

**Online Supporting Information for**

**Light driven carbon dioxide reduction coupled with conversion of acetylenic group to ketone by a functional Janus catalyst based on Keplerate {Mo<sub>132</sub>}**

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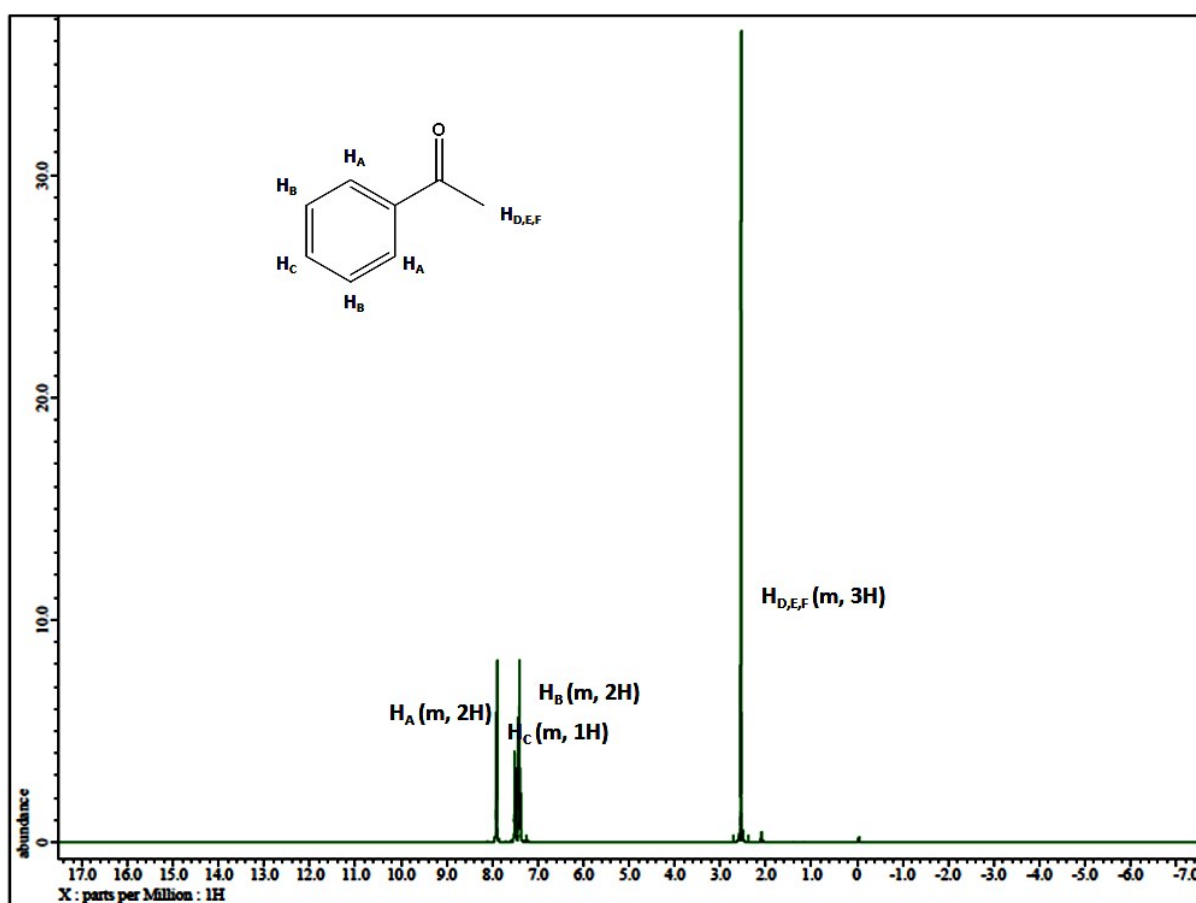
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and

