Supporting Information

PEG radical-initiated oxidation of benzylic alcohols in compressed carbon dioxide

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Supporting information

1. General information

The alcohols were purchased from J&KCHEMICA. Carbon dioxide with a purity of 99.99% was commercially available. The other organic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

NMR spectra were recorded on a Bruker 300 or Varian 400 spectrometer in $CDCl_3$. ^1H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to TMS. ^1H and ^{13}C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC-MS were measured on a Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m×0.25 μm) using a flame ionization detector. Column chromatography was performed by using silica gel 200-300 mesh with ethyl acetate/petroleum as eluent. The EPR experiments were performed on a Bruker EMX-6 with the following condition: microwave frequency 9.86 GHz, microwave power: 20.0 mW, center field 3520 G, magnetic field range 3520 G, modulation amplitude 2.00 G, time constant 10.24 ms, and receiver gain 2.00e+005.

2. Supporting figures

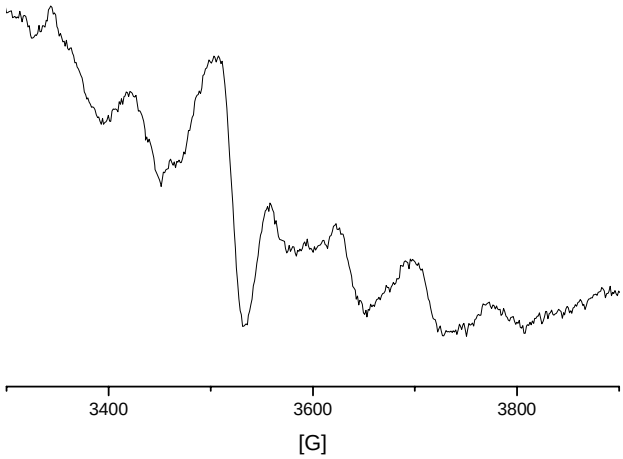


Fig. S1. EPR spectrum chart for oxygenation mixture of benzyl alcohol induced by PEG oxidative degradation in PEG/O_2/CO_2 system. Reaction conditions: benzyl alcohol (5.7 mmol); PEG (2.1 mmol); O_2 1atm; temperature 100 ^oC; time 4 h.

