

Efficient Photocatalytic Chlorides Dehalogenation by Planar Conjugated Microporous Polymers with Enhanced Charge Separation and Transport

Hao Zhang,^a Sizhe Li,^a Zhuangfei Qian,^a Jie Yin,^a Wenxin Wei,^{a*} Yan Zhao,^{a, b*} and
Kai A I Zhang^{a†}

^a. Department of Materials Science, Fudan University, Shanghai 200438, PR China.

^b. State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

* Corresponding author.

E-mail addresses: weiwenxin@fudan.edu.cn, zhaoy@fudan.edu.cn.

1. Experiment section

1.1 Materials

All chemicals and solvents were purchased from commercial sources and directly used as received unless noted. The reactions yield was monitored by GC–MS. Column flash chromatography was conducted with silica gel (200–300 mesh).

1.2 Methods

Fourier-transform infrared (FT-IR) spectroscopy. FT-IR spectra were recorded on a VARIAN 1000 FT-IR spectrometer in the region of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} . The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), and strong (s).

Solid-state ^{13}C cross-polarization magic-angle-spinning (^{13}C CP-MAS) NMR. ^{13}C CP-MAS NMR experiments were conducted on a Bruker ADVANCE III 500M spectrometer at ^{13}C resonance frequency of 500 MHz at ambient pressure using a standard cross-polarization total sideband suppression (CP-TOSS) pulse sequence probe with 4 mm (outside diameter) zirconia rotors. The ^{13}C ninety-degree pulse widths were 4 μs . The decoupling frequency corresponded to 72 kHz. The TOSS sample-spinning rate was 5 kHz.

Solution NMR. ^1H and ^{13}C NMR spectra were recorded on a Bruker (Rheinstetten, Germany) Avance 500 instrument at room temperature in chloroform-d (CDCl_3 , $\delta = 7.26$). The chemical shifts (δ) were reported in ppm referenced to tetramethylsilane

(TMS). Coupling constant values (J) were given in hertz (Hz), the multiplicity was abbreviated in the following way: s (singlet), d (doublet), triplet (t), and m (multiplet).

Ultraviolet-visible (UV-vis) absorption. Solid-state UV-vis absorption spectra were collected at room temperature on a Shimadzu UV-vis NIR diffuse reflectance spectrophotometer (referenced to barium sulfate as the optical standard) at a photometric range of 300–800 nm. Band gap values were calculated from the reflectance data using the Kubelka–Munk equation.

Field Emission scanning electron microscopy (FE-SEM). SEM SE (secondary electron) detector images were obtained on either a Zeiss Merlin or a VEGA TS 5130MM (TESCAN) with a SEMEDX using a Si/Li detector (10 kV acceleration voltage, Oxford). Samples were prepared by dispersing on mica substrate. The sample was then carbon coated using a Leica EM SCD 500 Sputter at 10–4 mbar of pressure in an argon atmosphere for 45 s while maintaining 15 mA of current. Sample was analyzed on a scanning electron microscope with accelerating voltages ranging from 1 to 15 kV. All the SEM images were taken from the same sample.

High-resolution Transmission electron microscopy (HRTEM). HRTEM was performed with a Philips CM30 ST (300kV, LaB6 cathode) at an accelerating voltage of 200 kV. To record the HRTEM images, dilute CMPs suspensions in ethanol were sonicated for 5 min, followed by drop-casting the sample on carbon-coated copper TEM grids (TED PELLA, INC. 200 line/inch Hexagonal mesh).

Nitrogen sorption isotherm, pore size, and surface area measurements. Low-pressure N₂ adsorption measurements were performed on the Micromeritics ASAP2460 volumetric analyzer. Before measurement, the samples were degassed in vacuum at 100 °C for 12 h. The amount of inert gas adsorbed to the surface of the sample was measured at varying relative pressures by this technique. As relative pressure increased to near saturation pressure (adsorption), accessible pores of increasing size filled with condensed gas. Once the pressure was reduced incrementally (desorption), the condensed gas evaporates from the pores. From the resulting isotherm, the Barrett-Joyner-Halenda (BJH) theory was used to determine the cylindrical equivalent pore volumes and pore areas from the amount of gas absorbed and desorbed. The surface area can also be determined using the Bruner-Emmet-Teller (BET) theory. The surface area calculated based on the BET model was normalized by the sample mass.

Thermogravimetric analysis (TGA). TGA of CMPs were run on a TA Instruments 5500 Thermogravimetric Analyzer (New Castle, DE 19720, USA) with samples held in platinum pans under an atmosphere of nitrogen. A 10 °C min⁻¹ ramp rate was used.

Electrochemical measurements: For cyclic voltammetry experiments, the CHI-610E electrochemical workstation from CH Instruments (USA) was employed to record electrochemical experiments. To conduct electrochemical measurements, a three-electrode system was used. The working electrode was made of indium tin oxide (ITO) glass plate coated with catalyst slurry with a diameter of 3 mm, the counter electrode was made of platinum wire, and the reference electrode was Hg/HgCl₂. To prepare

working electrode, the ITO glasses were first cleaned by being sonicated in acetone for 30 minutes and then dried under nitrogen flow. A slurry was then created by mixing 5 mg of CMP powder with 1 mL of ethanol and 10 μ L 10 wt.% Nafion perfluorinated resin powder, which was ultra-sonicated for 30 minutes. Next, 200 μ L of the slurry was spread onto the ITO glass ($1 \times 2 \text{ cm}^2$), and the uncoated area of the electrode was isolated using epoxy resin, forming a film that was allowed to dry under ambient temperature and pressure for 12 h. A 0.2 M aqueous solution of Na_2SO_4 (pH 6.8) was utilized as the electrolyte, which was purged with argon gas for 1 h before the measurements. The working electrode was then allowed to immerse in the electrolyte for a period of 60 seconds before any measurement was conducted. The x -intercepts of the linear fits in the voltammograms were used to extract the reduction onset potentials.

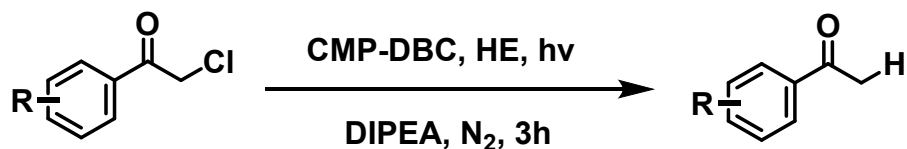
To test the influence of the polymer thin film thickness on the photocurrent, we took the photocurrent test as follows: The polymer (4.0 mg) was dispersed in ethanol (0.5 mL) containing 1 % nafion by ultrasound for 1 hour. Since the polymer cannot be dissolved in the ethanol solution, it is difficult to prepare uniform thickness films. To qualitatively illustrate the effect of polymer film thickness on photocurrent, the work electrodes with different thickness films were prepared by adding different drops of the above mixture solution on the same area of FTO substrate, and then being filmed at 80 $^\circ\text{C}$ in vacuum oven. The Pt plate served as the counter electrode, and a saturated Ag/AgCl electrode as a reference electrode. A 0.5 M Na_2SO_4 solution was used as the electrolyte. A 300 W Xenon lamp equipped with a 420 nm cut-off filter (100 mW cm^{-1}) was used as the light source in the photocurrent response measurement.

1.3 Preparation of CMP-DBC and CMP-TPE

In a typical procedure, 4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (338 mg, 1 mmol), 2,7,10,15-tetrabromodibenzo[*g,p*]chrysene (322 mg, 0.50 mmol), Pd(PhCN)₂Cl₂ (19.2 mg, 0.025 mmol), and K₂CO₃ (1.37 g, 10 mmol) were dissolved in anhydrous DMF (15 mL). After evacuating, nitrogen was introduced and repeated 3 times. The mixture was stirred at 150 °C for 3 days. The resulting precipitate was filtered and washed with deionized water to remove the inorganic salt, which was further purified by Soxhlet extraction with methanol and THF, separately. Finally, after being dried at 80 °C under vacuum, a red powder was obtained and denoted as CMP-DBC in 75% yield.

CMP-TPE was obtained according to the same procedures by performing 1,1,2,2-tetrakis(4-bromophenyl)ethene as the starting monomer instead of 2,7,10,15-tetrabromodibenzo[*g,p*]chrysene. The desired product was obtained as a yellow solid in 78% yield.

1.4 General Procedure of the Photocatalytic Reactions Using CMPs



In a 10 ml vial was charged with 2-chloro-1-phenylethan-1-one derivatives (0.2 mmol), Hantzsch ester (HE) (55.7 mg, 0.22 mmol), DIPEA (51.7 mg, 0.4 mmol) CMPs (5 mg), and CH₃CN (2 mL). Then, the vial was placed under N₂ condition in front of a blue LED lamp (460 nm, 1.2 W/cm²). The yields were determined by GC-MS. After completion of the reaction, the solvent was removed under reduced pressure. Then,

water (20 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL).

The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via silica gel column chromatography (petroleum ether/ethyl acetate ratios of 10:1 to 5:1) to generate the

corresponding

final

product

2. Supplementary Figures

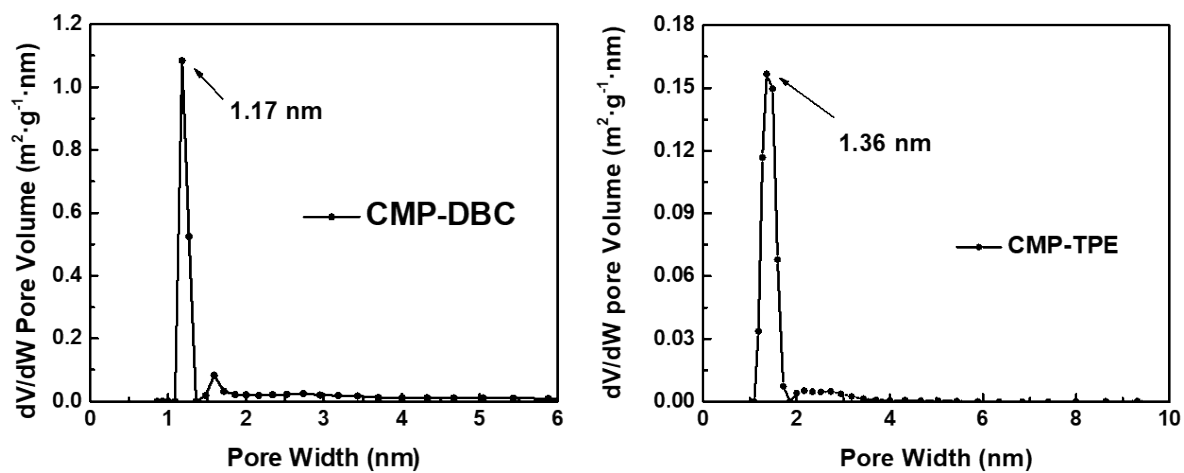


Fig. S1 Pore size distributions of CMP-DBC and CMP-TPE.

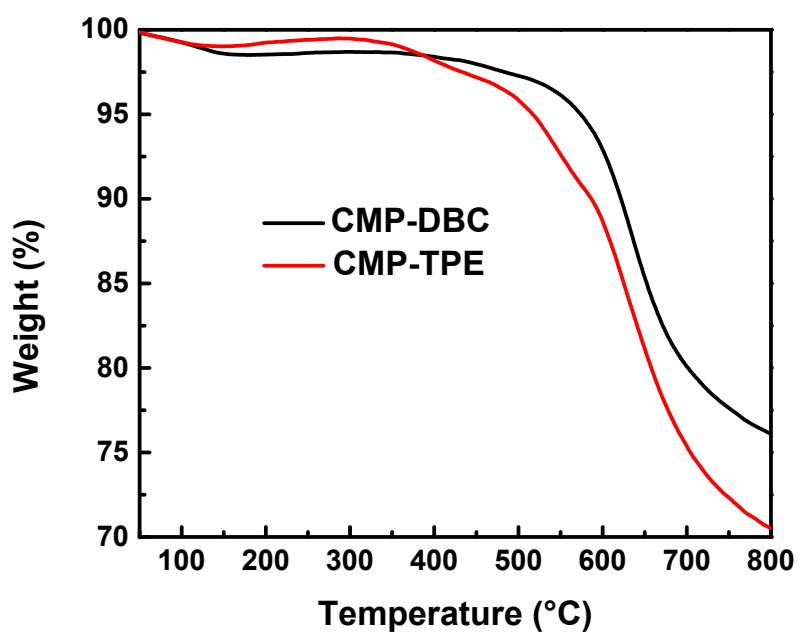


Fig. S2 Thermogravimetric analysis tests of the CMPs.

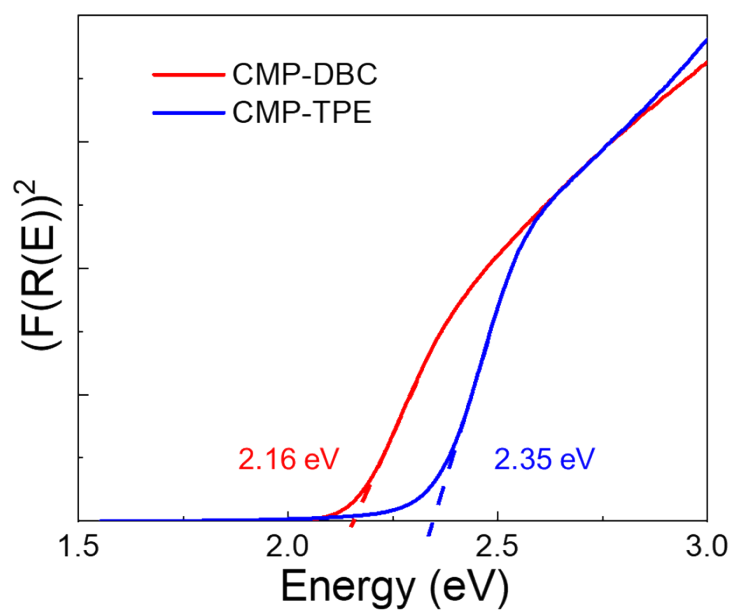


Fig. S3 Optical bandgap calculated by Kubelka-Munk function for CMP-DBC and CMP-TPE.