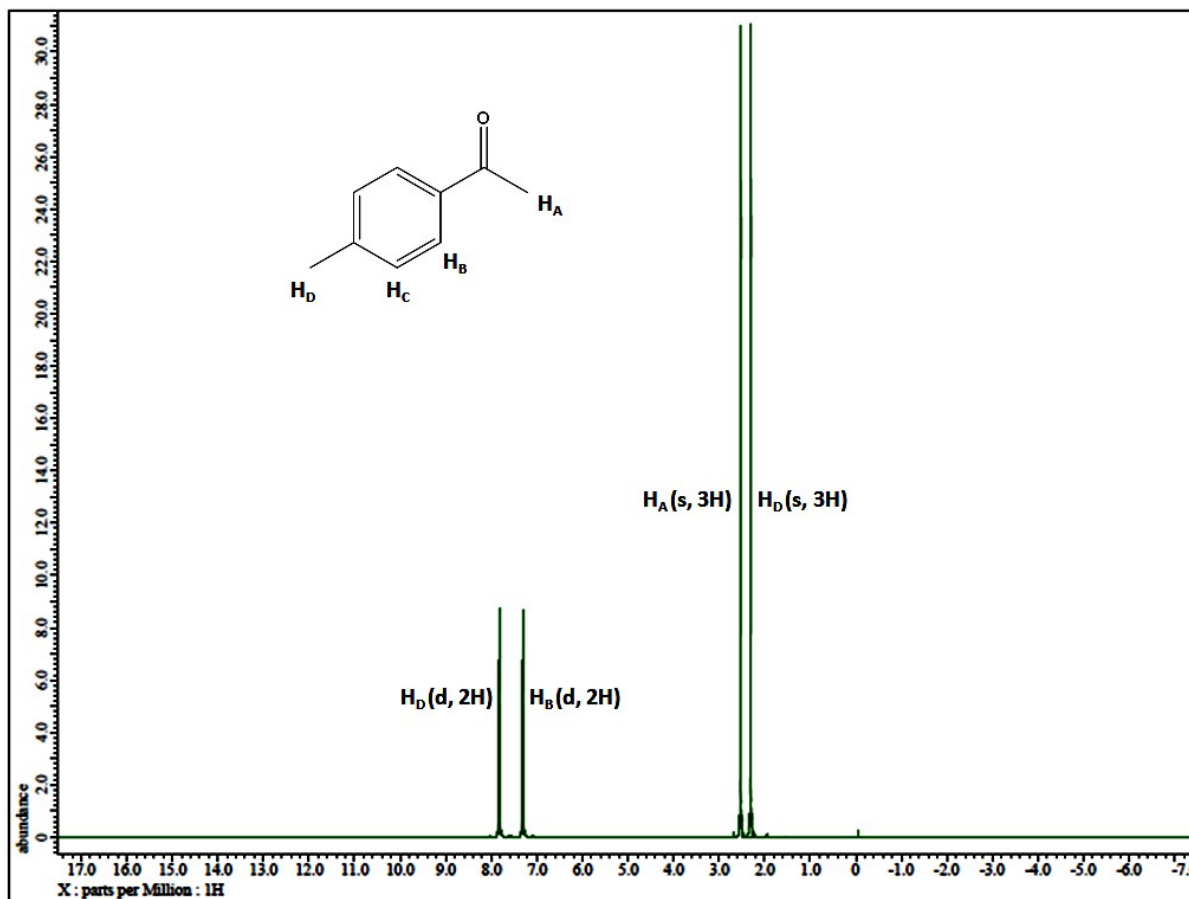
EFAML, Materials Science Centre, Department of Chemical Sciences, Indian Institute of Science Education & Research, Mohanpur Campus, Kolkata, India. \*E-mail: [s.roy@iiserkol.ac.in](mailto:s.roy@iiserkol.ac.in)

All the reactions have been performed as per the experimental procedure mentioned in the article:

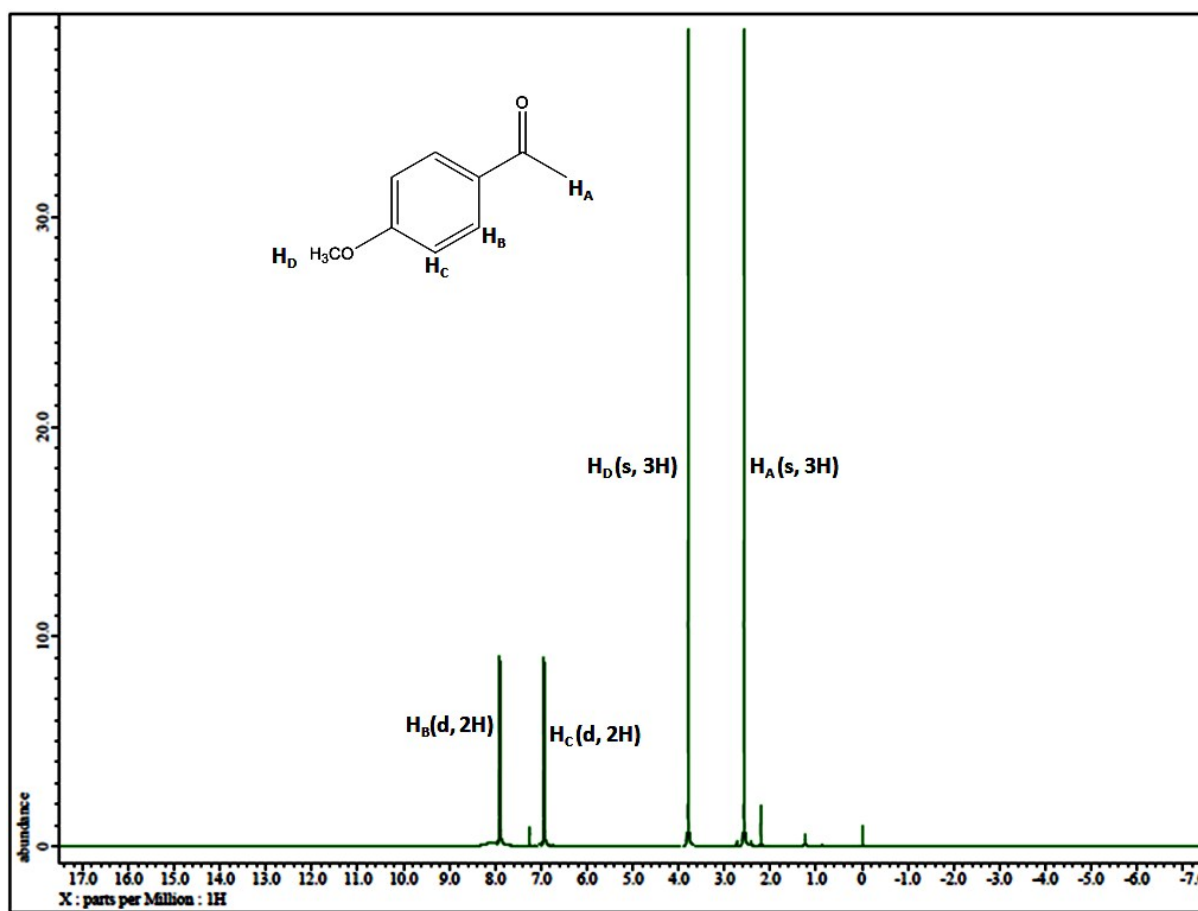
Acetophenone  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98- 7.96 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 2.61 (s, 3H)