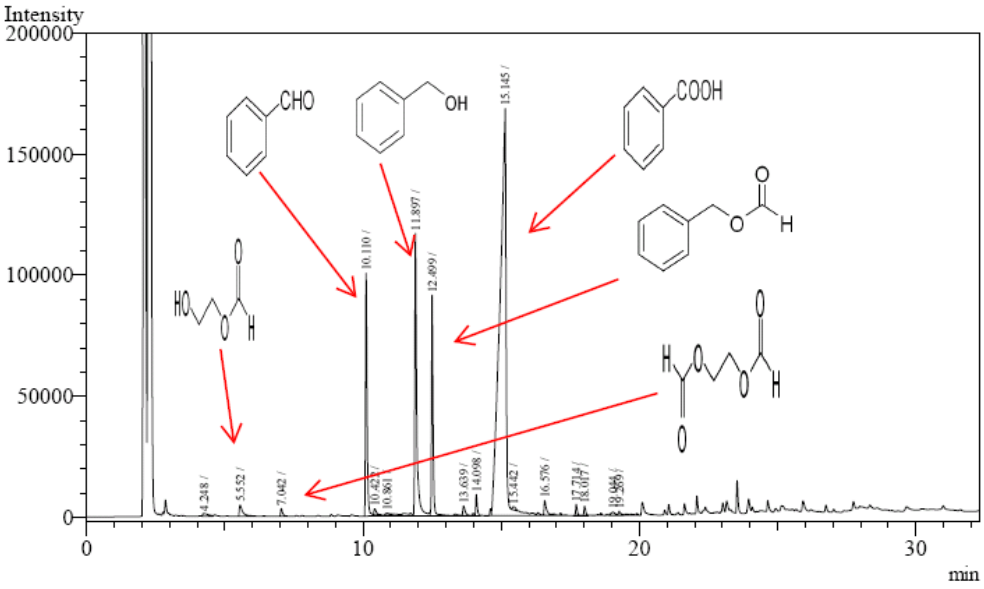
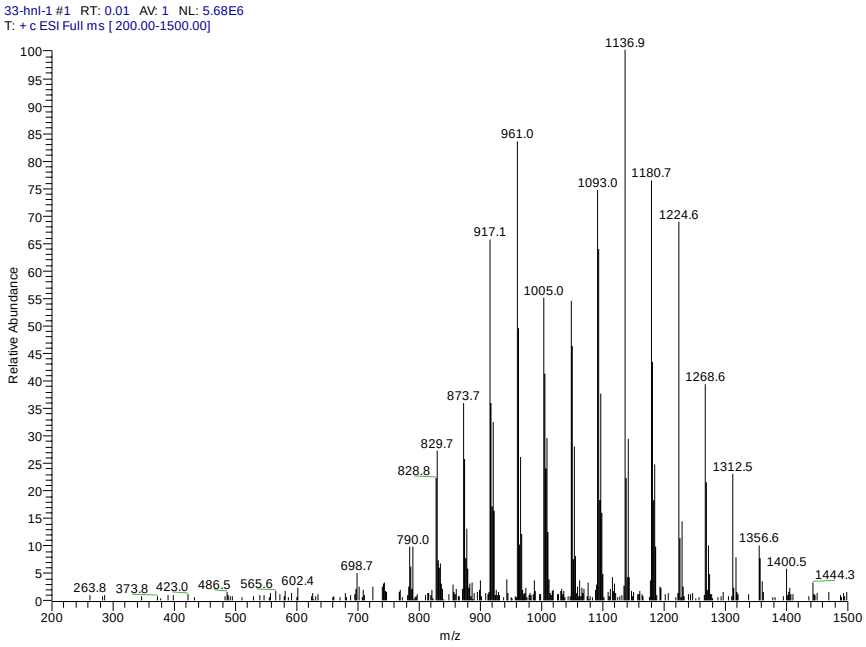
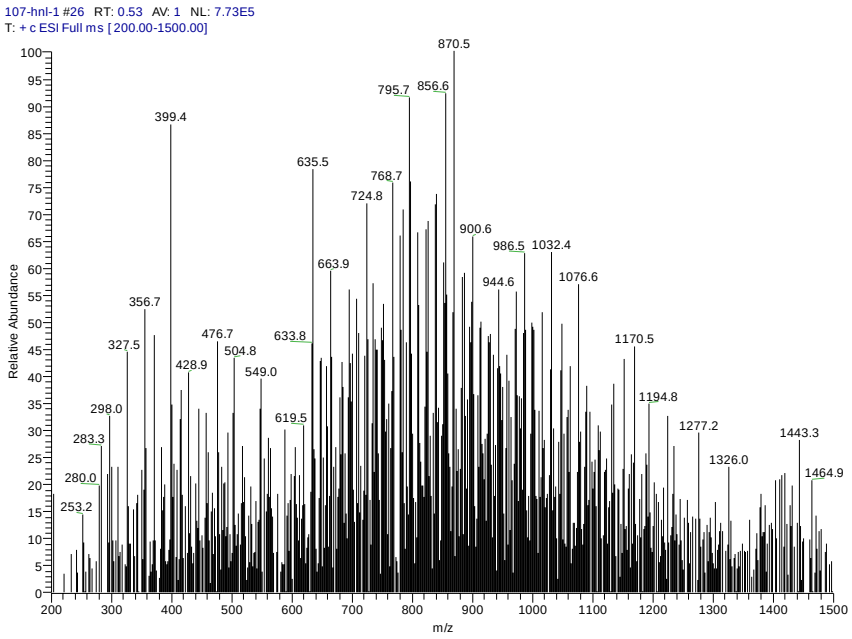


Fig. S2. GC Charts for oxygenation mixture of ethyl benzene induced by PEG oxidative degradation in PEG/O_2/CO_2 system. Reaction conditions: benzyl alcohol (0.2 g, 1.93 mmol); PEG (0.7 g, 0.7 mmol); O_2 2.5 MPa; total pressure (pO_2+pCO_2) 16 MPa; temperature 100 ^oC; time 12 h.