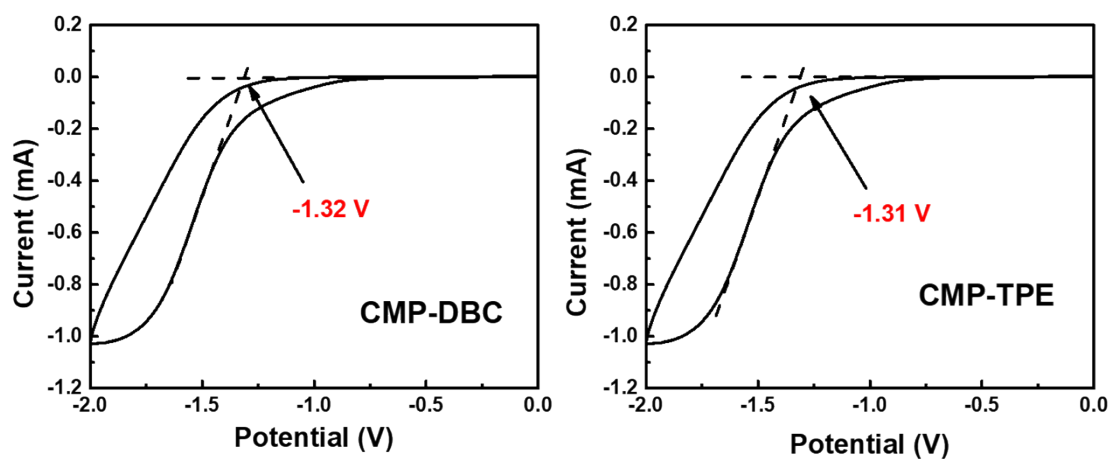


Fig. S4 Cyclic voltammetry measurement for CMP-DBC and CMP-TPE.

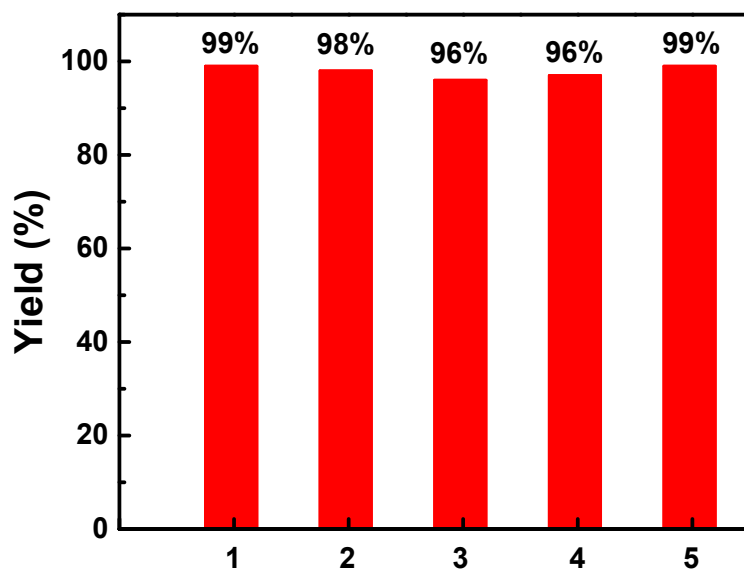


Fig. S5 Recyclability tests of CMP-DBC in photocatalytic Chlorides Dehalogenation.

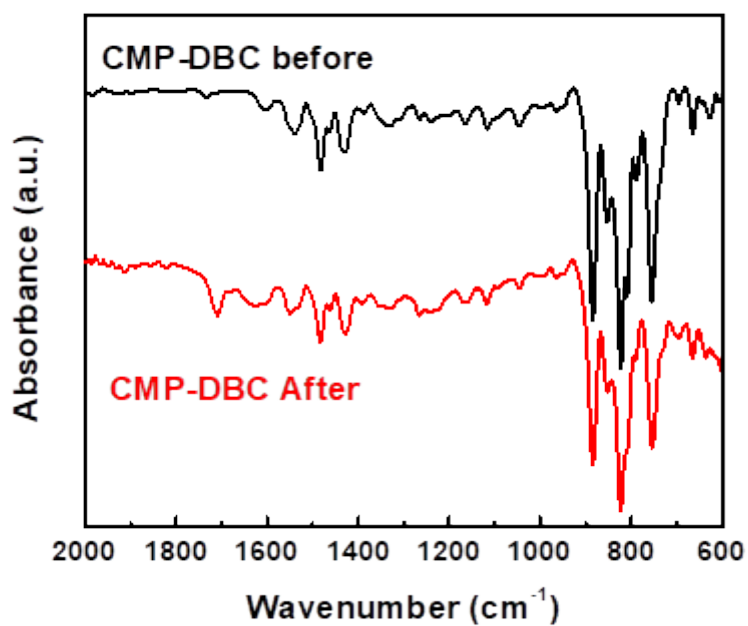


Fig. S6 The FT-IR spectra of CMP-DBC before and after five photocatalytic reaction.

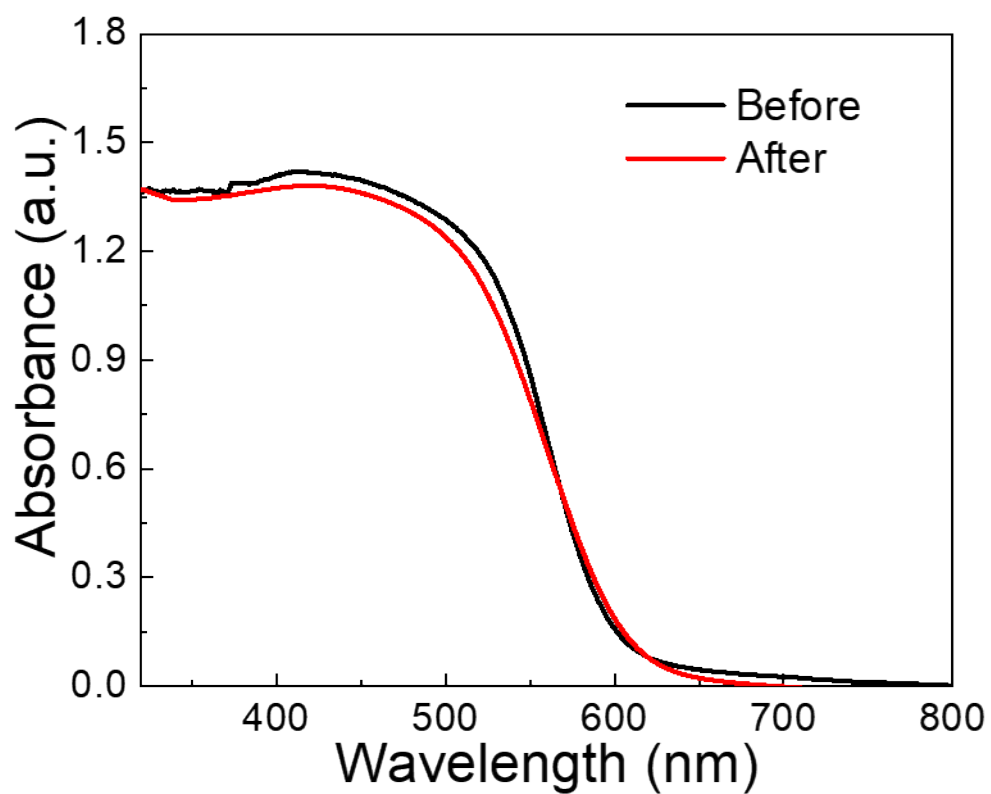


Fig. S7 The UV-vis spectra of CMP-DBC before and after five photocatalytic reactions.

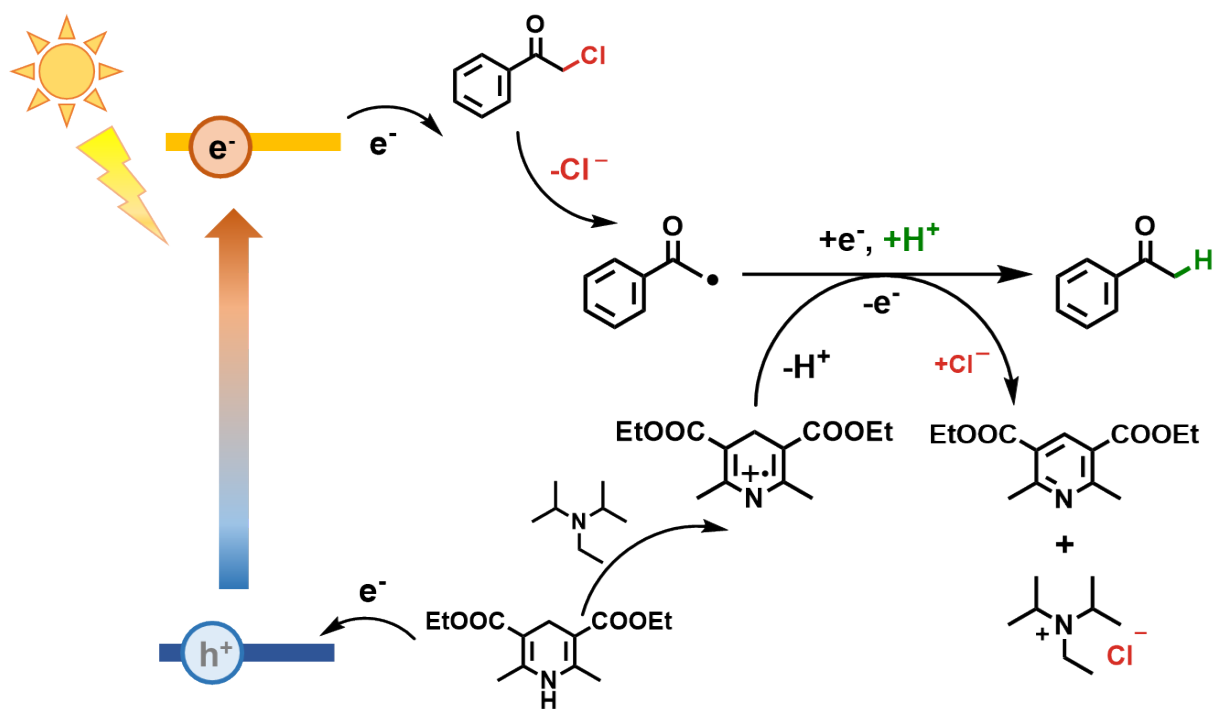


Fig. S8 Proposed reaction mechanisms for the photocatalytic chlorides dehalogenation.

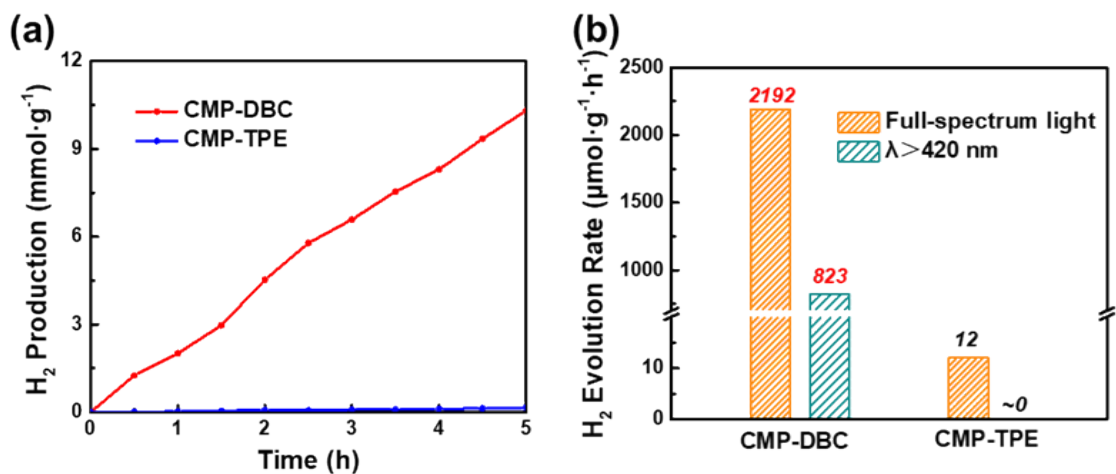
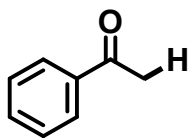


Fig. S9 Time course for photocatalytic H₂ production under UV-visible irradiation of CMPs. (b)

Average H₂ evolution rates on CMPs.

Table. S1 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) of the two CMPs.