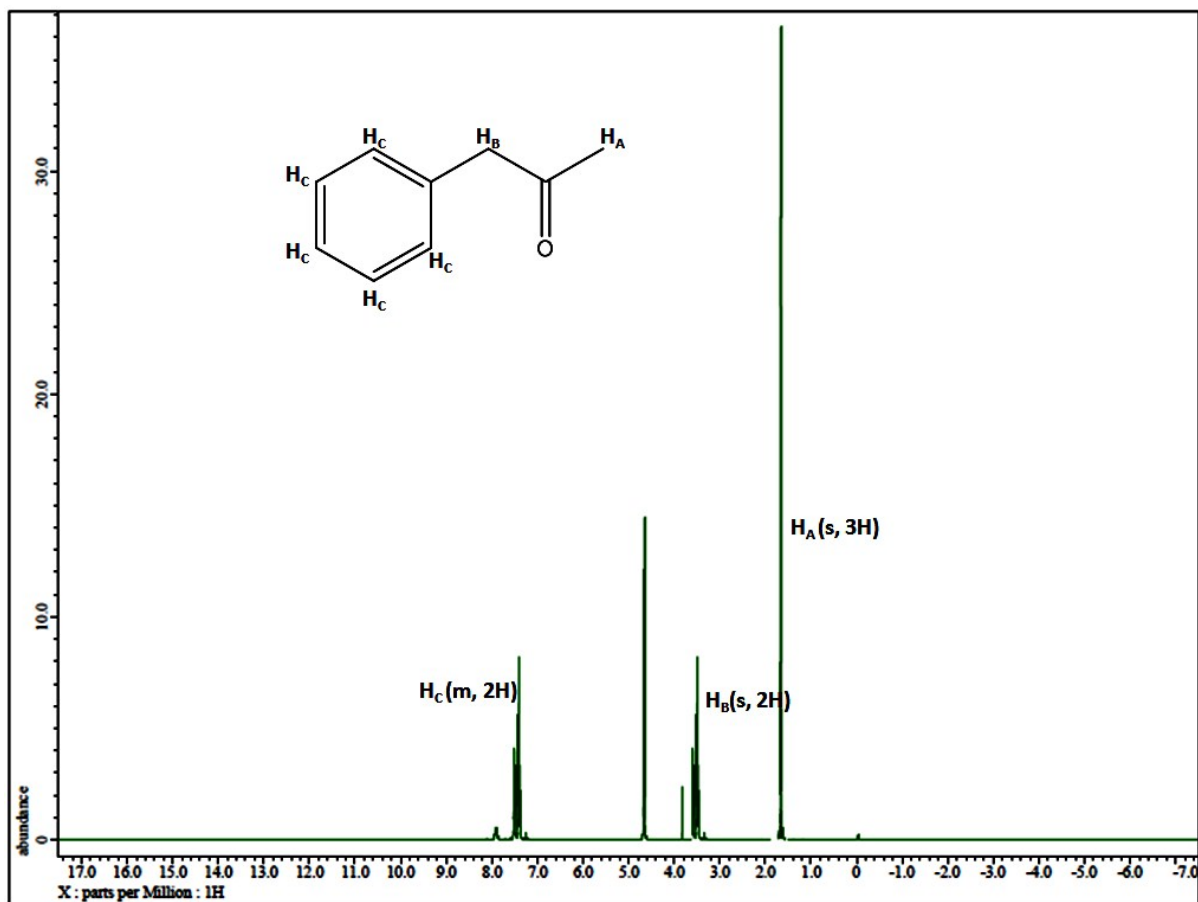
4-Methylacetophenone  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.75 (d,  $3 J = 7.9$  Hz, 2 H), 7.14 (d,  $3 J = 7.9$  Hz, 2 H), 2.46 (s, 3 H), 2.29 (s, 3 H).



