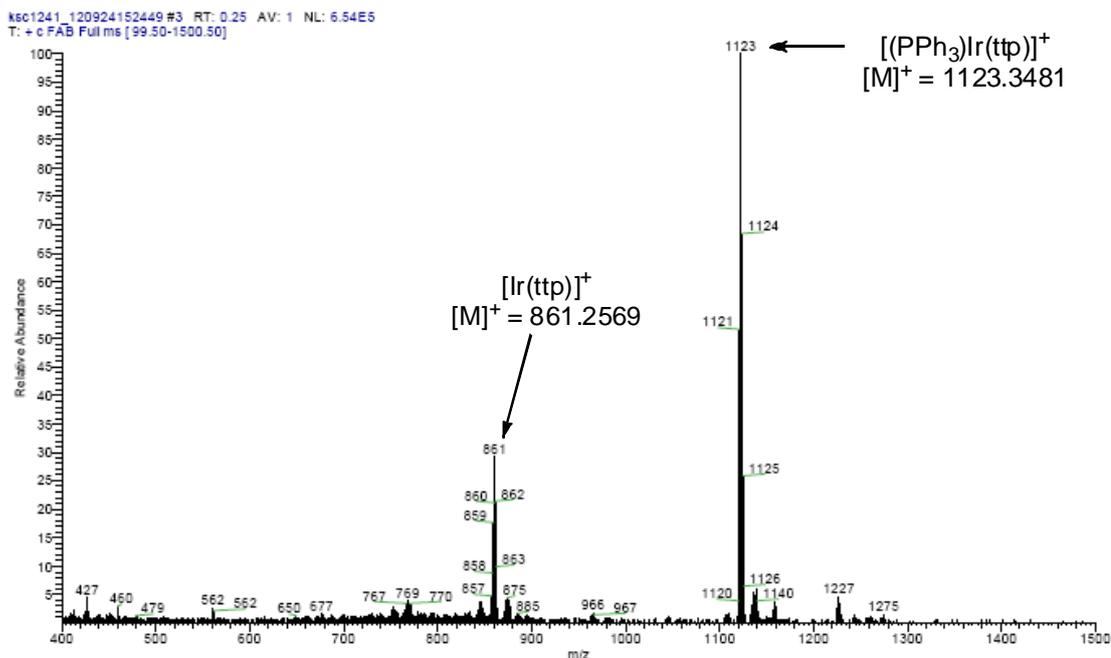
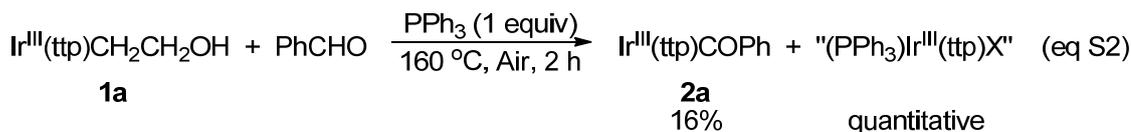


Figure S2(a). Mass Spectrum of the Unknown “(PPh₃)Ir(tp)X”