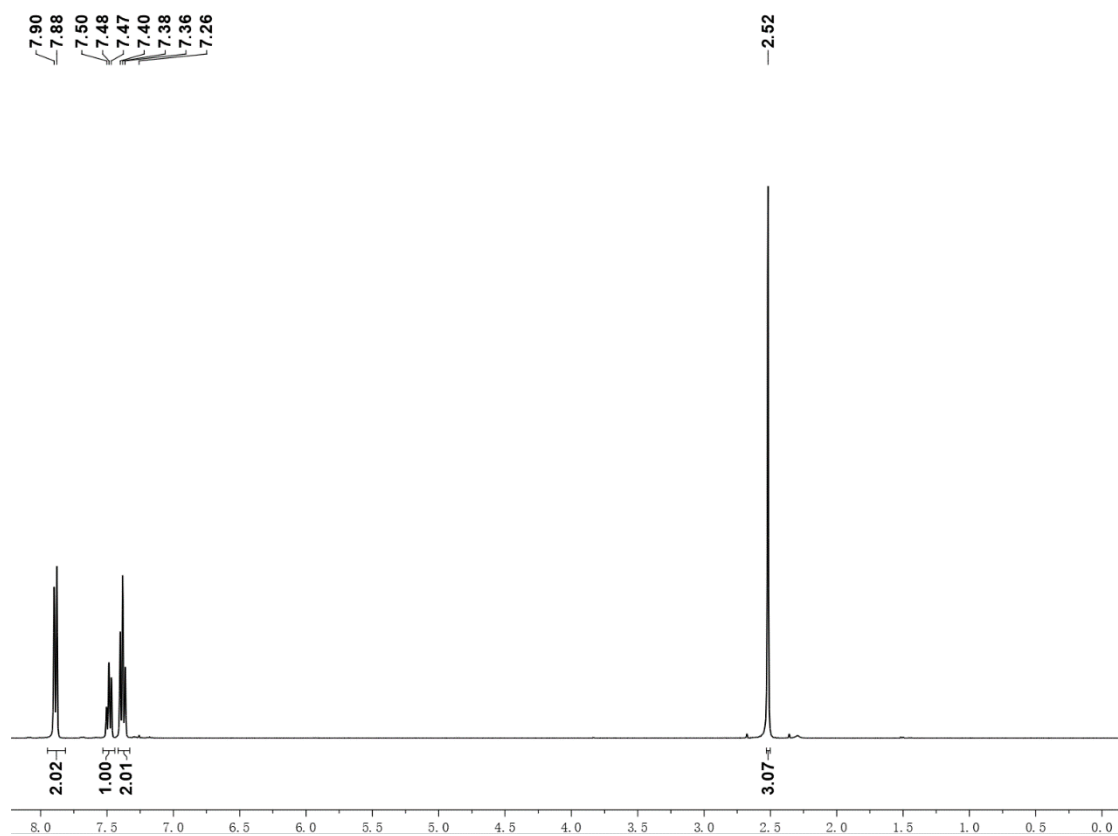
Sample	Mass (mg)	Volume (mL)	Concentration C ₀ (mg/L)	Dilution Ratio f	Element concentration in digestion solution C ₁ (mg/L)	Element content C _x (mg/kg)	Element content W (%)
CMP-DBC	11.2	50	0.463	1	0.463	2066.96	0.207
CMP-TPE	12.5	50	0.564	1	0.564	2256.00	0.226

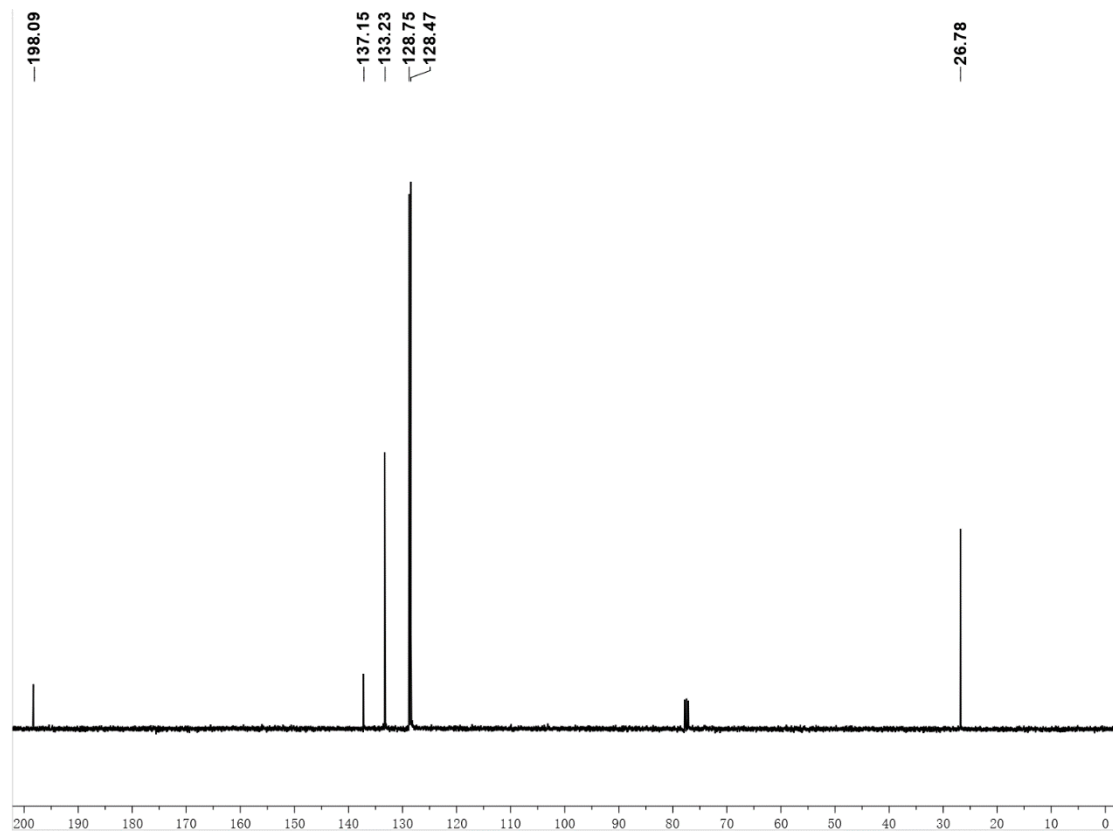


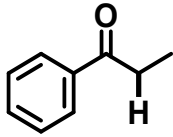
Acetophenone:

^1H NMR (CDCl_3 , 400 MHz): δ 7.90-7.88 (d, 2H), 7.50–7.47 (m, 1H), 7.40-7.36 (m, 2H), 2.52 (s, 3H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 198.1, 137.1, 133.2, 128.7, 128.5, 26.8 ppm.



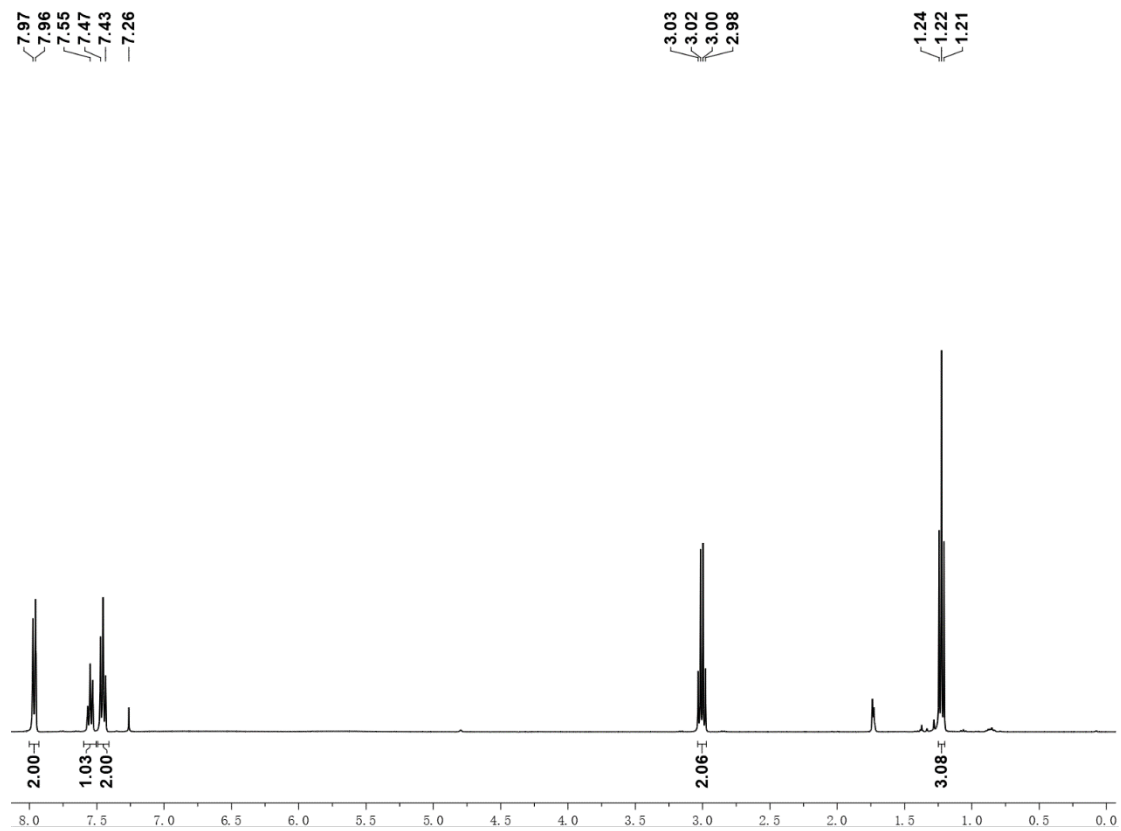




1-phenyl-propan-1-one:

^1H NMR (CDCl_3 , 400 MHz): 7.97-7.97 (m, 2H), 7.55 (m, 1H), 7.47-7.43 (t, 2H), 3.03-2.98 (m, 2H), 1.24-1.21 (t, 3H).

^{13}C NMR (CDCl_3 , 400 MHz): δ 201.1, 137.1, 140.0, 133.1, 128.8, 128.2, 32.1, 8.2 ppm.