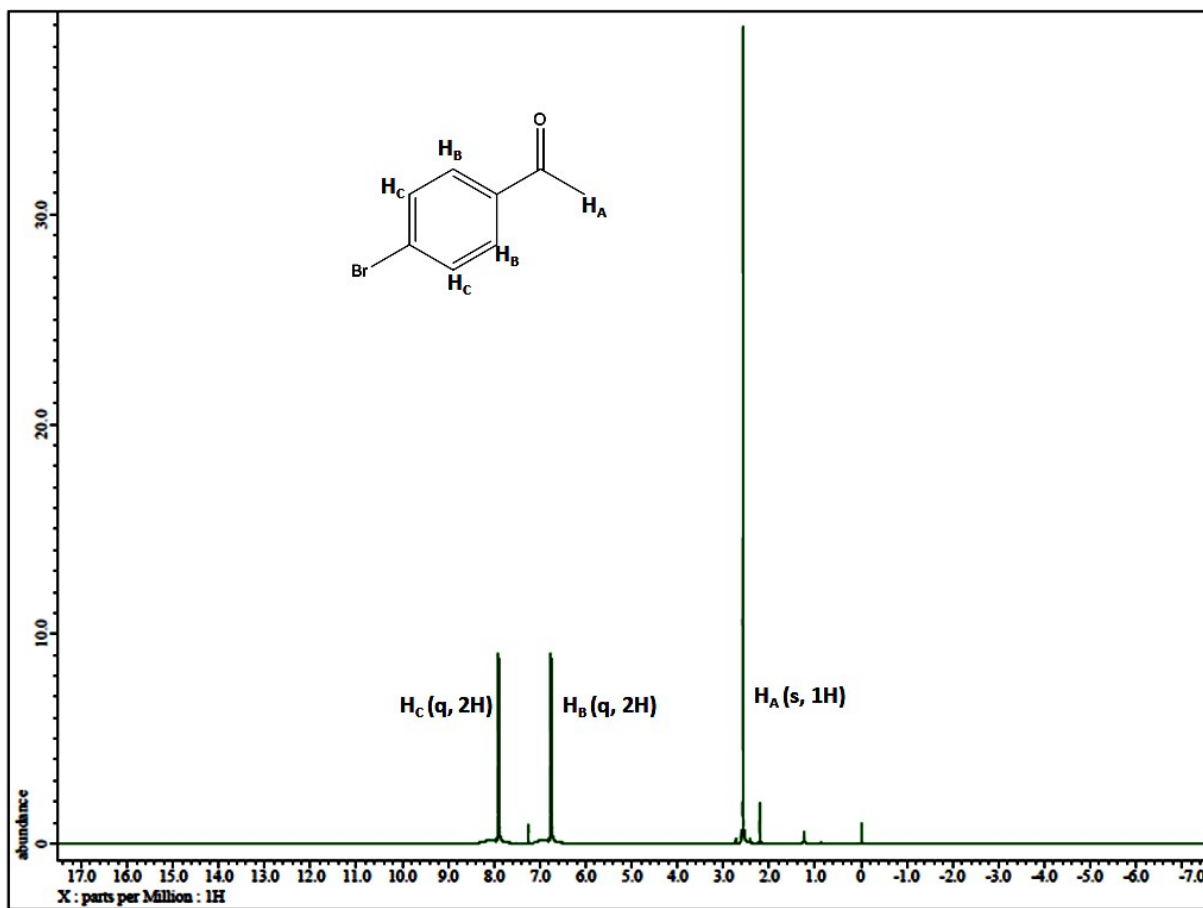
4-Methoxyacetophenone  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.84–7.79 (m, 2 H), 6.84–6.74 (m, 2 H), 3.74 (s, 3 H), 2.42 (s, 3 H).



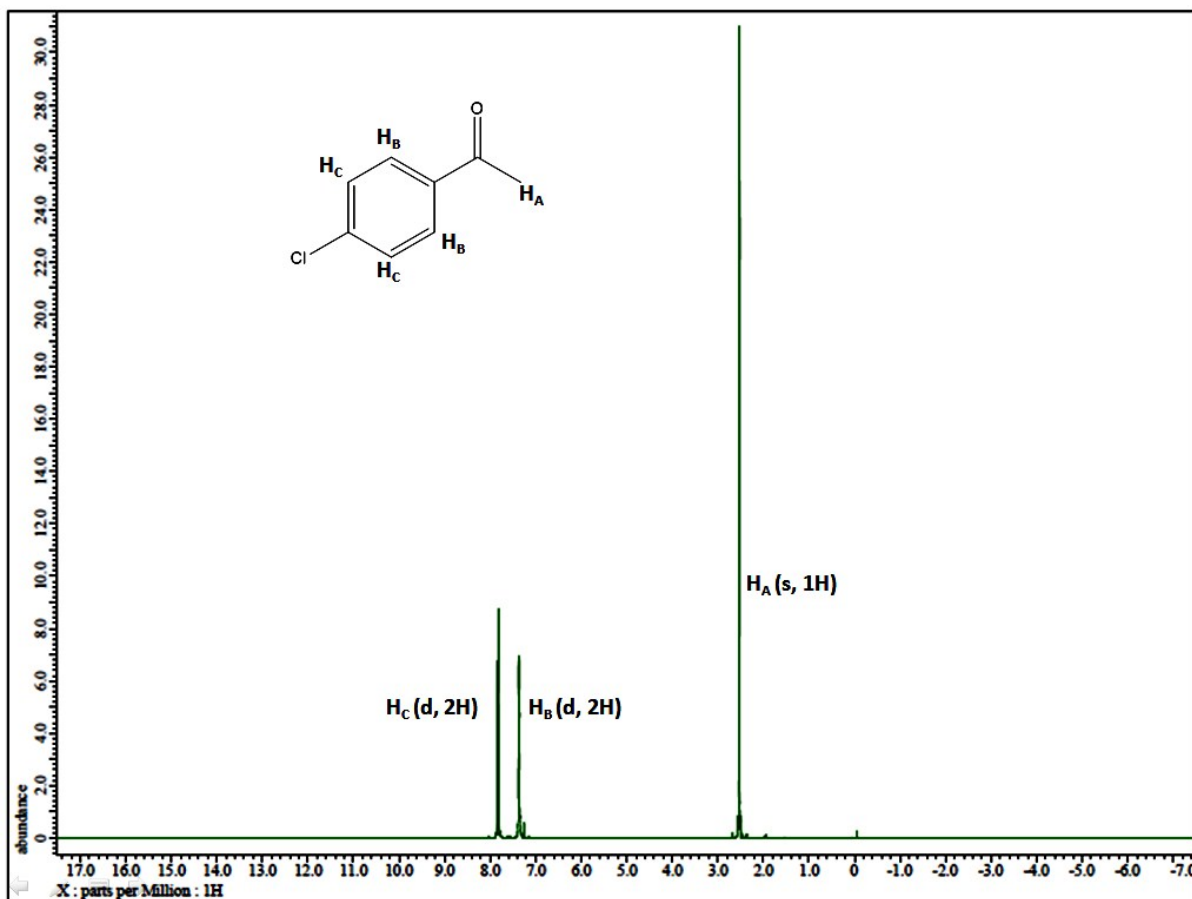
1-Phenylpropan-2-one  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.15-7.40 (m, 5H), 3.68 (s, 2H), 2.14 (s, 3H).