(a)

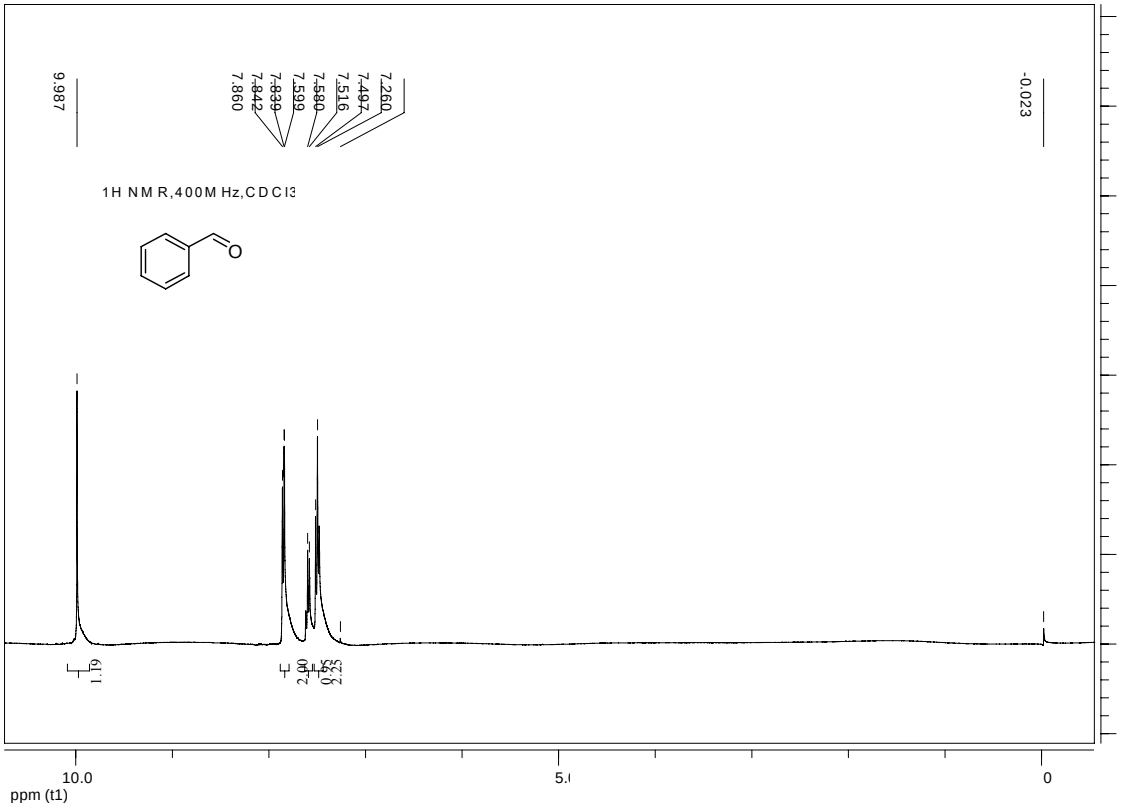


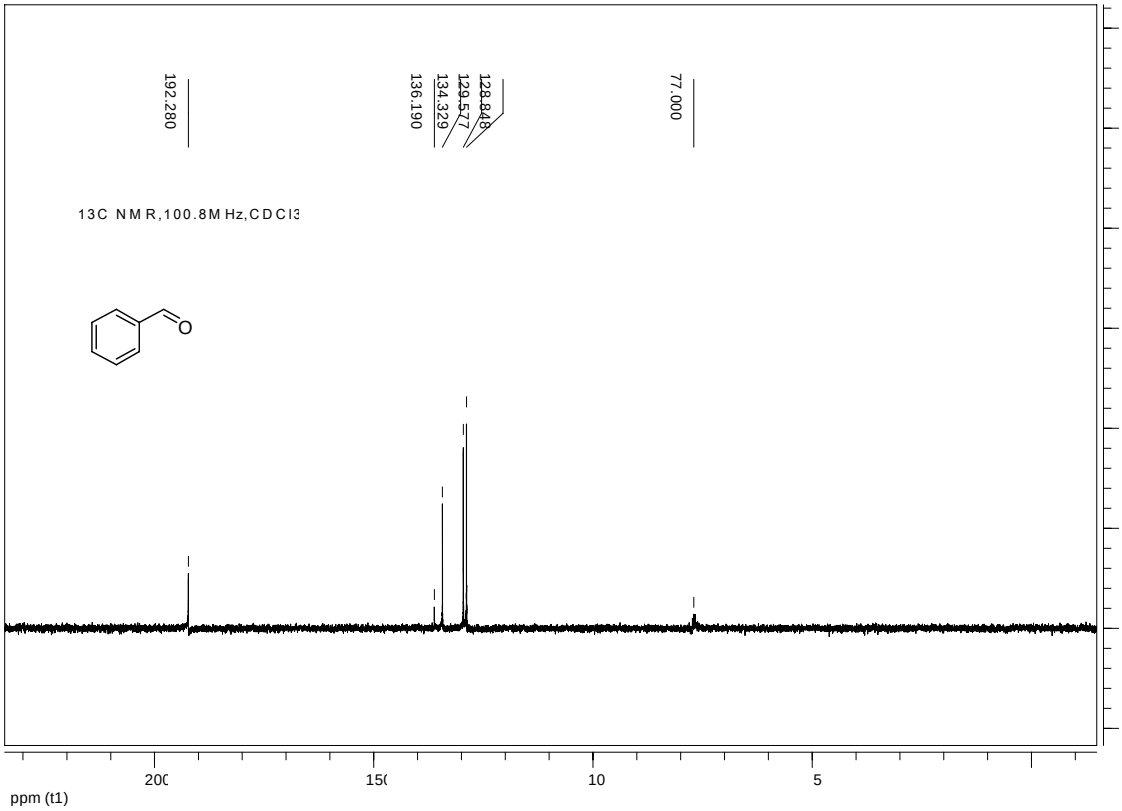
(b)

Fig. S3 The ESI-MS in the positive mode for fresh PEG-1000 (a) and spent PEG-1000 (b) after the reaction induced by PEG oxidative degradation in PEG/O_2/CO_2 system. Reaction conditions: benzyl alcohol (0.2 g, 1.93 mmol); PEG (0.7 g, 0.7 mmol); O_2 2.5 MPa; total pressure (pO_2+pCO_2) 16 MPa; temperature 100 ^oC; time 12 h.