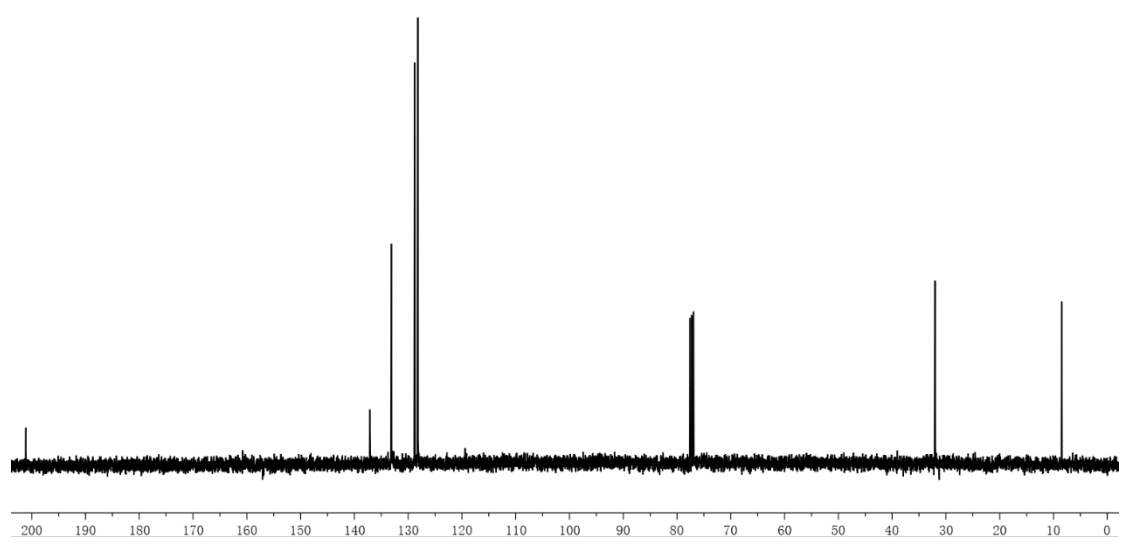


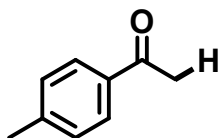
—201.06

—137.12
—133.11
—128.77
—128.19

—32.09

—8.16

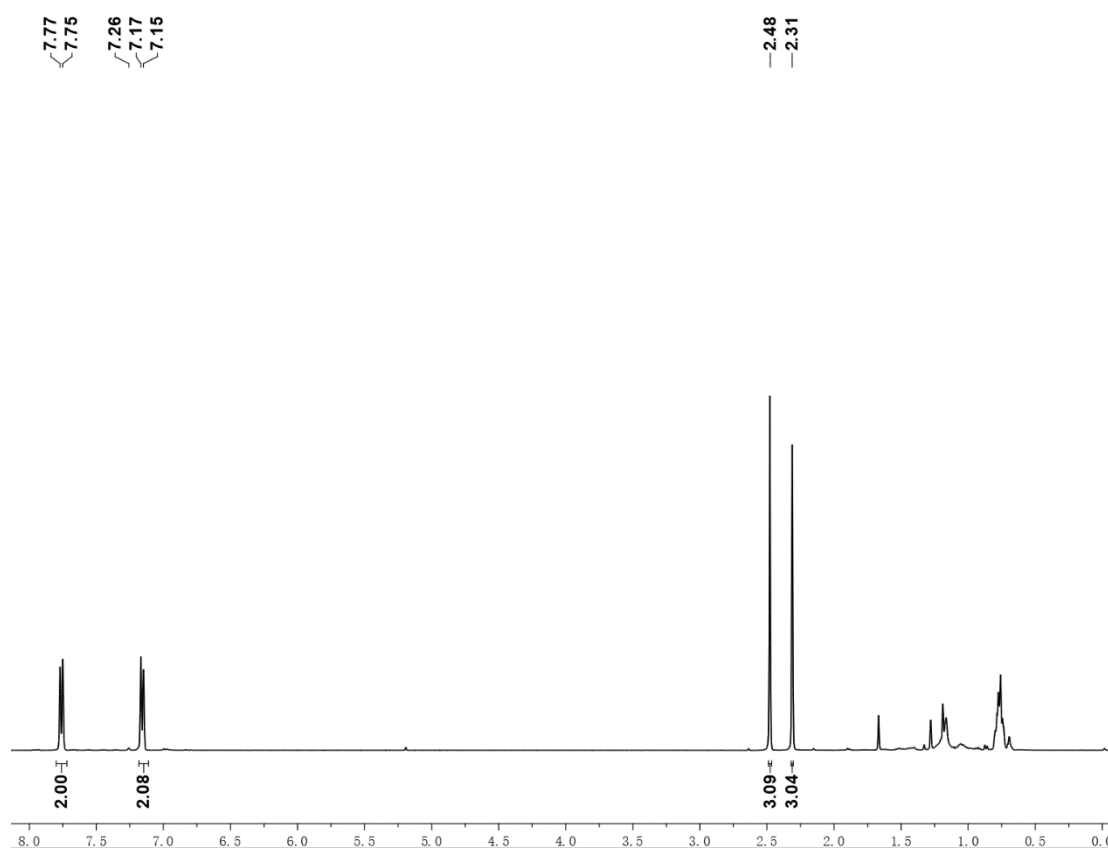


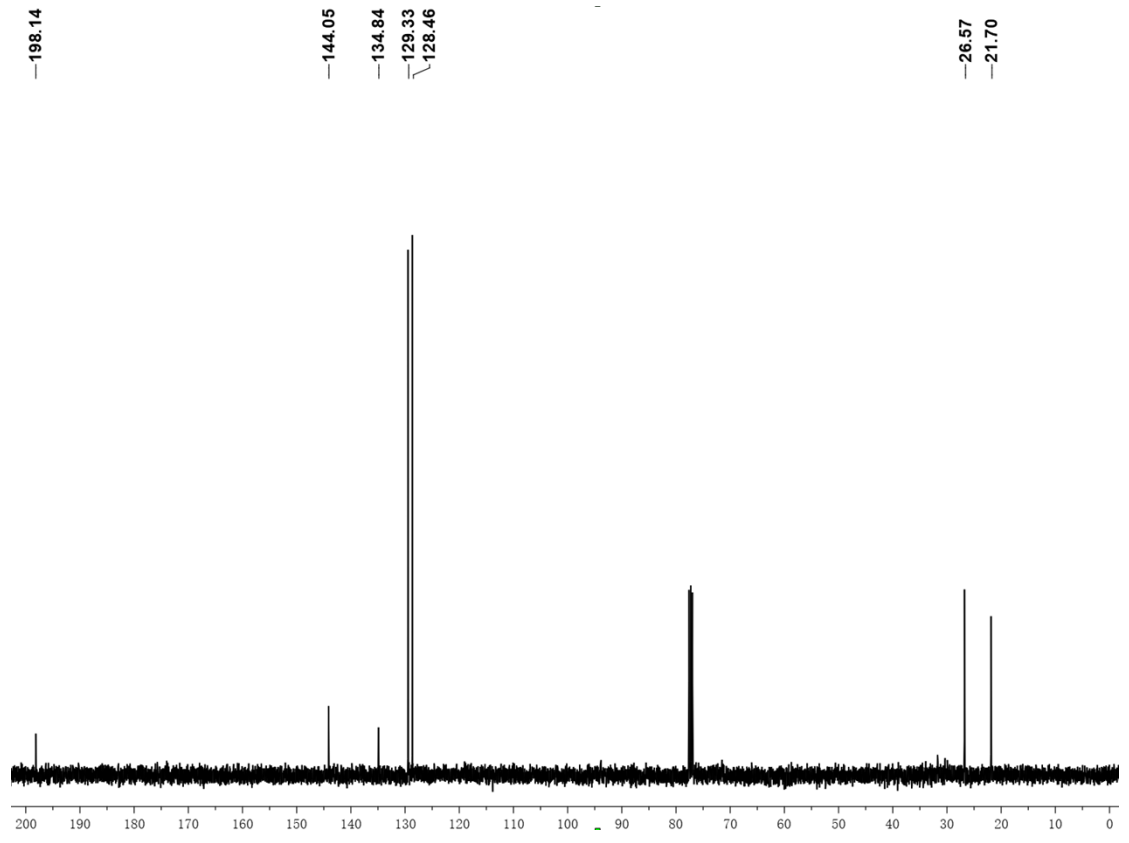


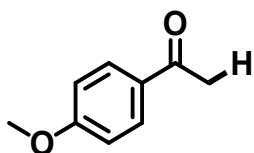
1-(p-tolyl)ethan-1-one:

^1H NMR (CDCl_3 , 400 MHz): δ 7.77 (d, $J = 8$ Hz, 2H), 7.17 (d, $J = 8$ Hz, 2H), 2.48 (s, 3H), 2.31 (s, 3H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 198.1, 144.0, 134.8, 129.3, 128.3, 26.6, 21.7 ppm.



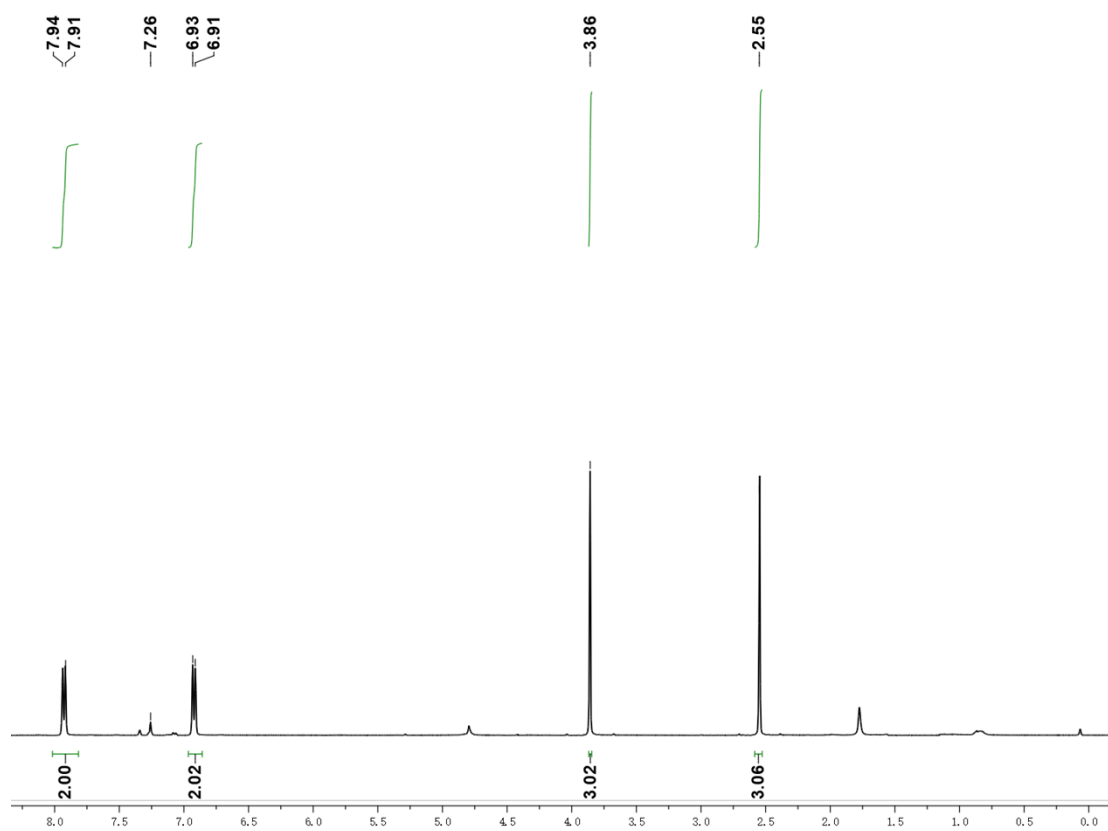


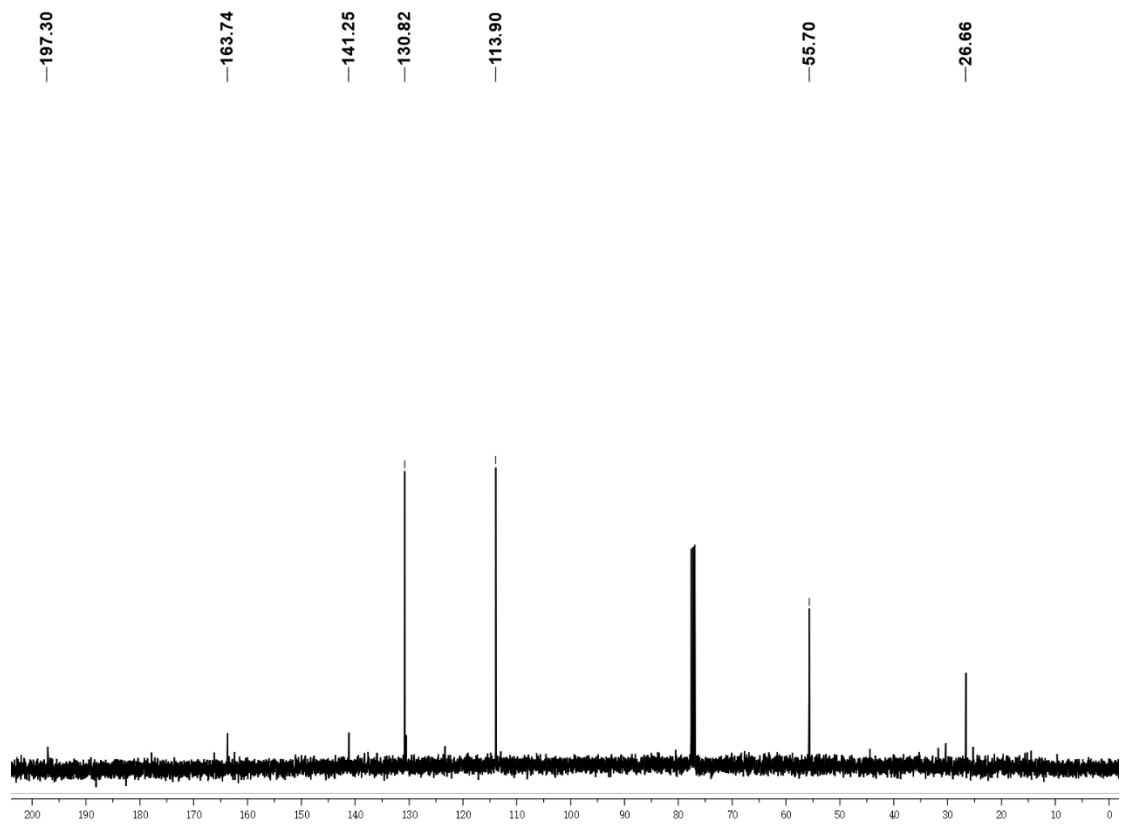


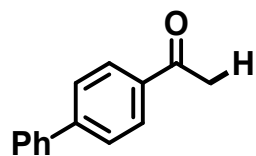
4-Methoxyacetophenone:

^1H NMR (CDCl_3 , 400 MHz): δ 7.94 (d, $J = 8$ Hz, 2H), 6.93 (d, $J = 8$ Hz, 2H), 3.86 (s, 3H), 2.55 (s, 3H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 197.3, 163.7, 141.2, 130.8, 113.9, 55.7, 26.6 ppm.