4-Bromoacetophenone  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.60 (s, 3H), 7.61-7.63 (q, 2H), 7.83-7.84 (q, 2H)



4-Chloroacetophenone  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.61 (s, 3H), 7.45 (d,  $J = 8.5$  Hz, 2H), 7.91 (d,  $J = 8.5$  Hz, 2H).



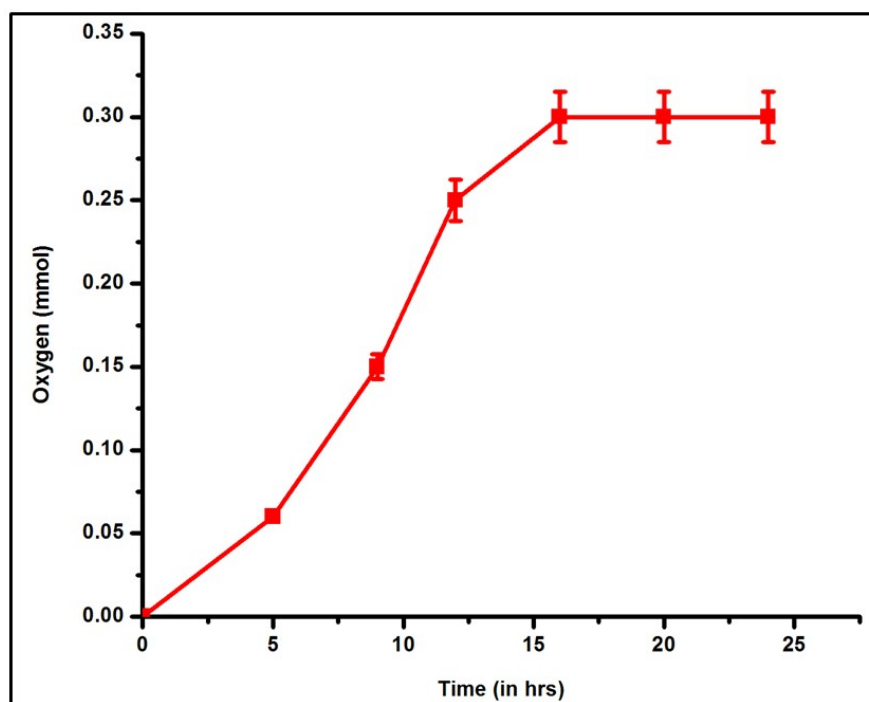


Fig. S1 Time dependent oxygen evolution at varying pH.