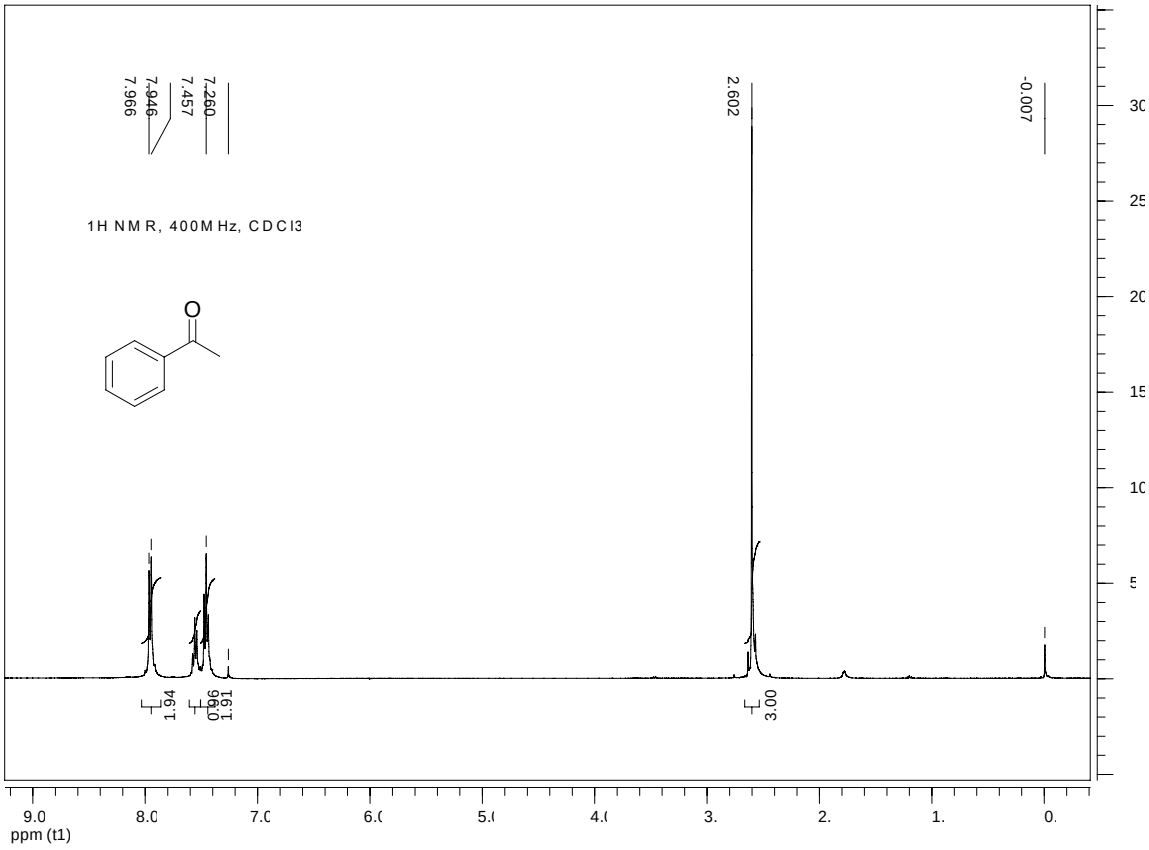
3. Supporting NMR charts

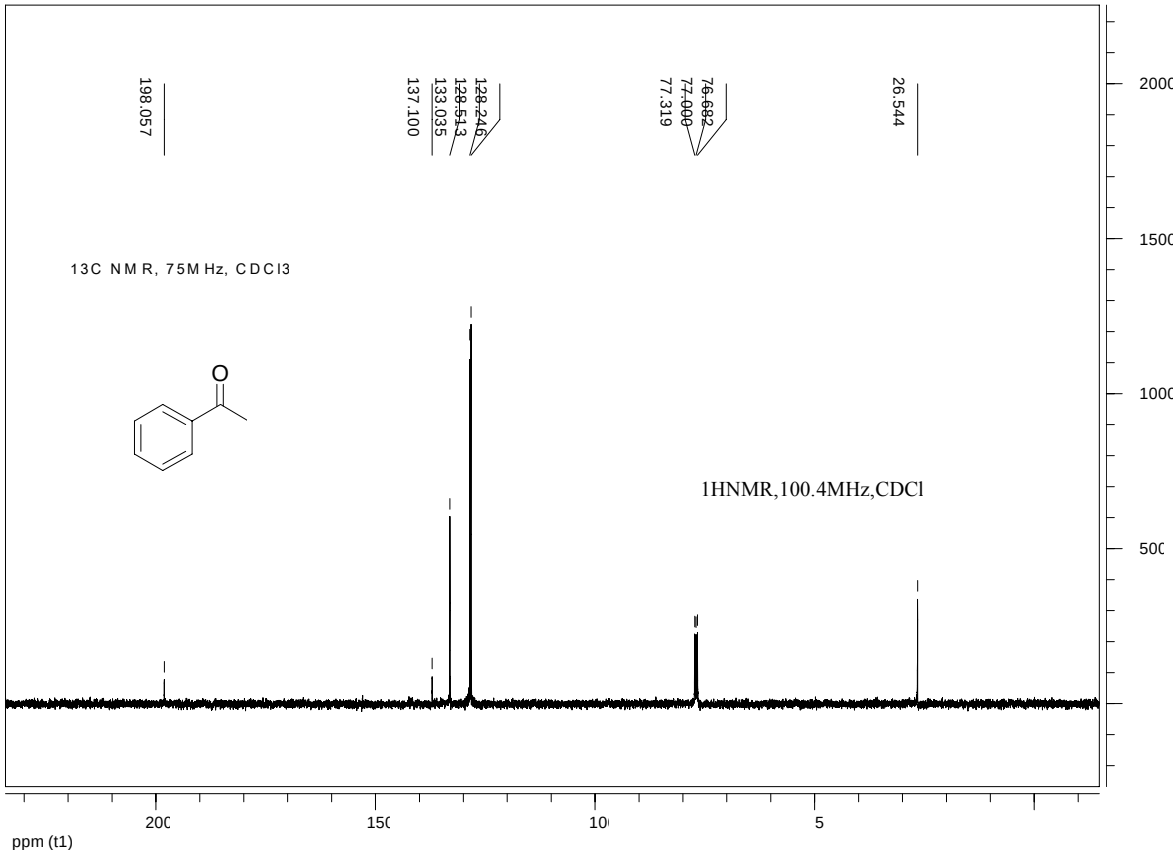
