Supplementary Material (ESI) for New Journal of Chemistry

Supplementary information

Polyethylene glycol radical-initiated benzylic C-H bond oxygenation in compressed carbon dioxide

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General information

The benzylic substrates were purchased from J&KCHEMICA. Carbon dioxide with a purity of 99.99% was commercially available. The other organic and inorganic 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 ($CDCl_3$: δC = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δH = 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.

Supporting Figures

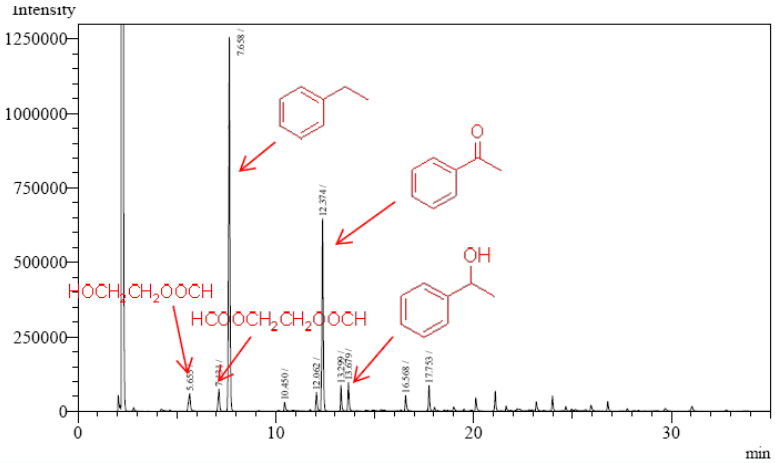


Figure S1. GC Charts for oxygenation mixture of ethyl benzene induced by PEG oxidative degradation in PEG/O_2/CO_2 system. Reaction conditions: ethyl benzene (0.2 g 1.93 mmol); PEG (0.7 g, 0.7 mmol); $Co(OAc)_2$ (10 mg, 2 mol%); O_2 2.5 MPa; total pressure (pO_2+pCO_2) 16 MPa; temperature 100 ^oC; time 12 h.