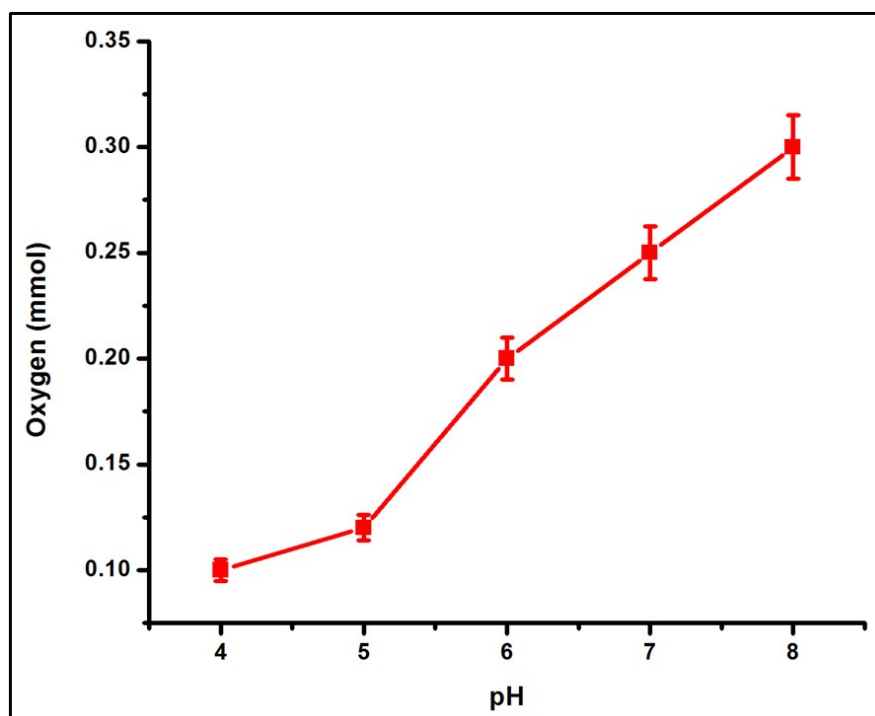


Fig. S2 pH dependent O<sub>2</sub> formation

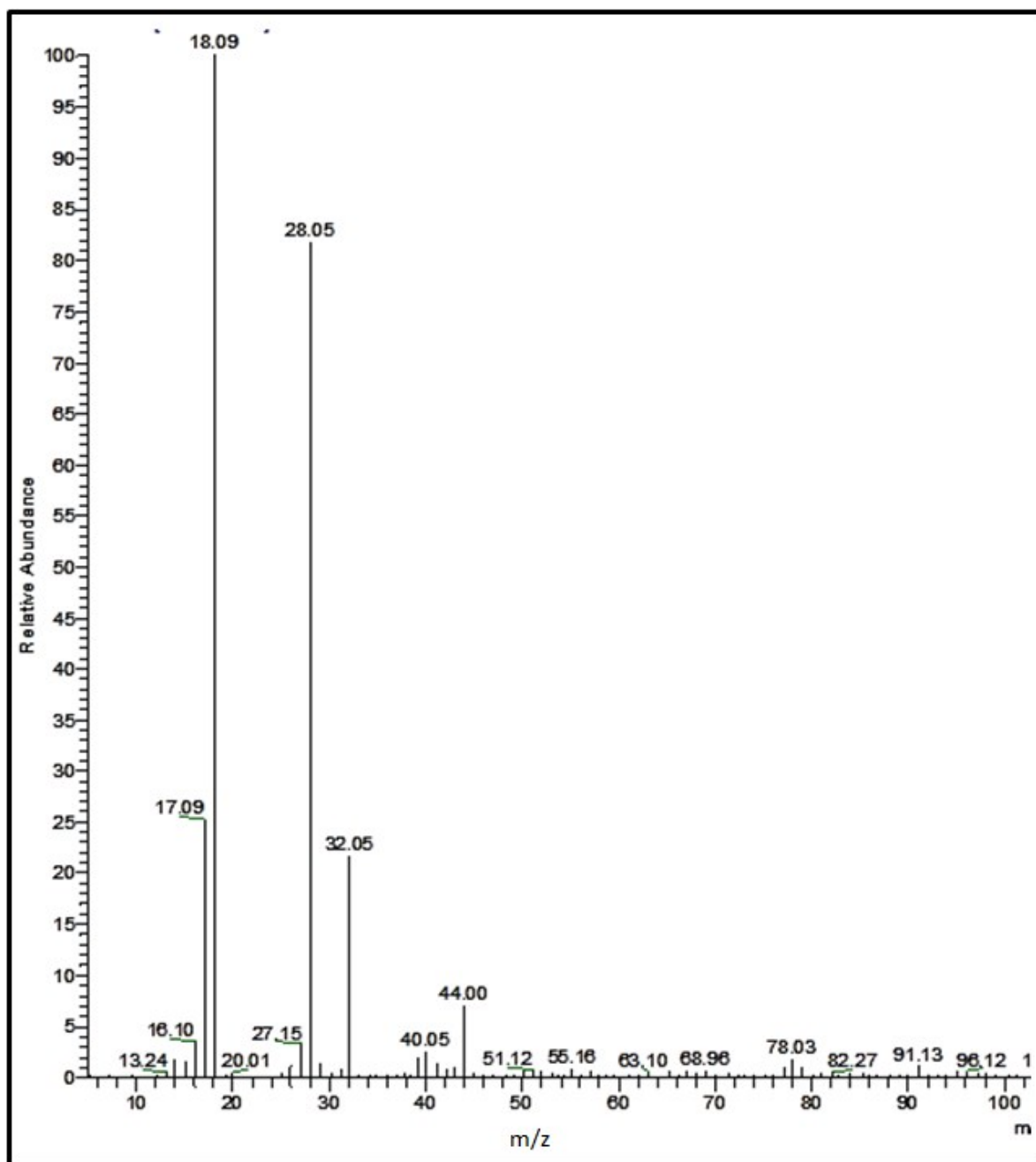


Fig. S3 Mass Spectra of Ethyl formate obtained during esterification