Benzaldehyde



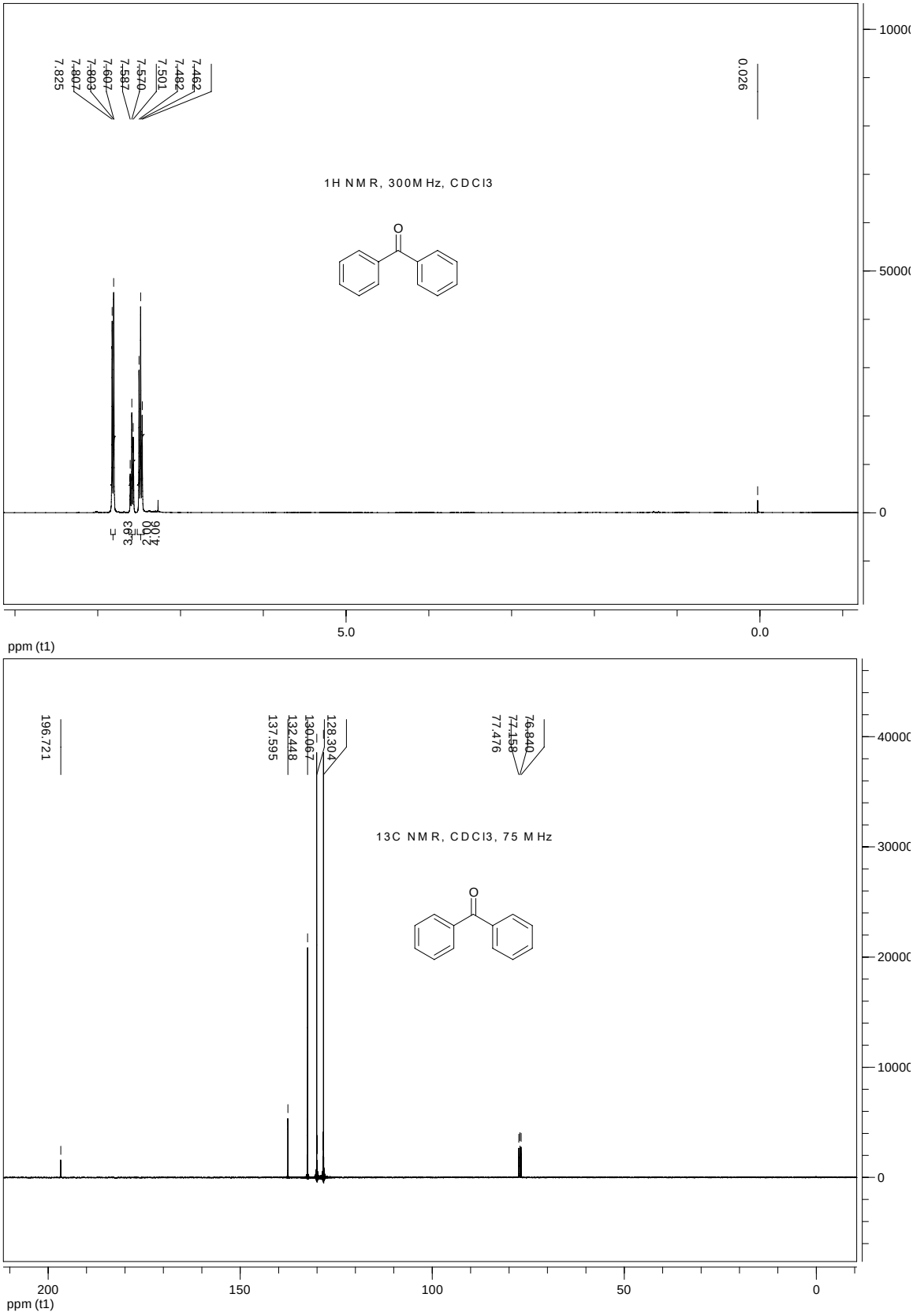


Acetophenone