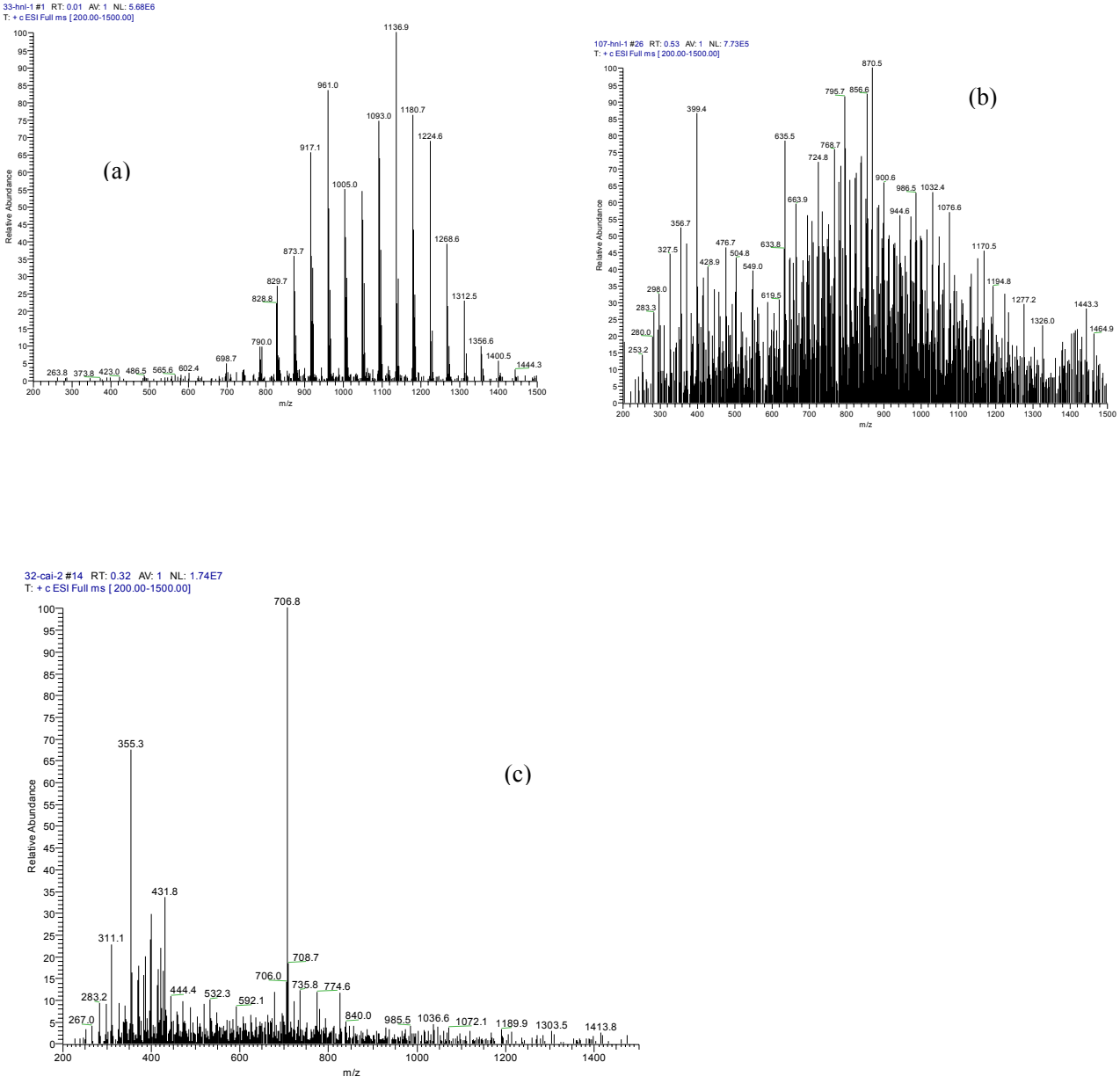


Figure S2. The ESI-MS in the positive mode for (a) fresh PEG-1000, (b) spent PEG-1000 after the reaction without $Co(OAc)_2$, (c) used PEG-1000 after the reaction with $Co(OAc)_2$ in PEG/O_2/CO_2 system. Reaction conditions: ethyl benzene (0.2 g, 1.93 mmol); PEG (0.7 g, 0.7 mmol); $Co(OAc)_2$ (10 mg, 2 mol%); O_2 2.5 MPa; total pressure (pO_2+pCO_2) 16 MPa; temperature 100 ^oC; time 12 h.