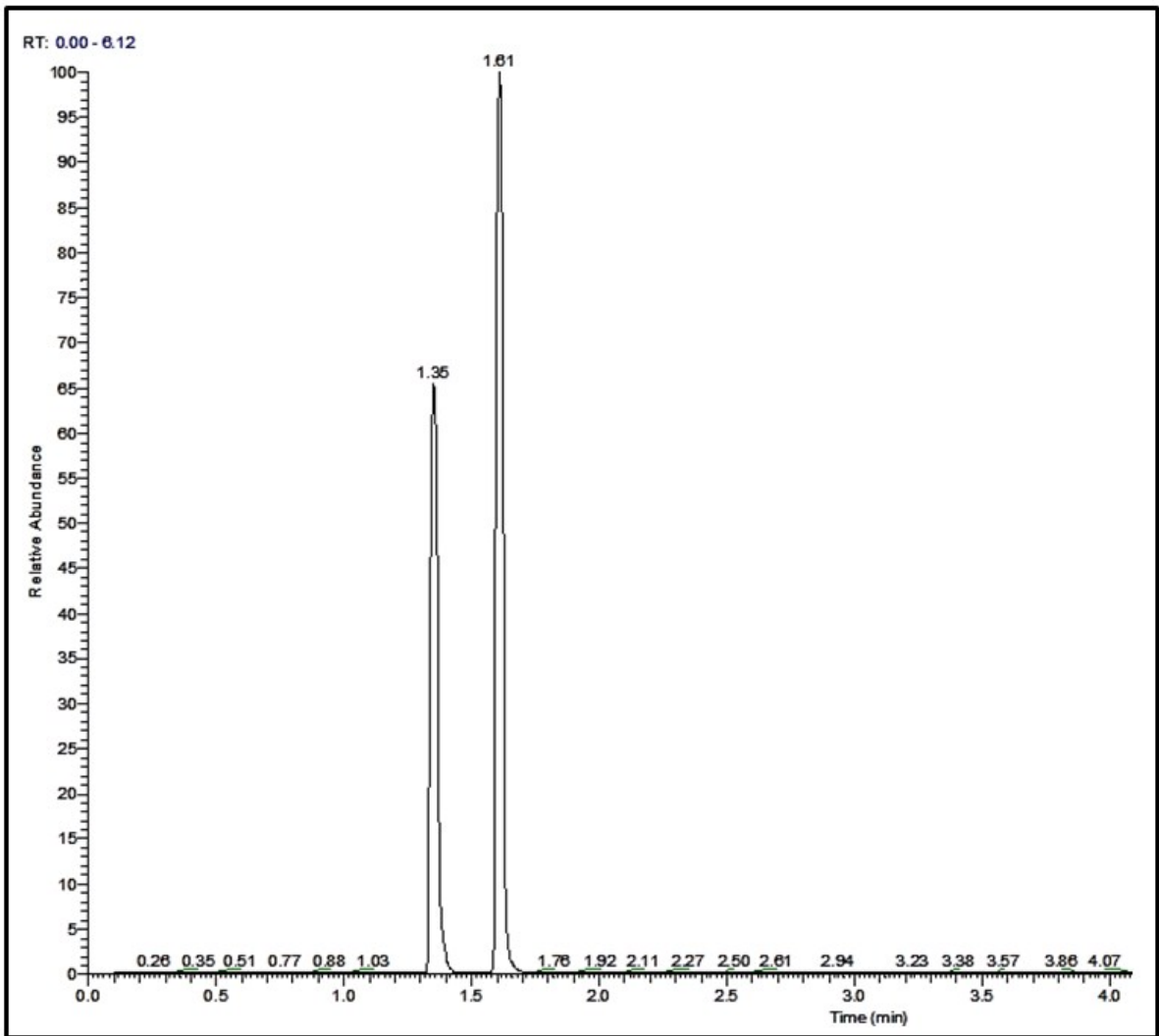


Fig. S4 Retention time of ethyl formate after esterification from GC-MS.

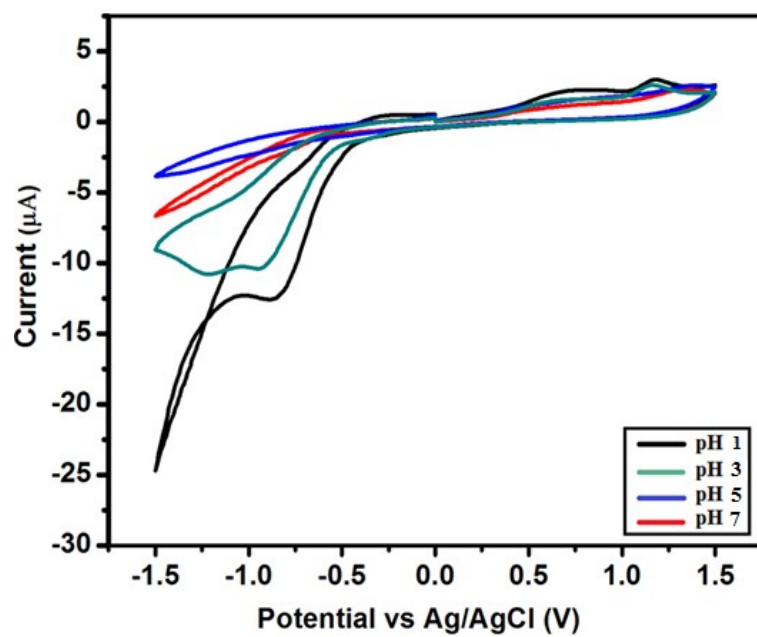


Fig. S5 Cyclic Voltammetry Graph at different pH .