Accurate Mass Measurement

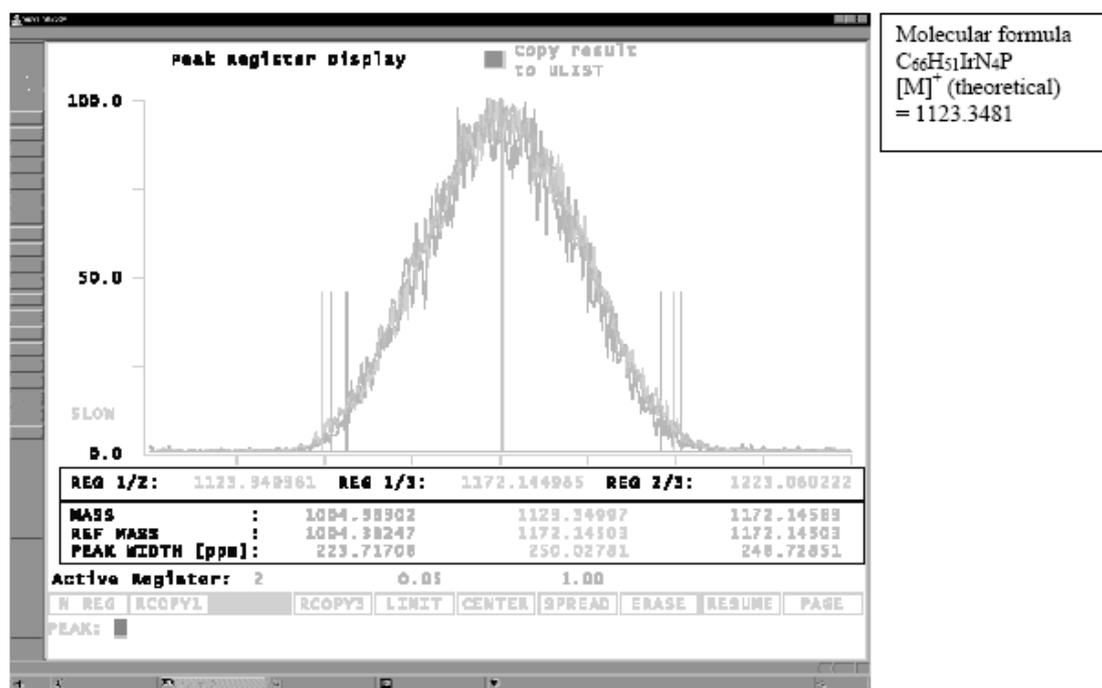
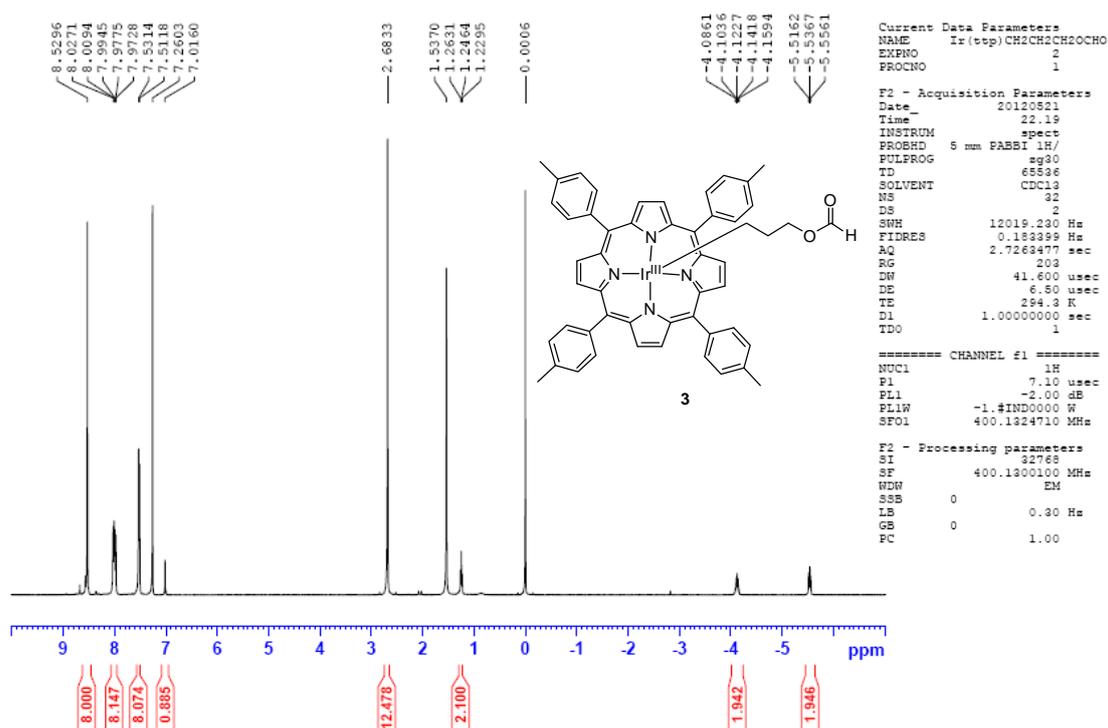