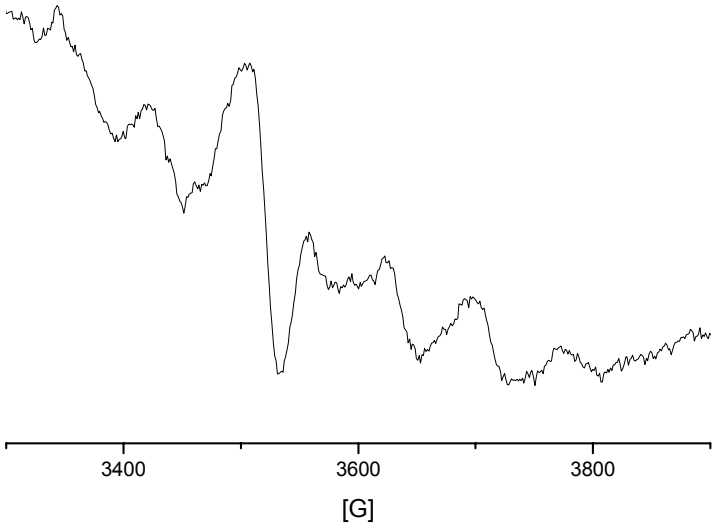
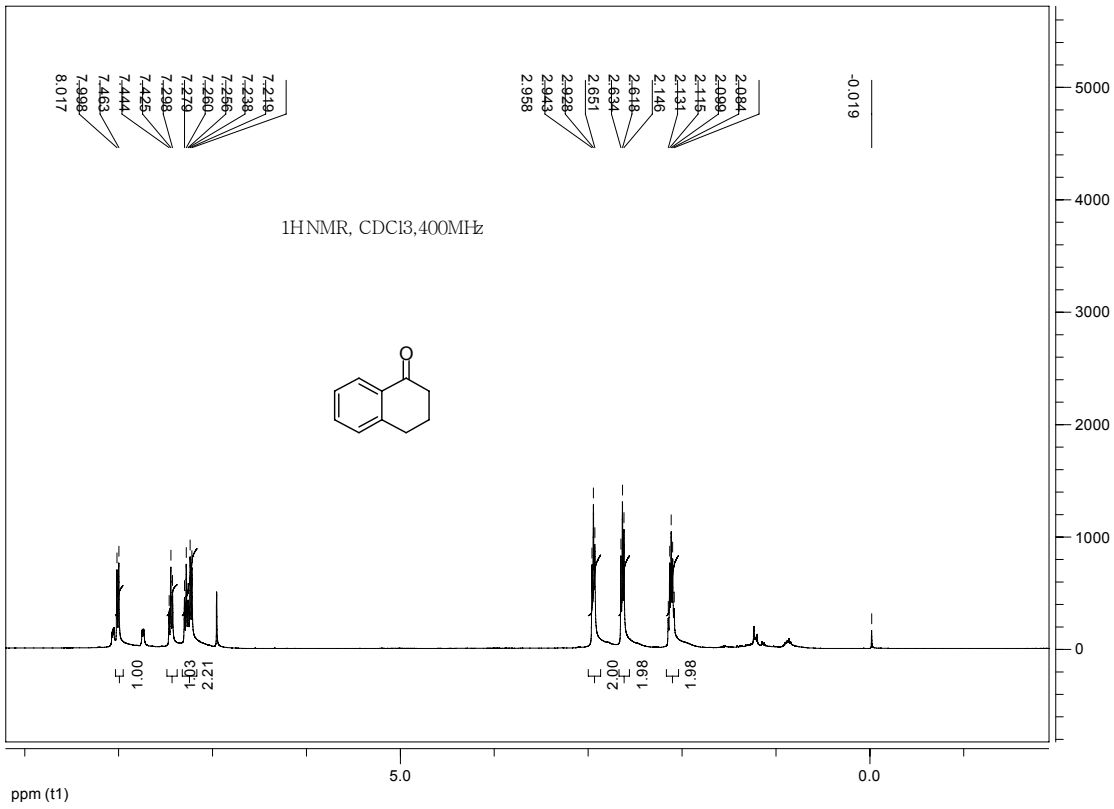
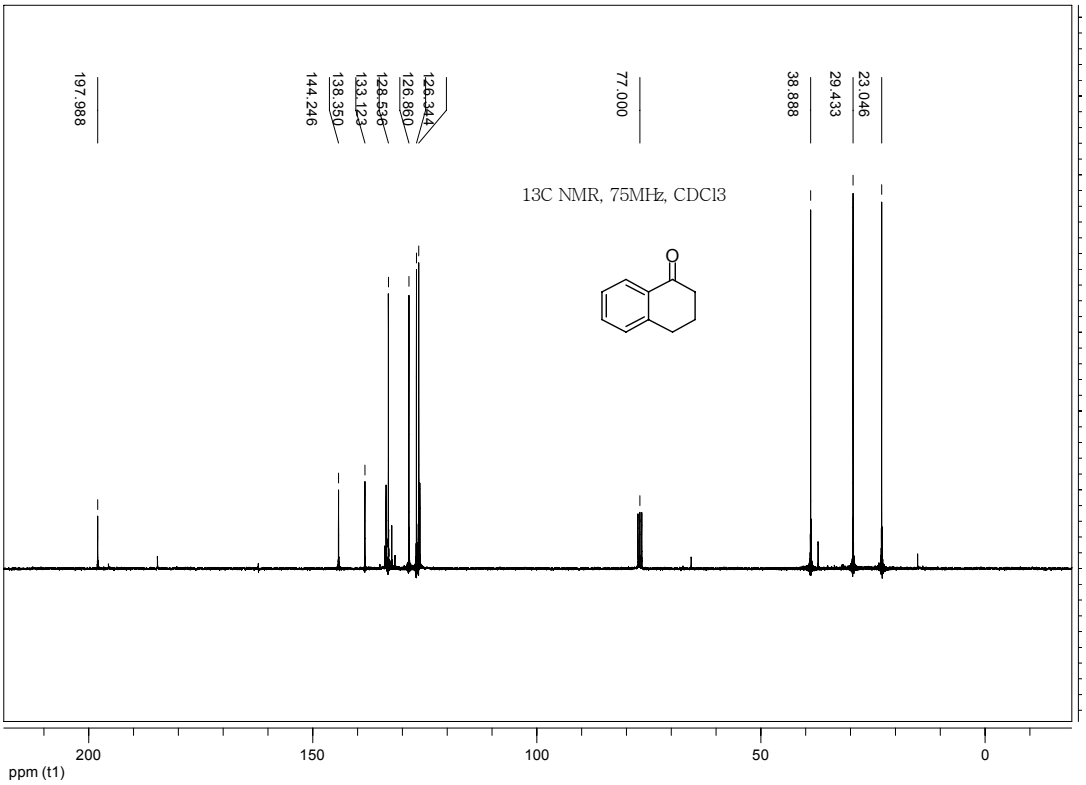