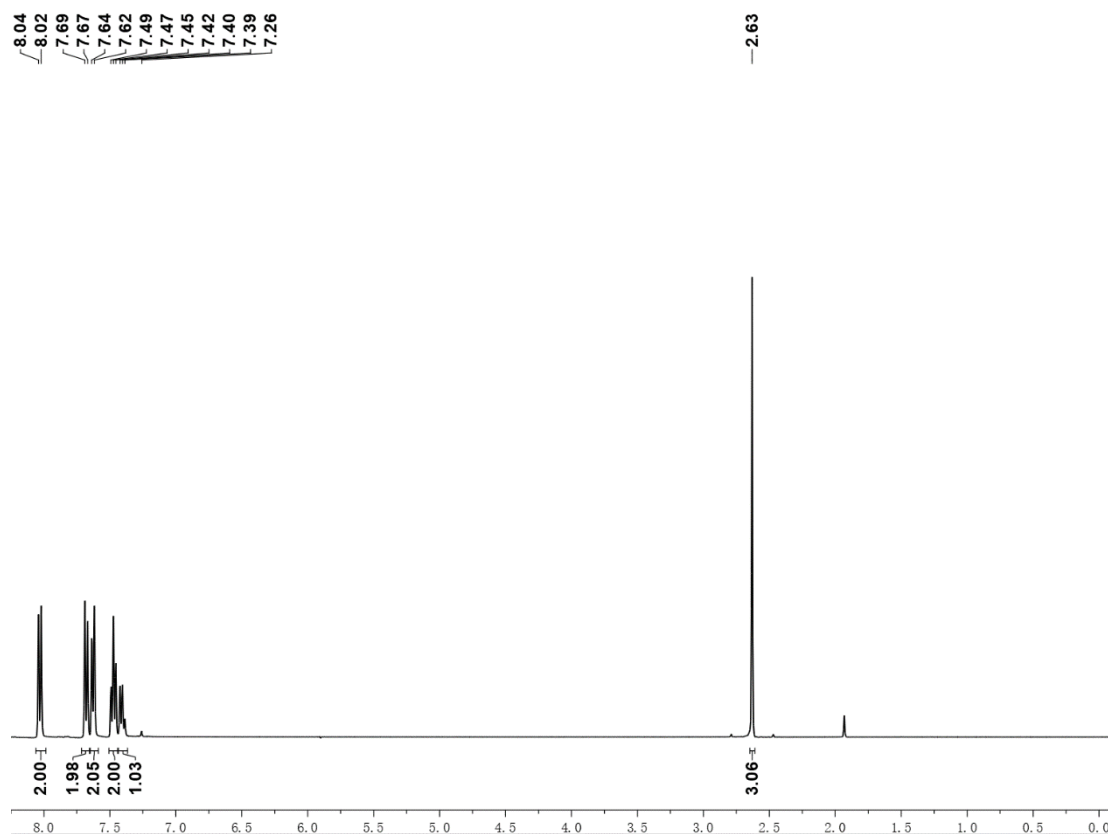


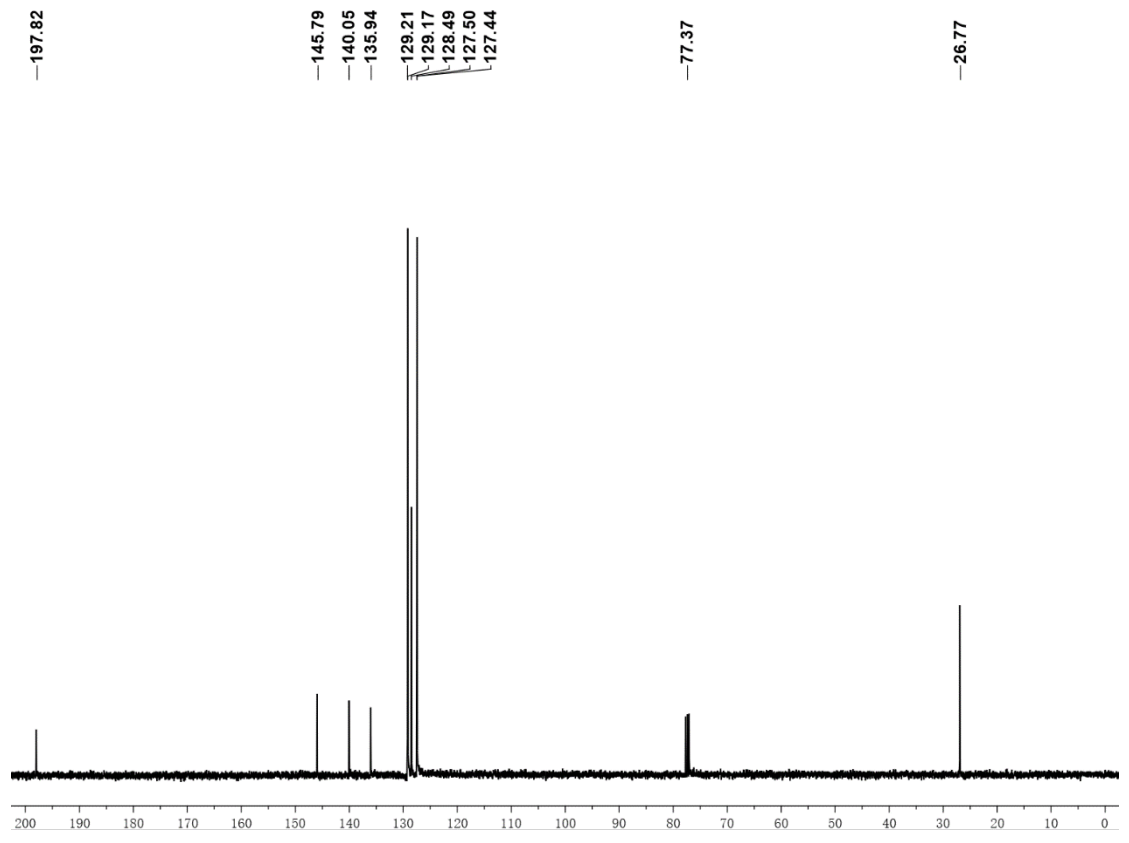


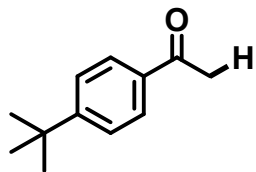
1-([1,1'-biphenyl]-4-yl)ethan-1-one:

^1H NMR (CDCl_3 , 400 MHz): δ 8.04-8.02 (m, 2H), 7.69-7.67 (m, 2H), 7.64-7.62 (m, 2H), 7.49-7.45 (m, 2H), 7.42-7.39 (m, 1H), 2.63 (s, 3H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 197.8, 145.8, 140.0, 135.9, 129.2, 129.17, 128.5, 127.5, 127.4, 26.7 ppm.





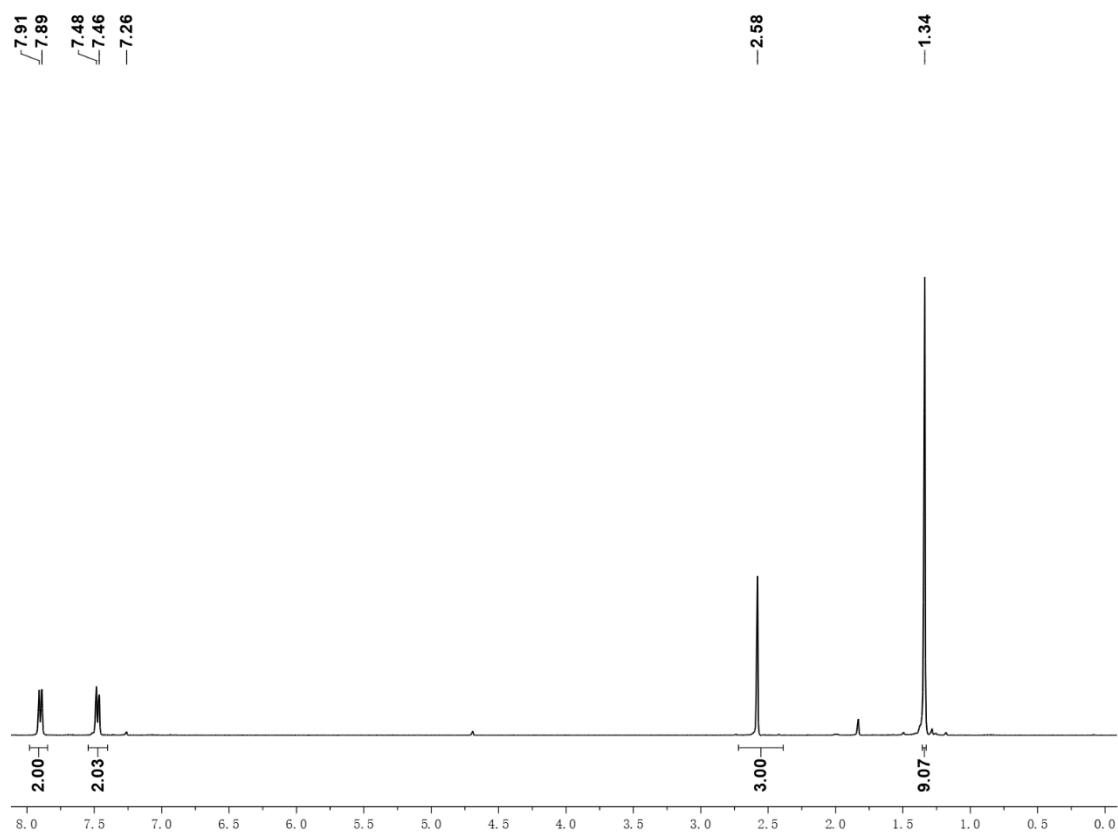


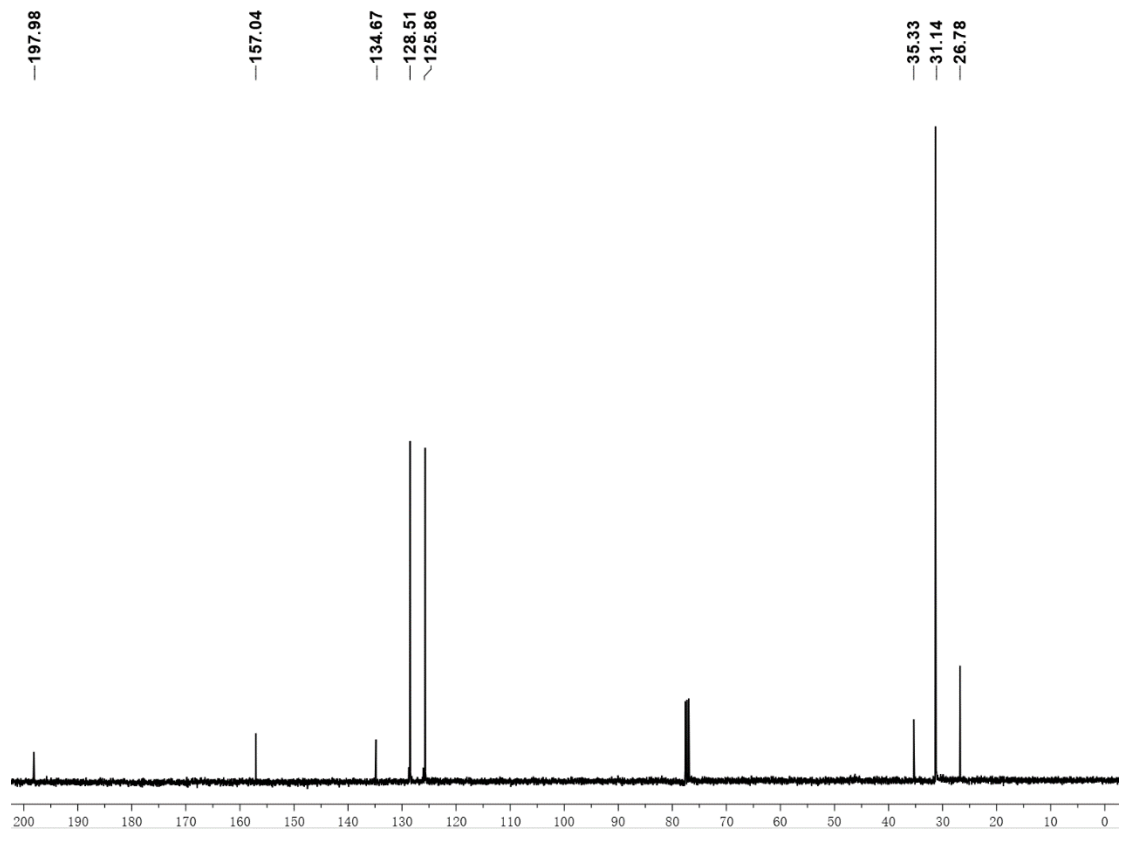
4'-tert-Butylacetophenone:

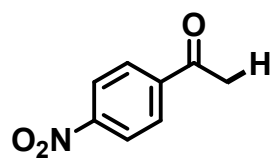
^1H NMR (CDCl_3 , 400 MHz): δ 7.91-7.89 (m, 2H), 7.48-7.46 (m, 2H), 2.58 (s, 3H), 1.34

(s, 9H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 197.9, 157.0, 134.6, 128.5, 125.9, 35.3, 31.1, 26.8 ppm.