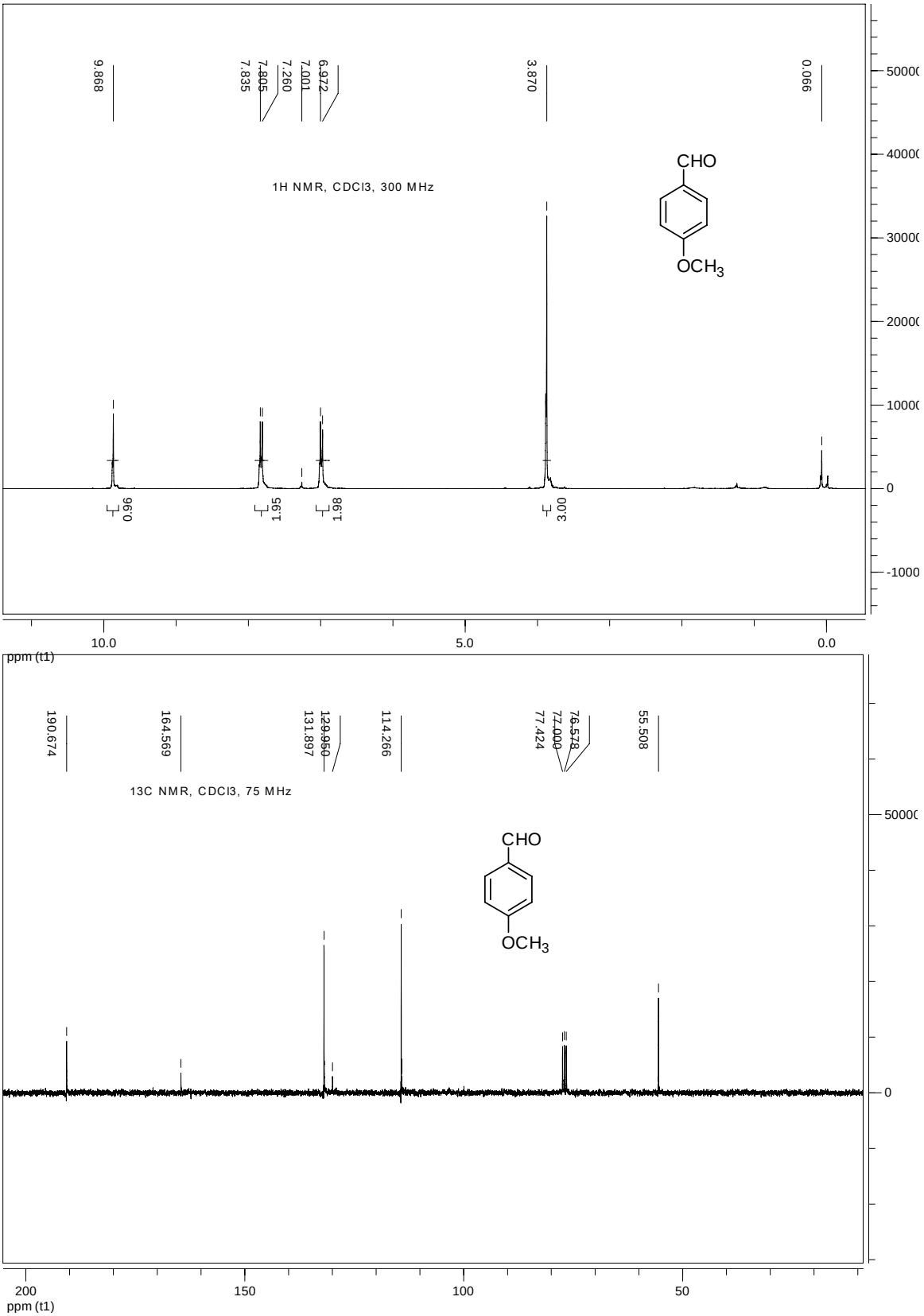




Diphenyl-methanone



4-Methoxy-benzaldehyde



Formic acid phenethyl ester