Figure S3. EPR spectrum chart for oxygenation mixture of ethyl benzyl induced by PEG oxidative degradation in PEG/O_2/CO_2 system. Reaction conditions: ethyl benzyl (5.7 mmol); PEG-300 (2.1 mmol); O_2 1 atm; temperature 120 ^{o}C; time 4 h.

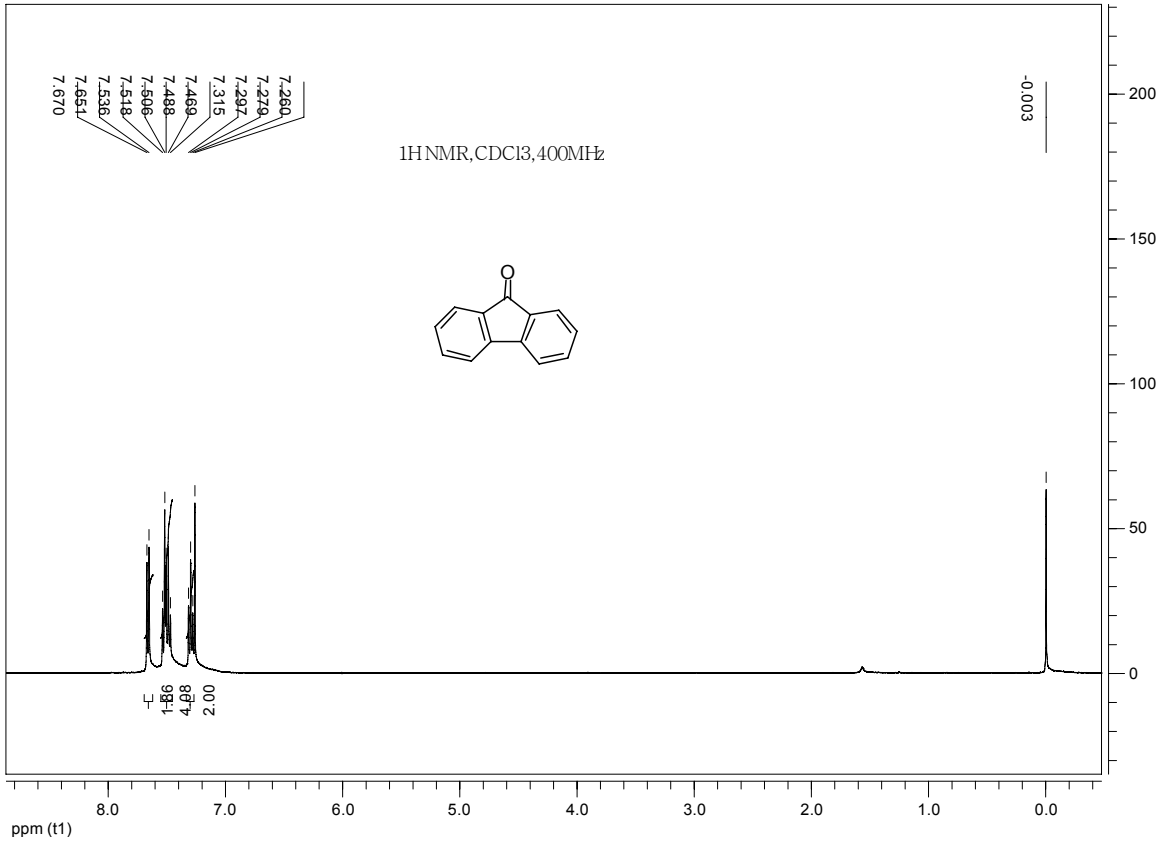
^{1}H NMR and ^{13}C NMR charts for products