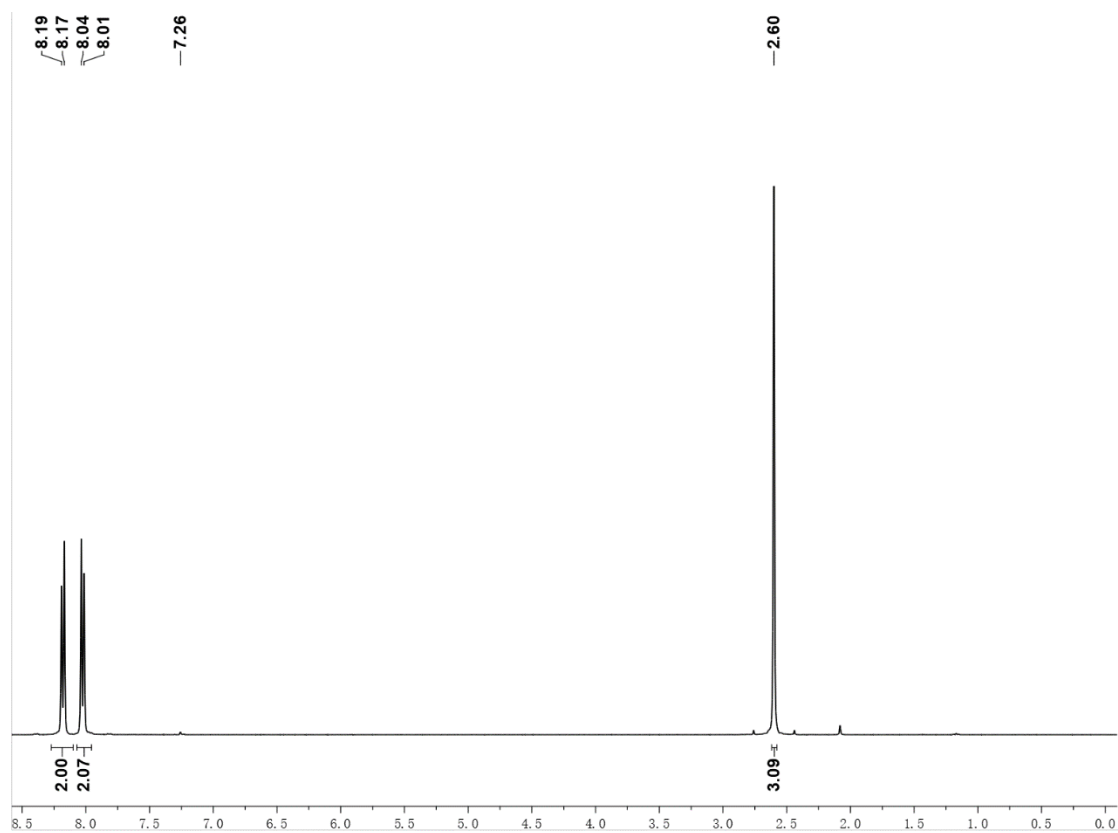


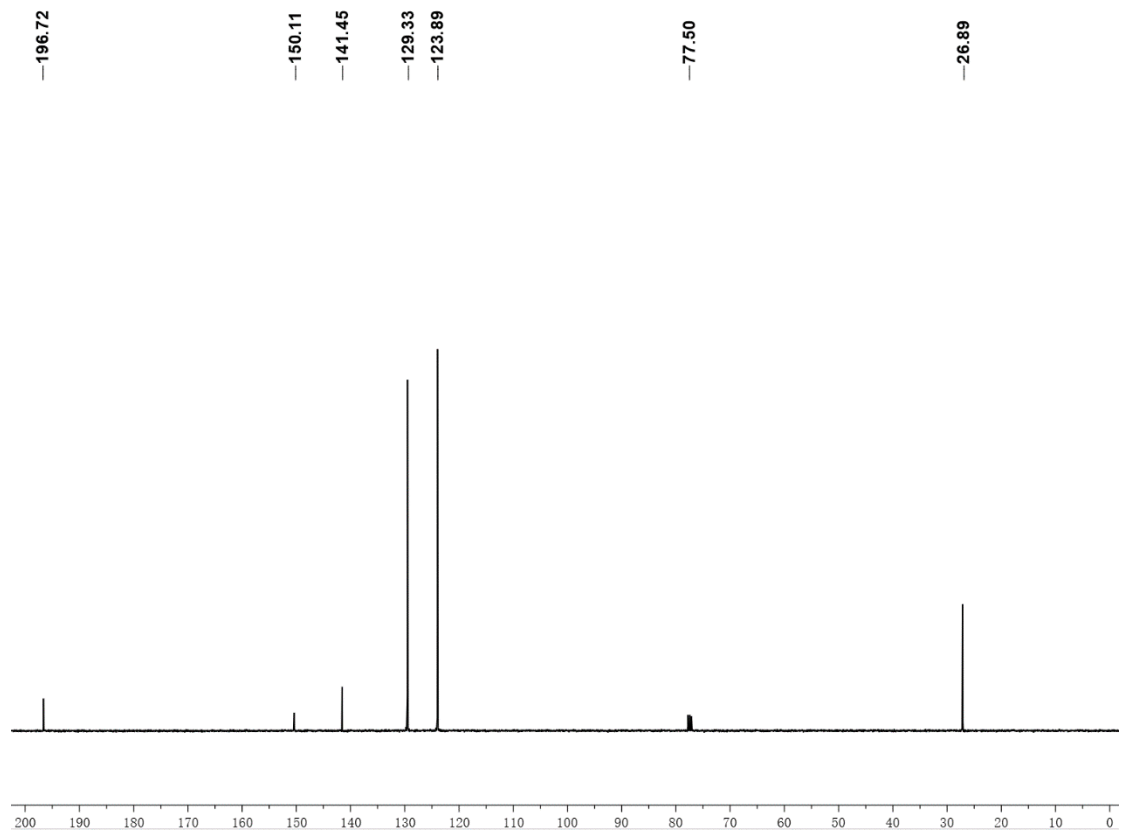


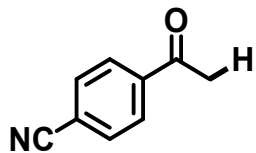
4-Nitroacetophenone:

¹H NMR (CDCl₃, 400 MHz): δ 8.19-8.17 (m, 2H), 8.04-8.01 (m, 2H), 2.60 (s, 3H) ppm.

¹³C NMR (CDCl₃, 400 MHz): δ 196.7, 150.1, 141.4, 129.3, 123.9, 26.9 ppm.



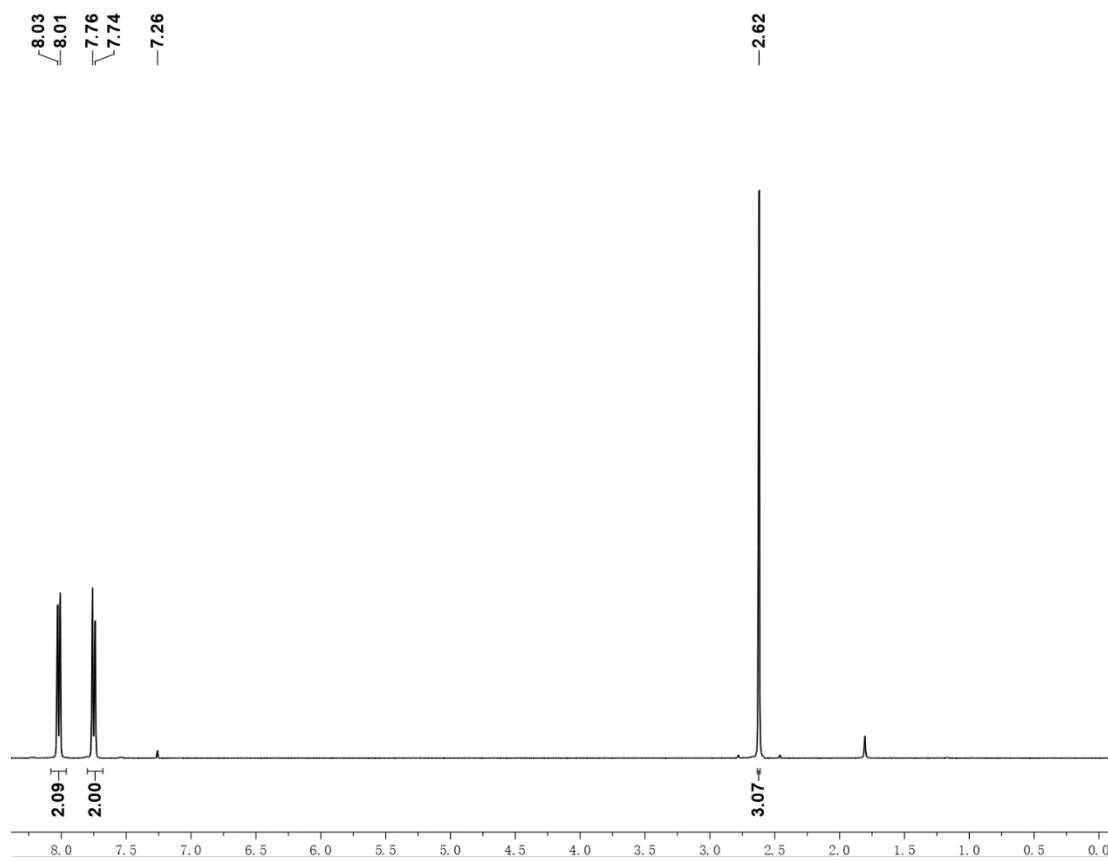


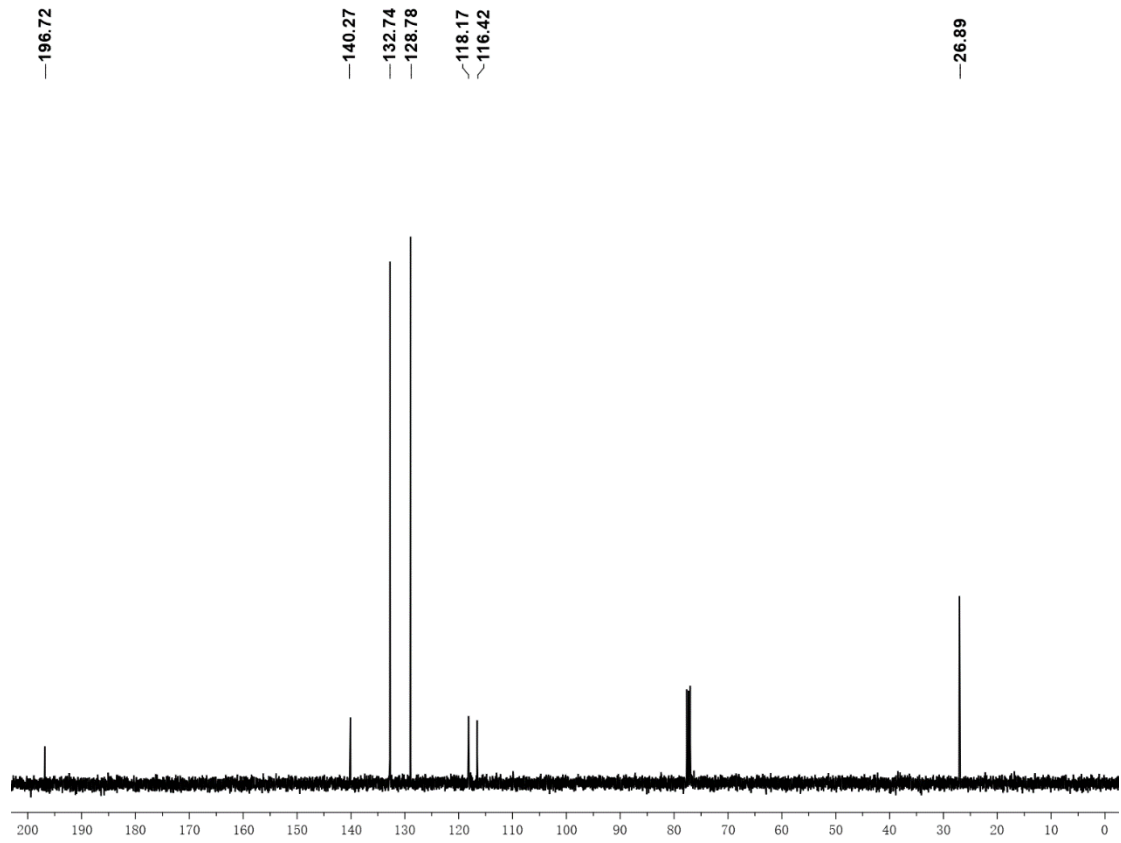


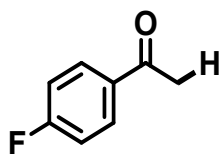
4-Acetylbenzonitrile:

^1H NMR (CDCl_3 , 400 MHz): δ 8.03 (d, $J = 8$ Hz, 2H), 7.76 (d, $J = 8$ Hz, 2H), 2.62 (s, 3H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 196.7, 140.2, 132.7, 128.8, 118.2, 116.4, 26.9 ppm.