Figure S2(b). High-Resolution Mass Spectrum of the Unknown “(PPh₃)Ir(ttp)X”

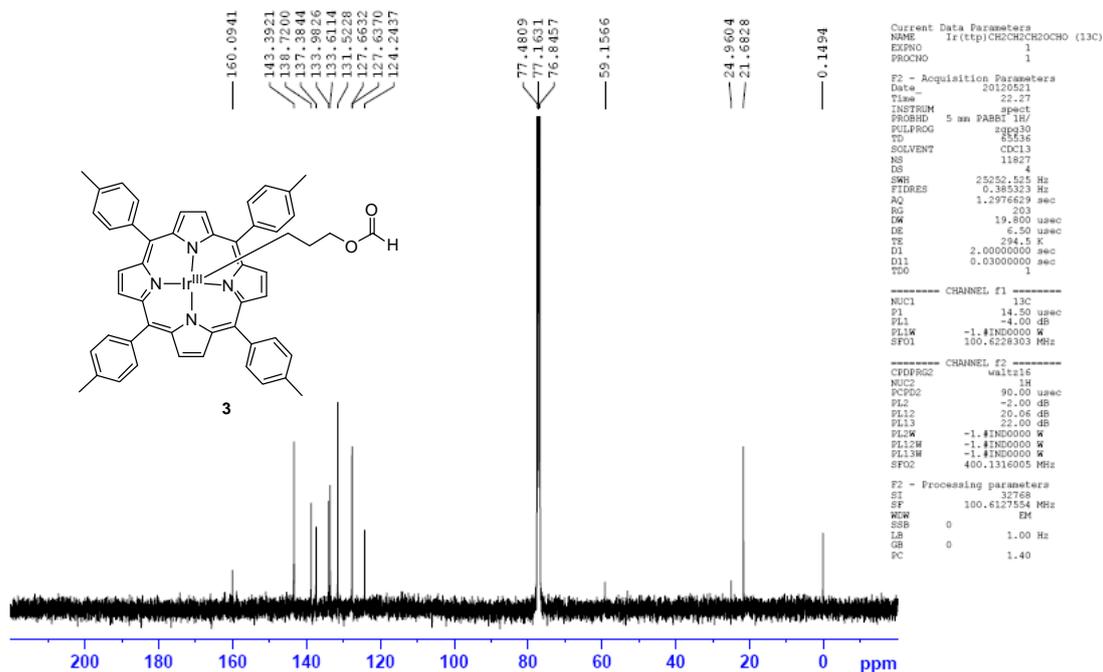
List of Spectra

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1	^1H NMR spectrum of $\text{Ir}^{\text{III}}(\text{ttp})(\text{CH}_2)_3\text{OCHO}$ 3	S5
2	^{13}C NMR spectrum of $\text{Ir}^{\text{III}}(\text{ttp})(\text{CH}_2)_3\text{OCHO}$ 3	S6
3	^1H NMR spectrum of $\text{Ir}^{\text{III}}(\text{ttp})\text{COC}_6\text{H}_4(p\text{-Me})$ 2b and $\text{Ir}^{\text{III}}(\text{ttp})\text{-CH}_2\text{C}_6\text{H}_4(p\text{-CHO})$ 4	S6
4	^1H NMR spectrum of Unknown “ $(\text{PPh}_3)\text{Ir}(\text{ttp})\text{X}$ ”	S7
5	^{31}P NMR spectrum of Unknown “ $(\text{PPh}_3)\text{Ir}(\text{ttp})\text{X}$ ”	S7