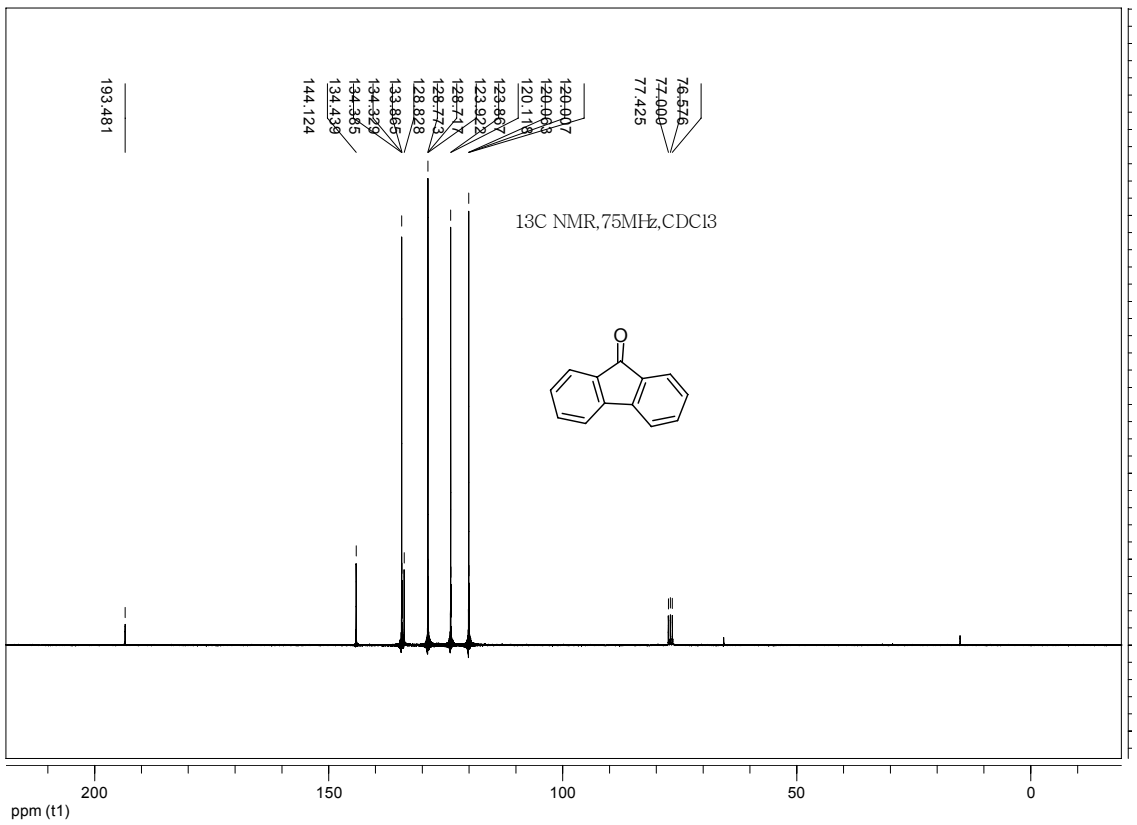
3.4-Dihydro-2H-naphthalen-1-one