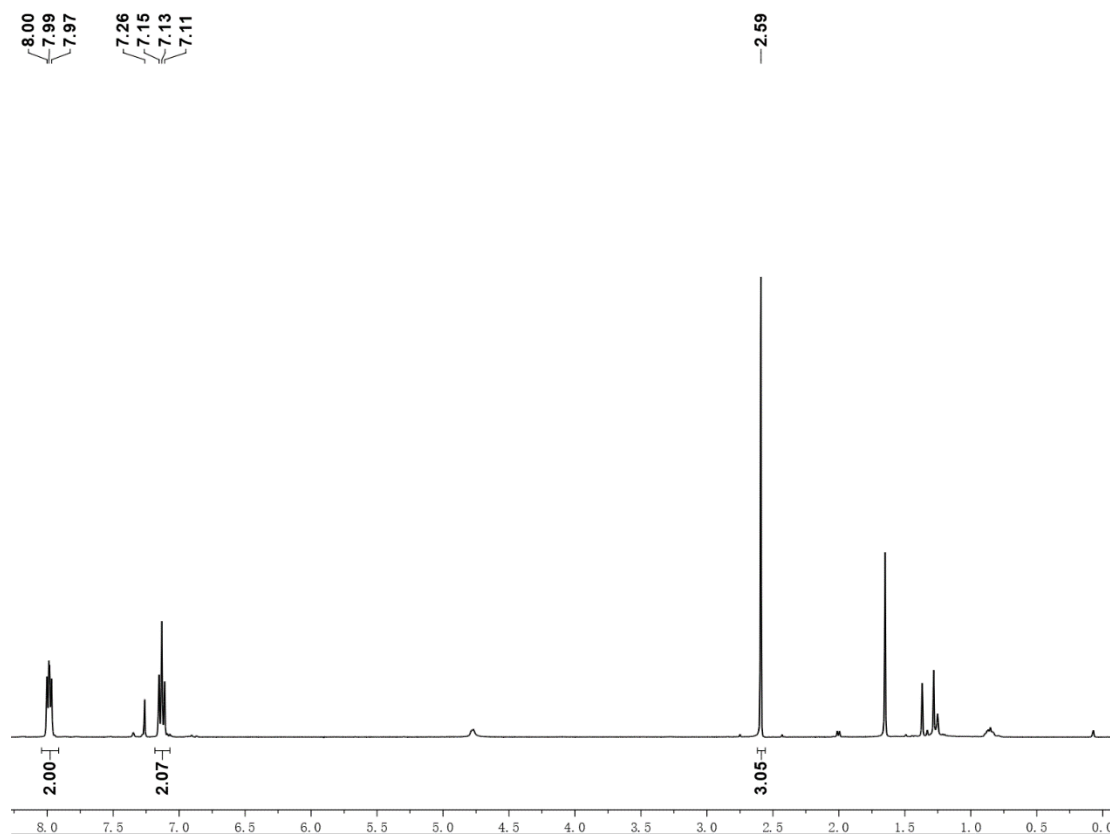


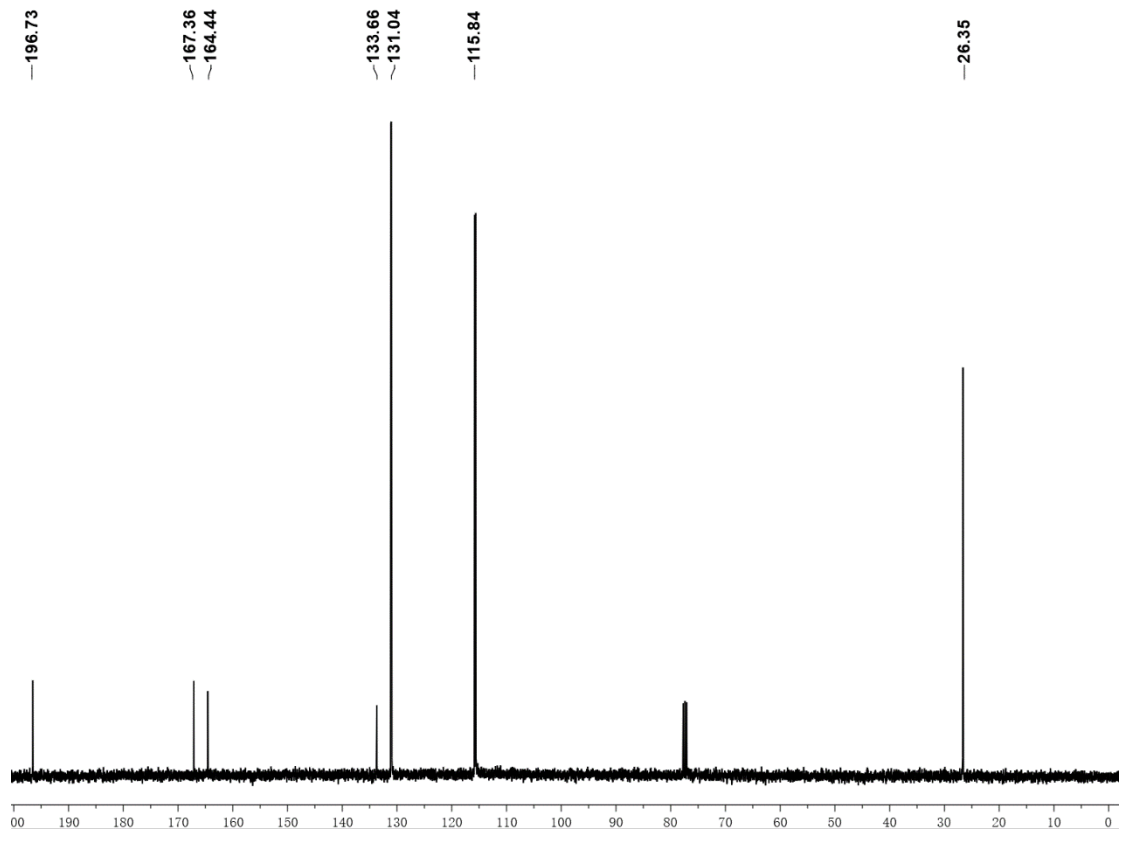
4-Fluoroacetophenone:

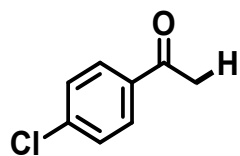
^1H NMR (CDCl_3 , 400 MHz): δ 8.00-7.97 (m, 2H), 7.15–7.11 (m, 2H), 2.59 (s, 3H)

ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 196.7, 167.3, 164.4, 133.6, 131.0, 115.8, 26.3 ppm.



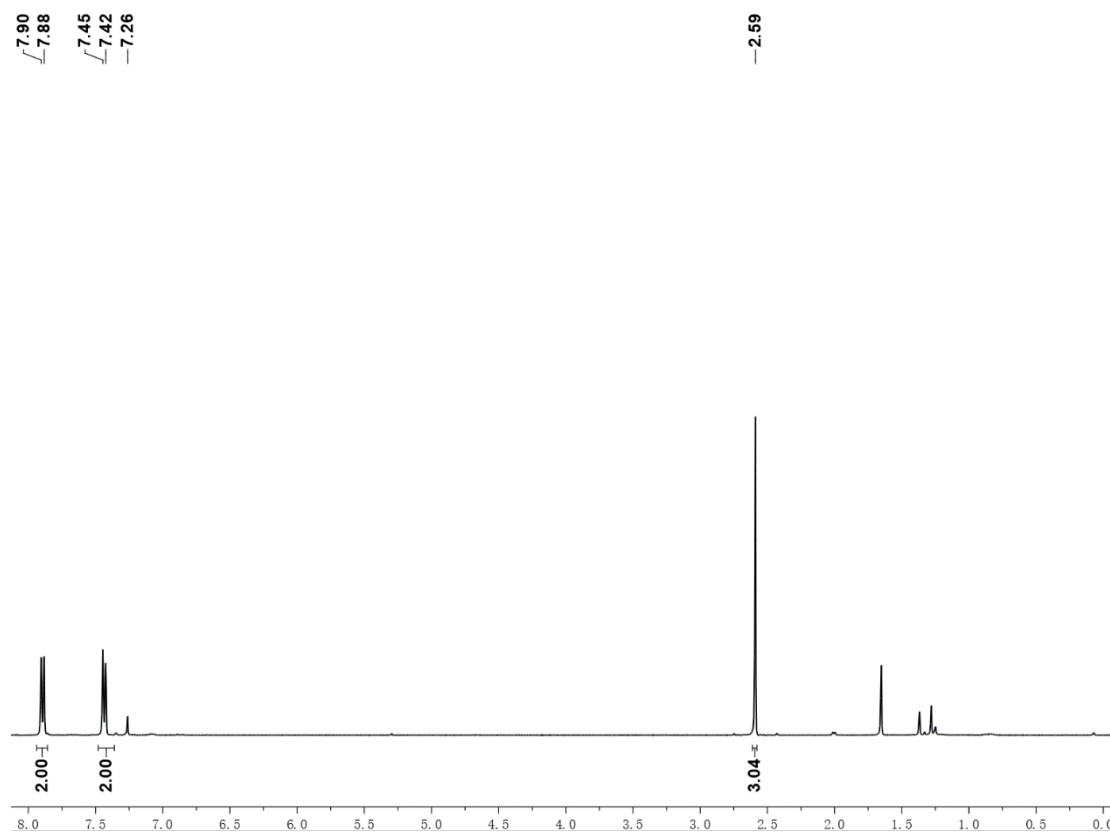


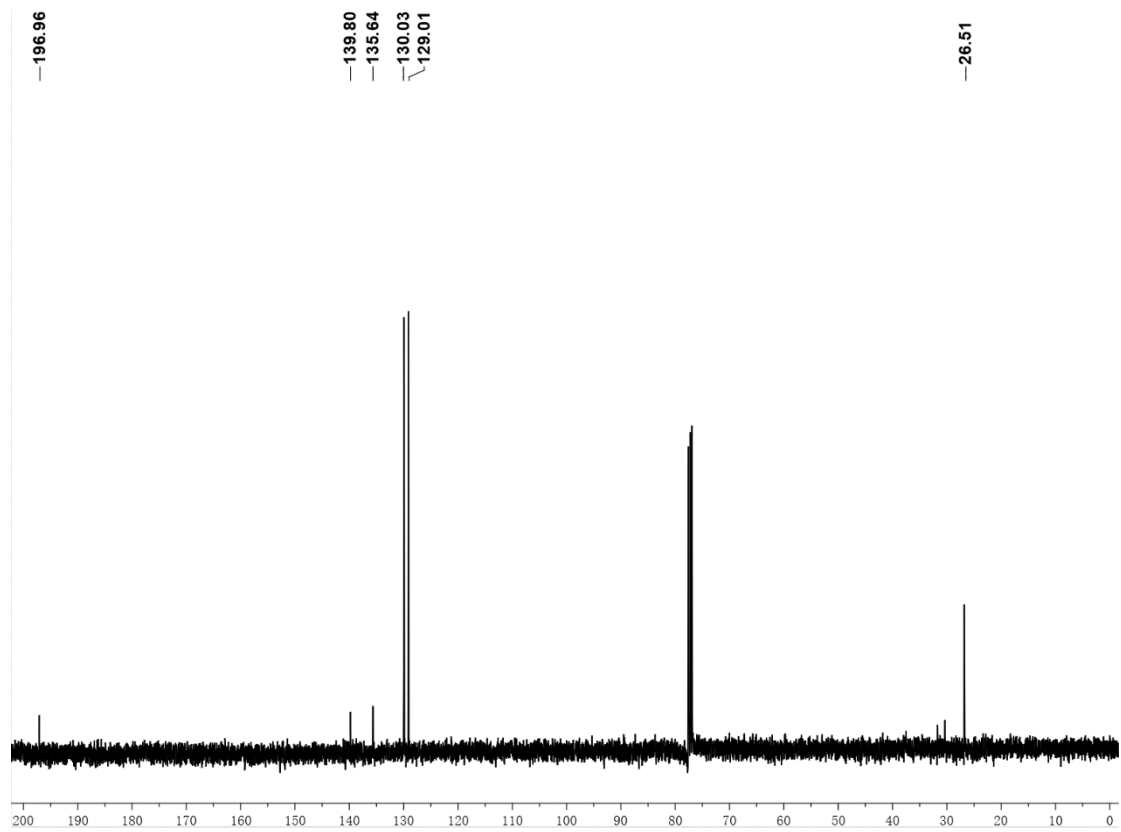


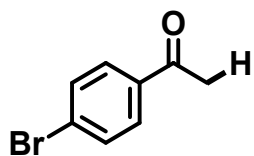
4-Chloroacetophenone:

^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, $J = 8$ Hz, 2H), 7.45 (d, $J = 8$ Hz, 2H), 2.59 (s, 3H) ppm.

^{13}C NMR (CDCl_3 , 400 MHz): δ 196.7, 139.8, 135.6, 130.0, 129.0, 26.5 ppm.



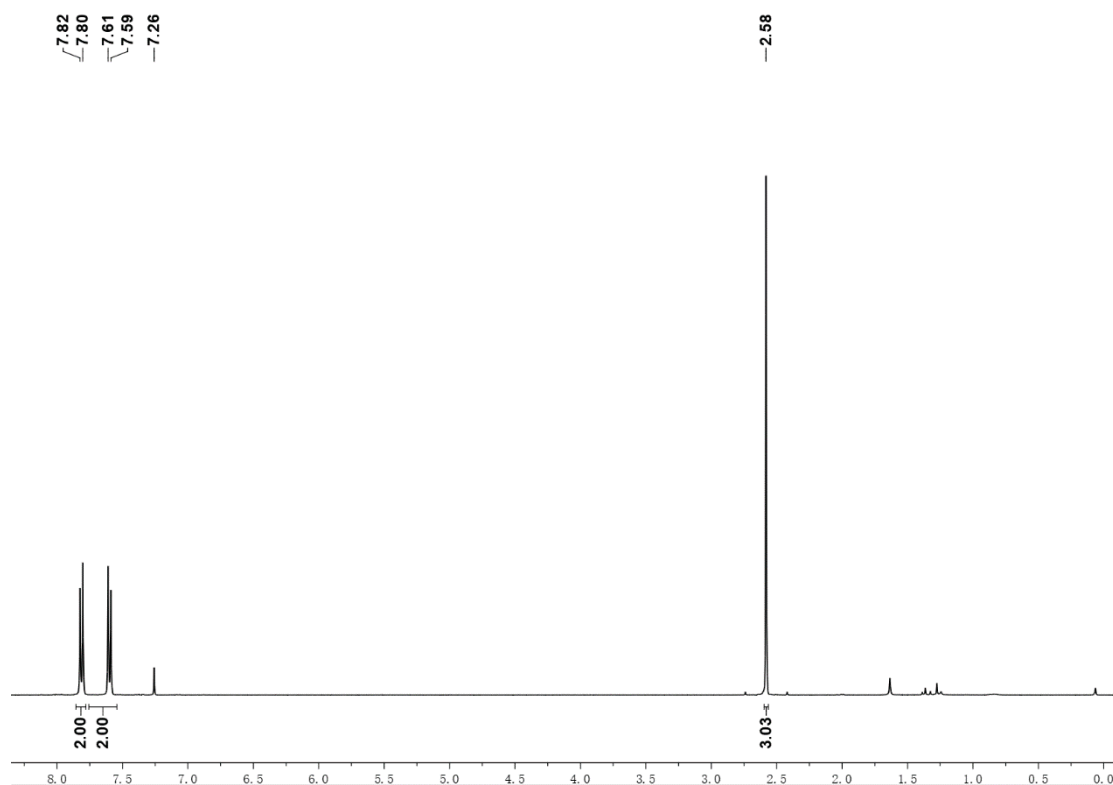




4-Bromoacetophenone:

^1H NMR (CDCl_3 , 400 MHz): δ 7.82 (d, $J = 8$ Hz, 2H), 7.61 (d, $J = 8$ Hz, 2H), 2.58 (s, 3H) ppm.