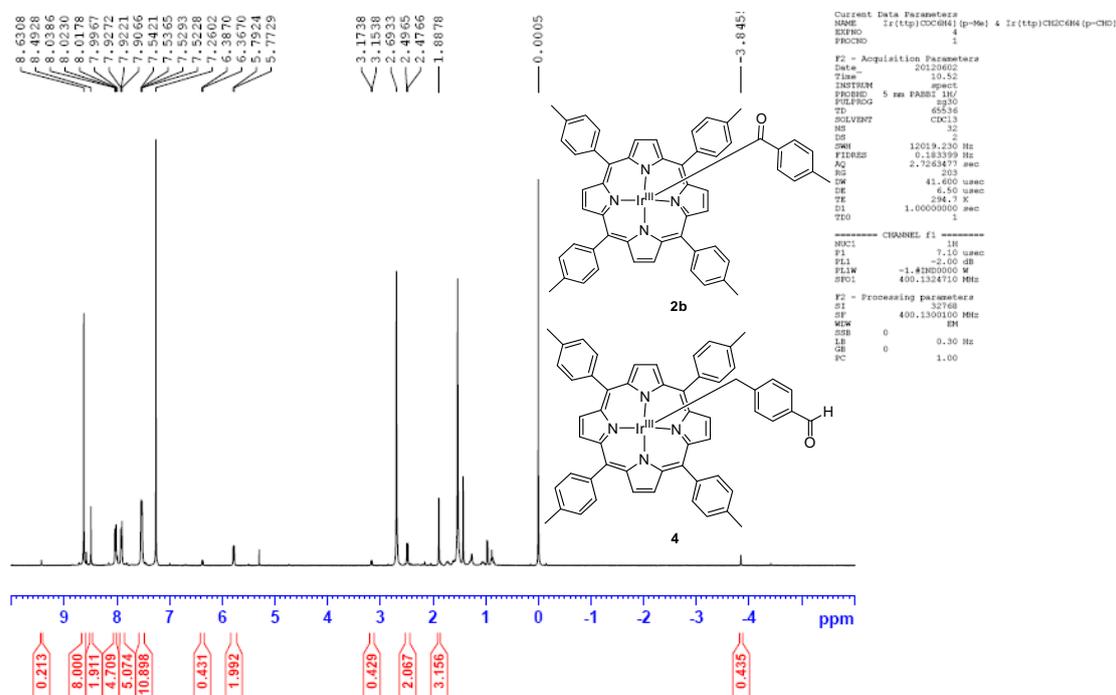
^1H NMR spectrum of $\text{Ir}^{\text{III}}(\text{ttp})(\text{CH}_2)_3\text{OCHO}$ **3**



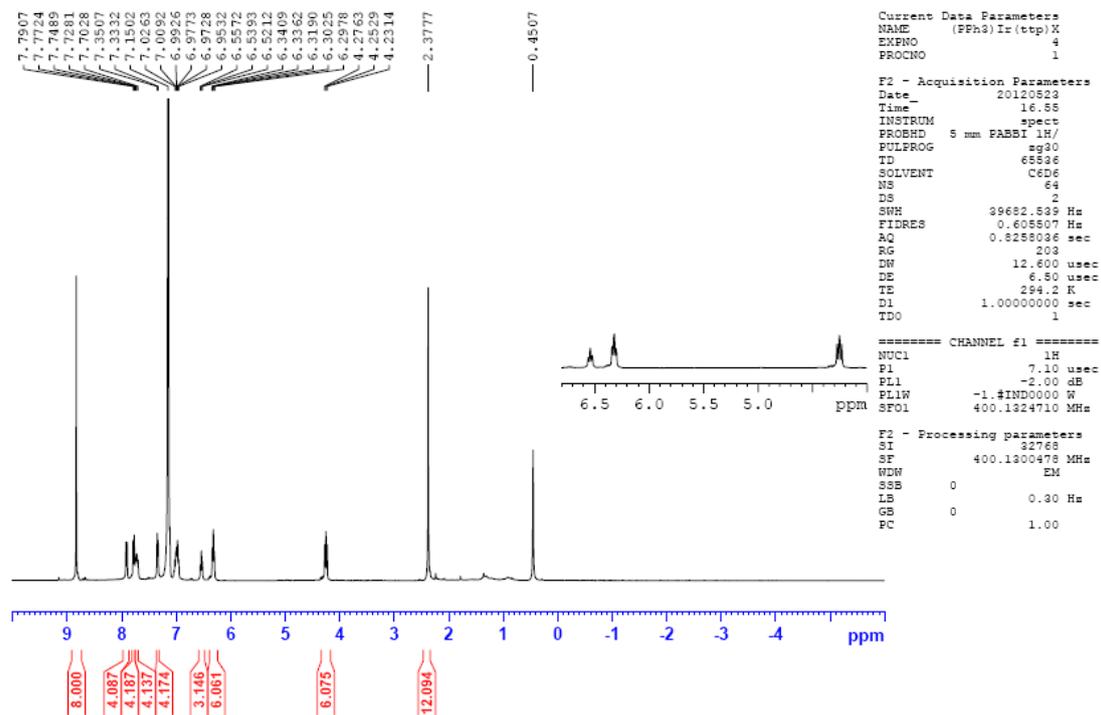
^{13}C NMR spectrum of $\text{Ir}^{\text{III}}(\text{ttp})(\text{CH}_2)_3\text{OCHO}$ **3**