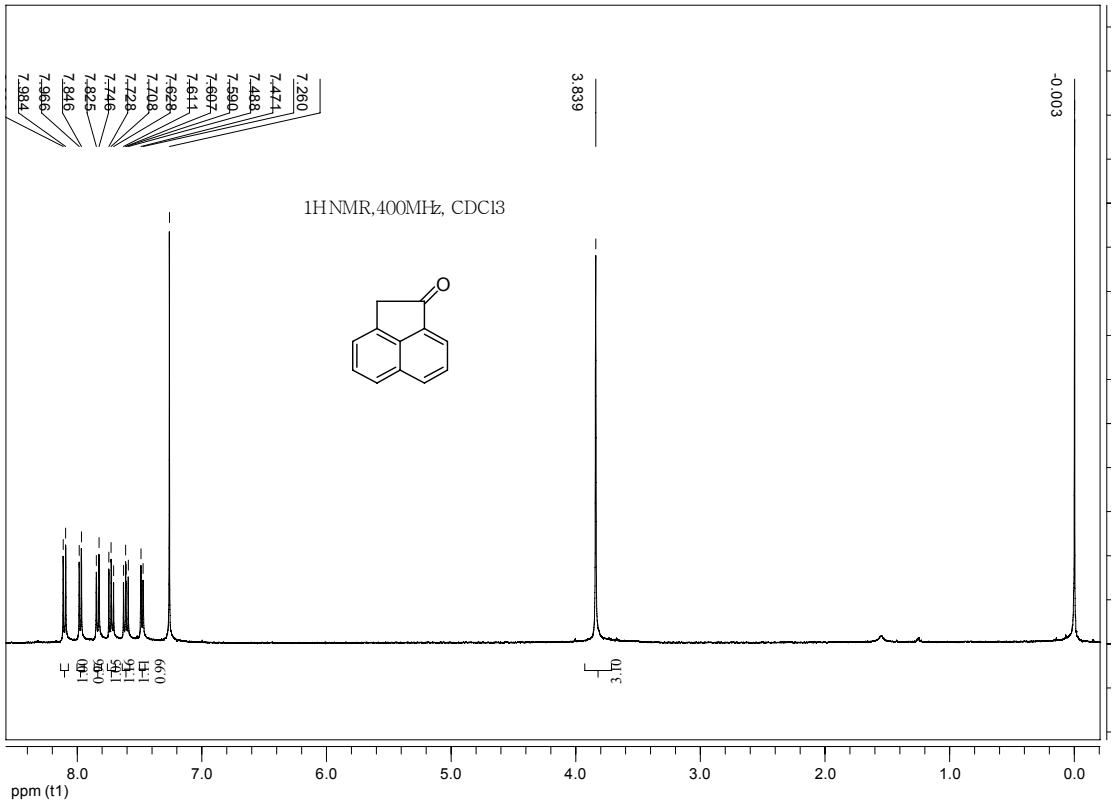


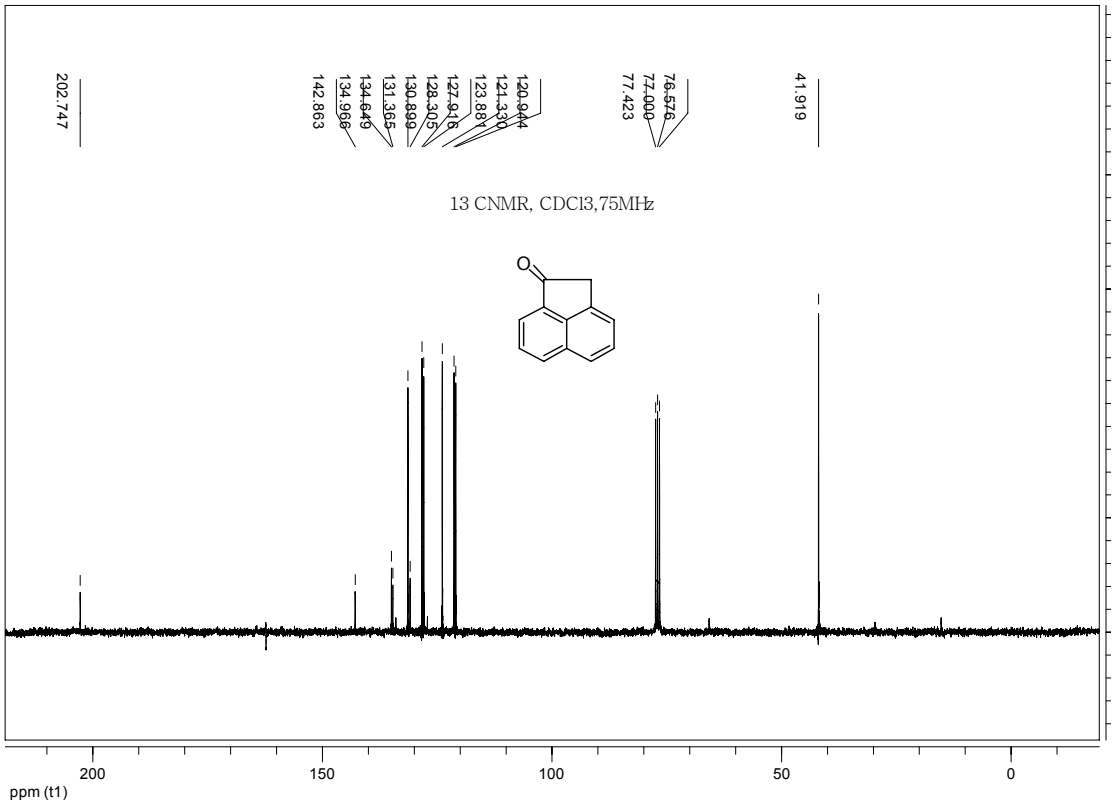