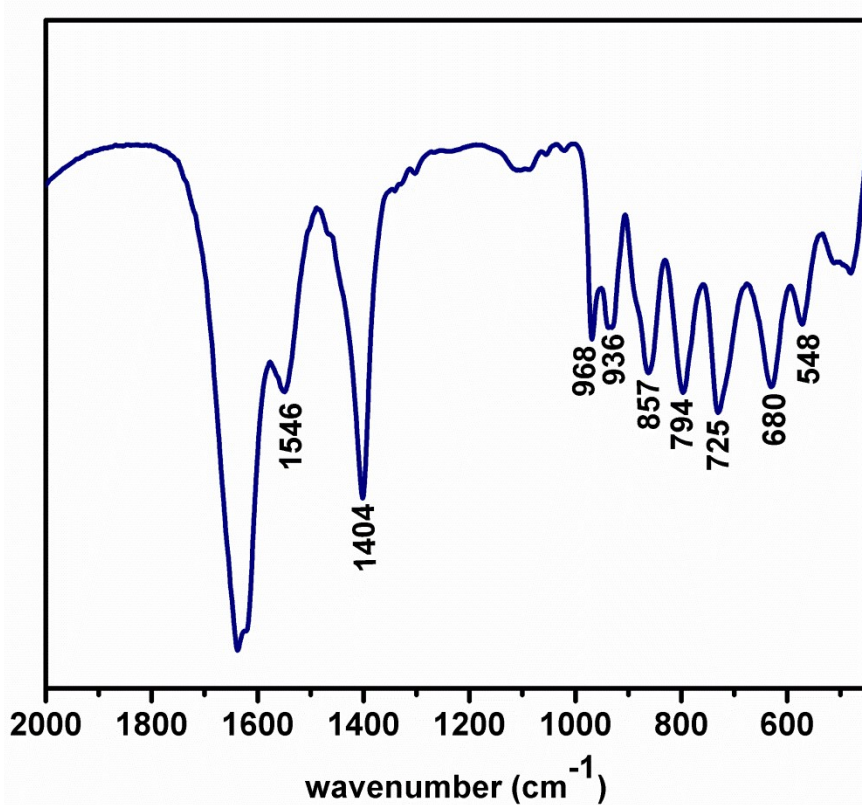


Fig. S6 FT-IR spectra for {Mo<sub>132</sub>}

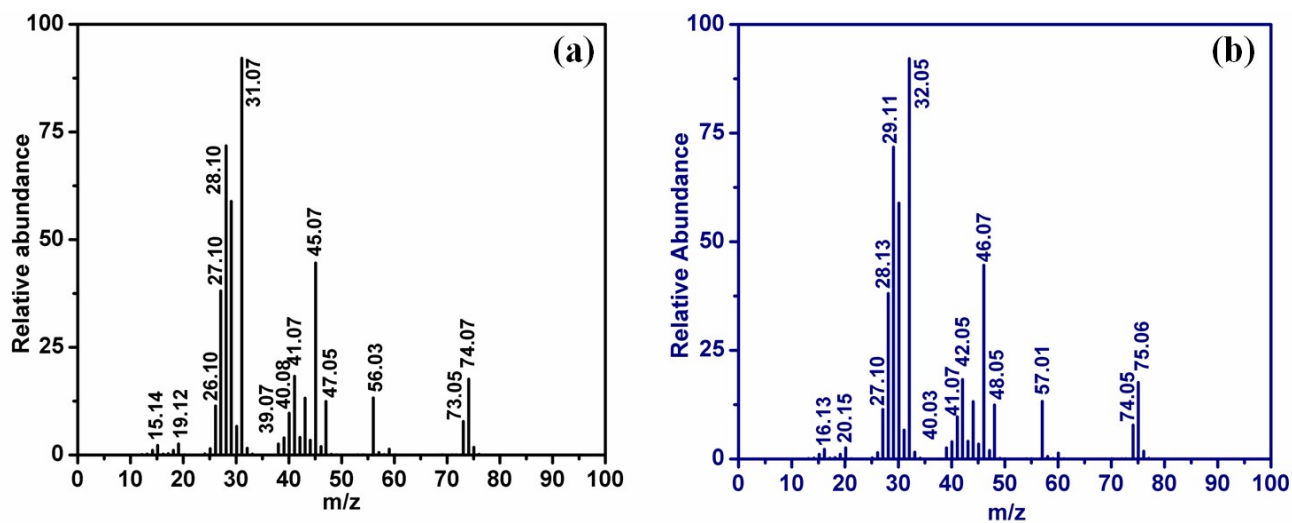


Fig.5 S7 Gas chromatogram analysis of formic acid formed from (a)  $^{12}\text{CO}_2$  and (b)  $^{13}\text{CO}_2$

#### TON & TOF for Formic acid

Turn over Number (TON) = Moles of product/ Moles of catalyst  $\{\text{Mo}_{132}\} = 0.12/0.4 \times 10^{-3} = 300$

Turn over Frequency (TOF) = TON/ Total time taken for the catalytic reaction =  $300/24 \text{ h} = 12.5 \text{ h}^{-1}$ .

#### TON & TOF for Acetophenone

Turn over Number (TON) = Moles of product/ Moles of catalyst  $\{\text{Mo}_{132}\} = 0.79/0.4 \times 10^{-3} = 1975$

Turn over Frequency (TOF) = TON/ Total time taken for the catalytic reaction =  $1975/24 \text{ h} = 82.29 \text{ h}^{-1}$ .