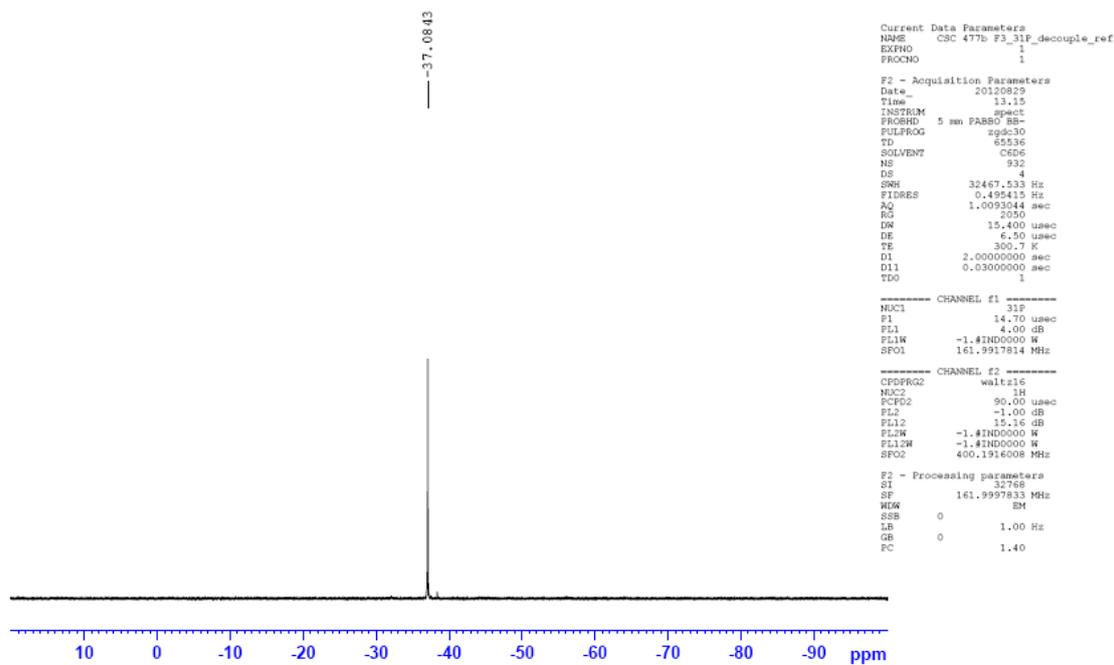
^1H NMR spectrum of $\text{Ir}^{\text{III}}(\text{ttp})\text{COC}_6\text{H}_4(p\text{-Me})$ **2b** and $\text{Ir}^{\text{III}}(\text{ttp})\text{CH}_2\text{C}_6\text{H}_4(p\text{-CHO})$ **4**



¹H NMR spectrum of Unknown “(PPh₃)Ir(ttp)X”



³¹P NMR spectrum of Unknown “(PPh₃)Ir(ttp)X”



References

- (1) (a) Cheung, C. W.; Chan, K. S. *Organometallics* **2011**, *30*, 4269-4283. (b) Tsang, J. Y. K.; Chan, K. S. *Can. J. Chem.* **2011**, *89*, 1506-1511.
- (2) (a) Lee, S. Y.; Lai, T. H.; Choi, K. S.; Chan, K. S. *Organometallics* **2011**, *30*, 3691-3693. (b) Yeung, S. K. *Ph. D Thesis*, The Chinese University of Hong Kong, **2005**.