Fluorene-9-one



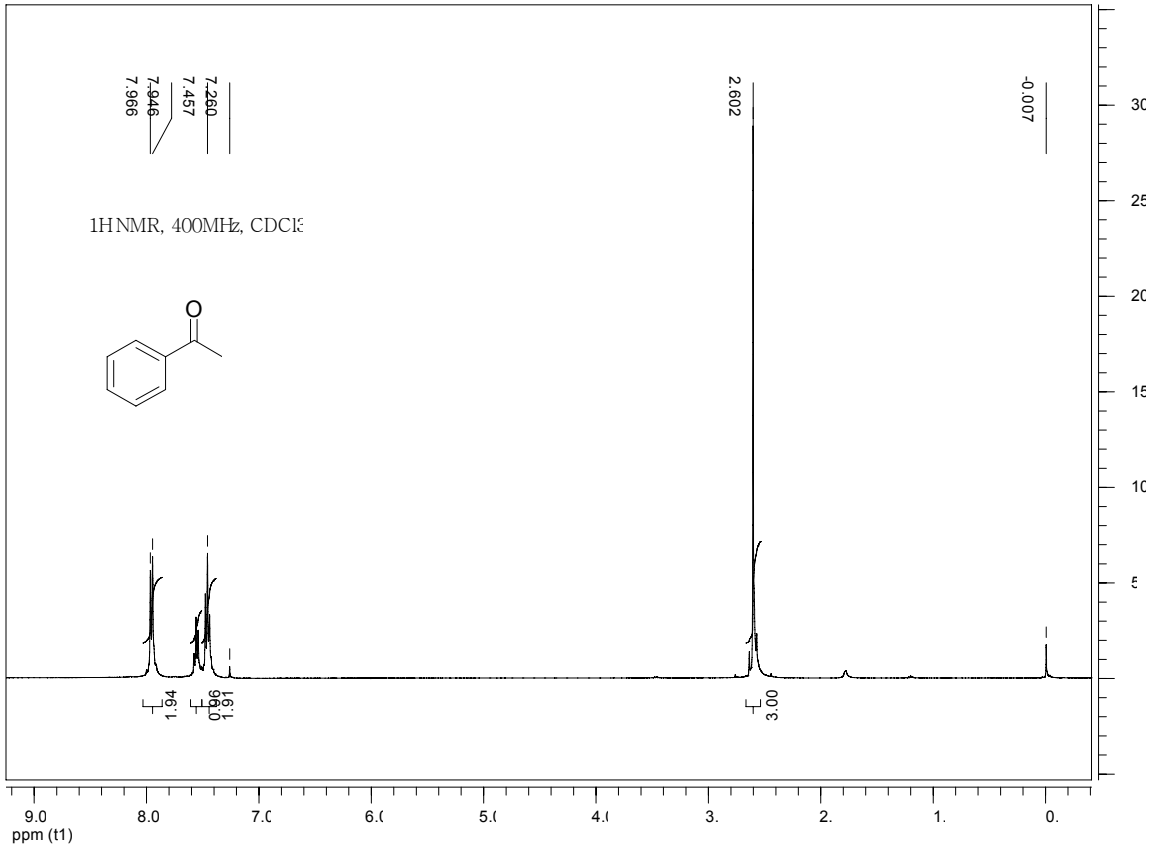


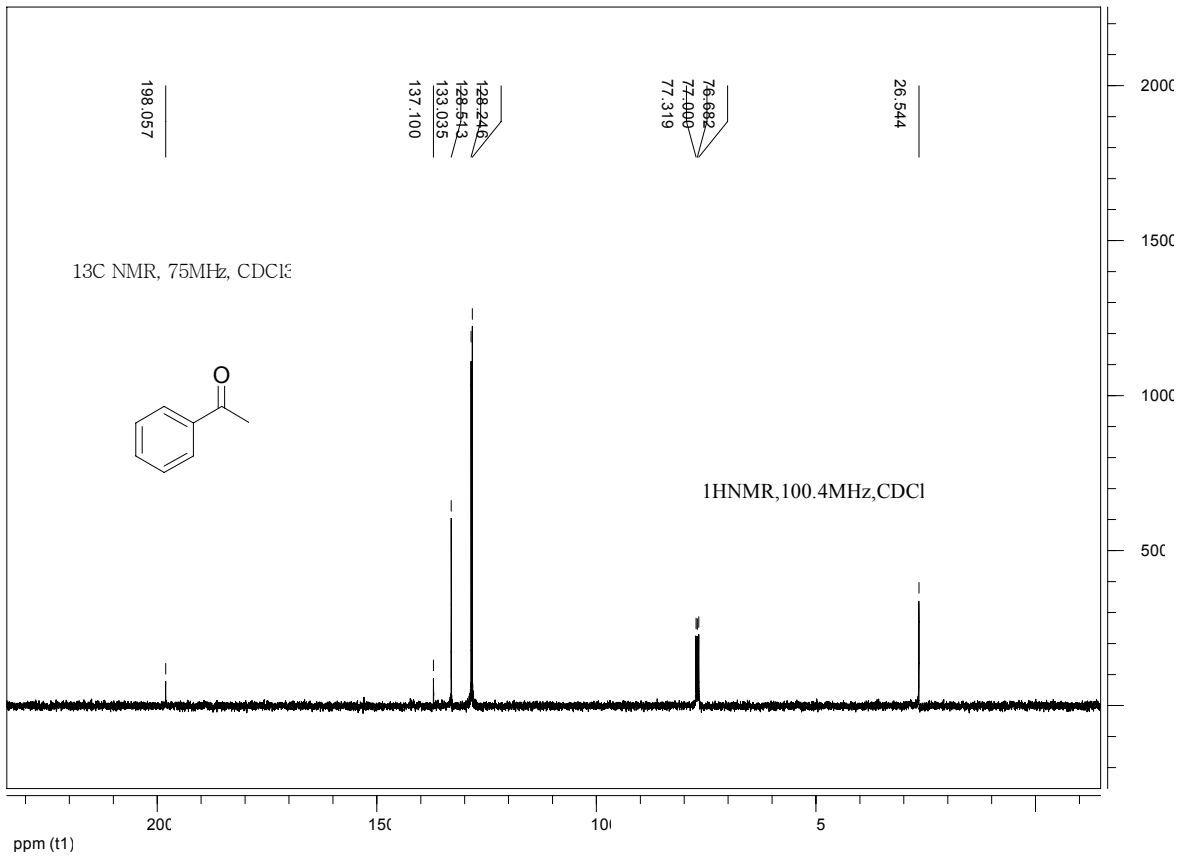
2H-acenaphthylen-1-one





Acetophenone





Benzaldehyde