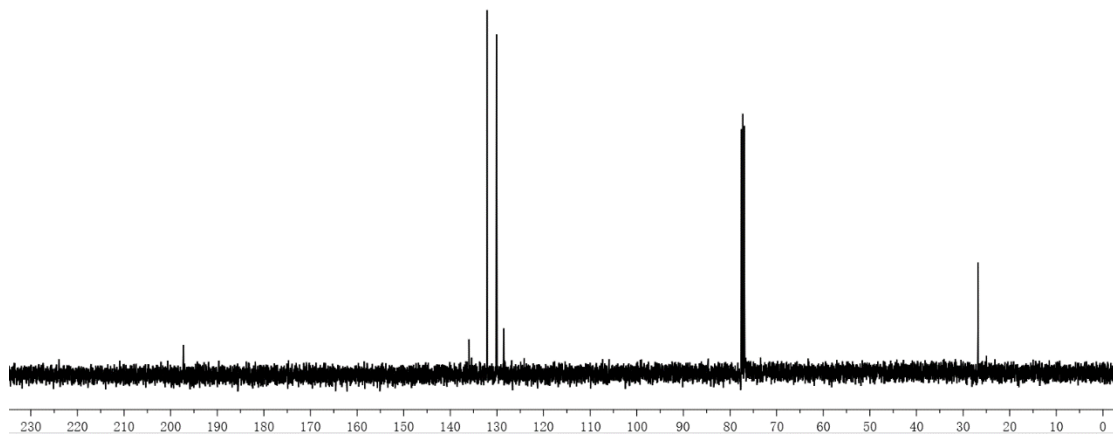
^{13}C NMR (CDCl_3 , 400 MHz): δ 197.3, 135.9, 132.5, 130.3, 128.5, 27.0 ppm.

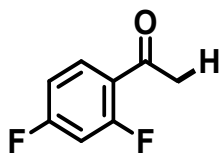


—197.34

135.93
132.56
130.27
128.53

—27.06

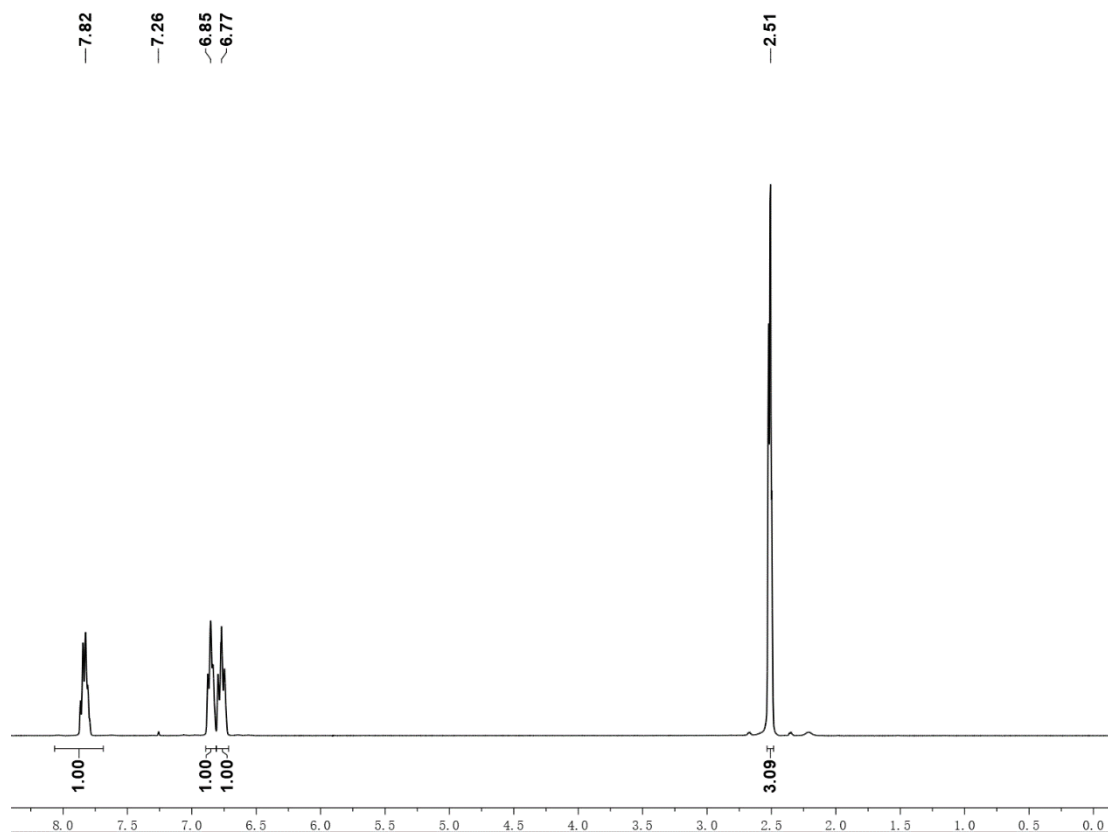


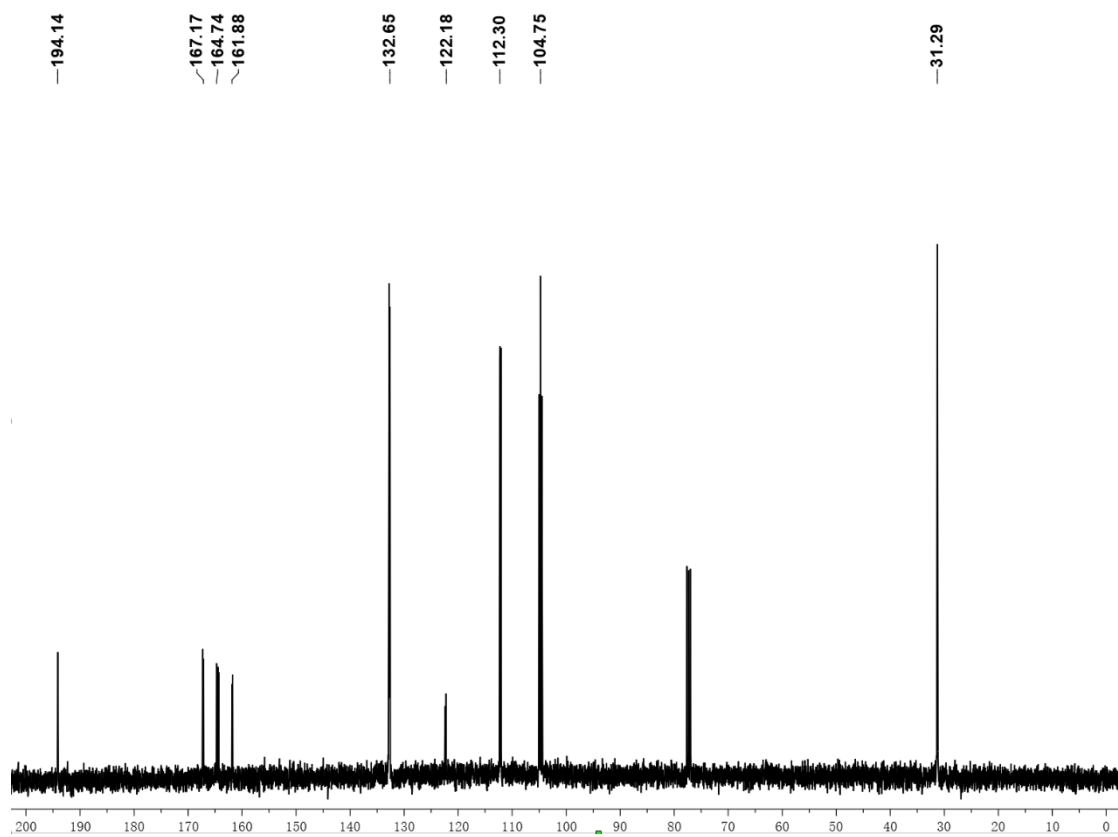


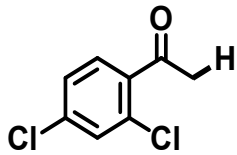
2',4'-Difluoroacetophenone:

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.82 (d, $J = 8$ Hz, 1H), 6.85 (d, $J = 12$ Hz, 1H), 6.77 (m, 1H), 2.51 (d, 3H) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 400 MHz): δ 194.1, 167.2, 164.7, 161.9, 132.6, 122.2, 112.3, 104.8, 31.3 ppm.



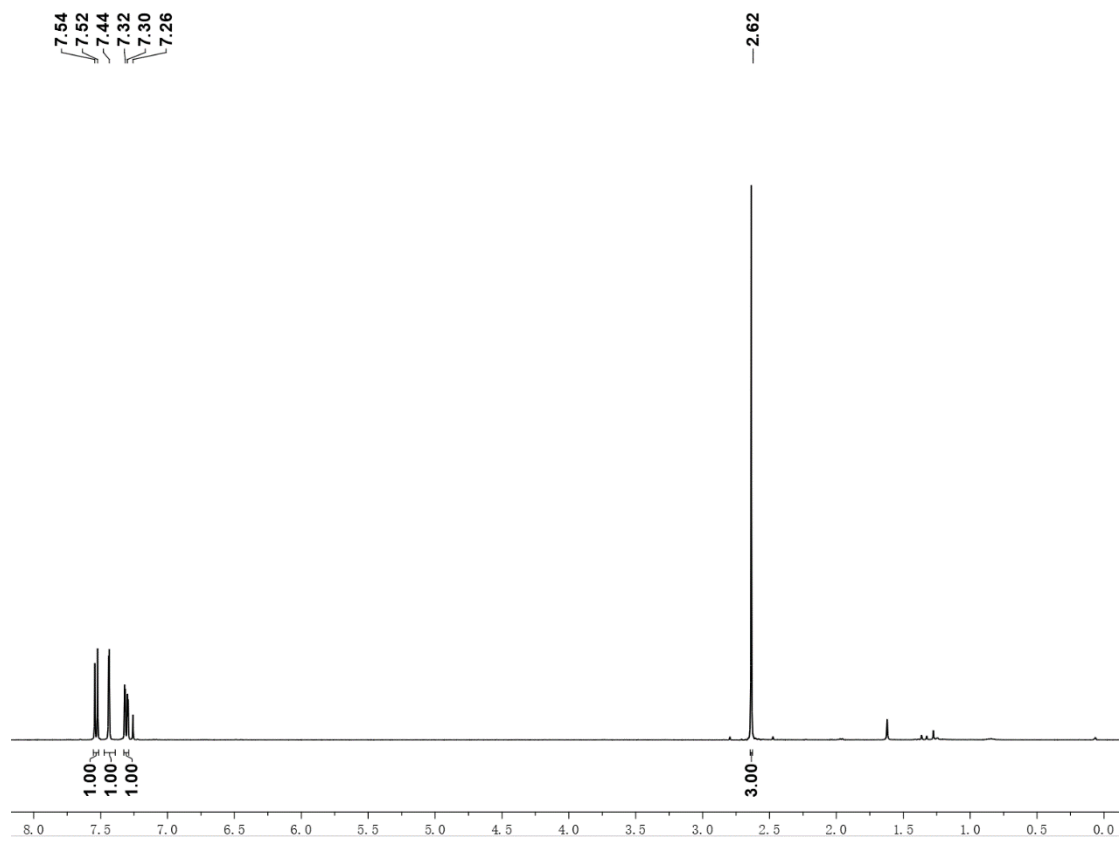




1-(2,4-dichlorophenyl)ethan-1-one:

^1H NMR (CDCl_3 , 400 MHz): δ 7.54 (d, $J=8.0$ Hz, 1H), 7.44 (d, $J=4.0$ Hz, 1H), 7.32-7.30 (dd, $J=4.0$ Hz, 1H), 2.62 (s, 3H).

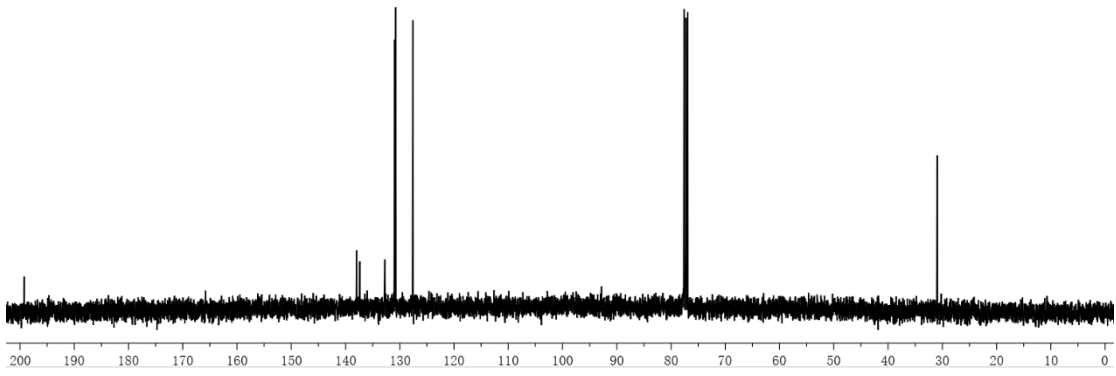
^{13}C NMR (CDCl_3 , 400 MHz): δ 199.2, 138.0, 137.4, 133.0, 130.9, 130.8, 127.5, 30.9.

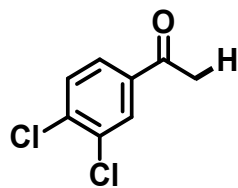


—199.16

138.02
137.37
133.02
130.94
130.77
127.53

—30.94

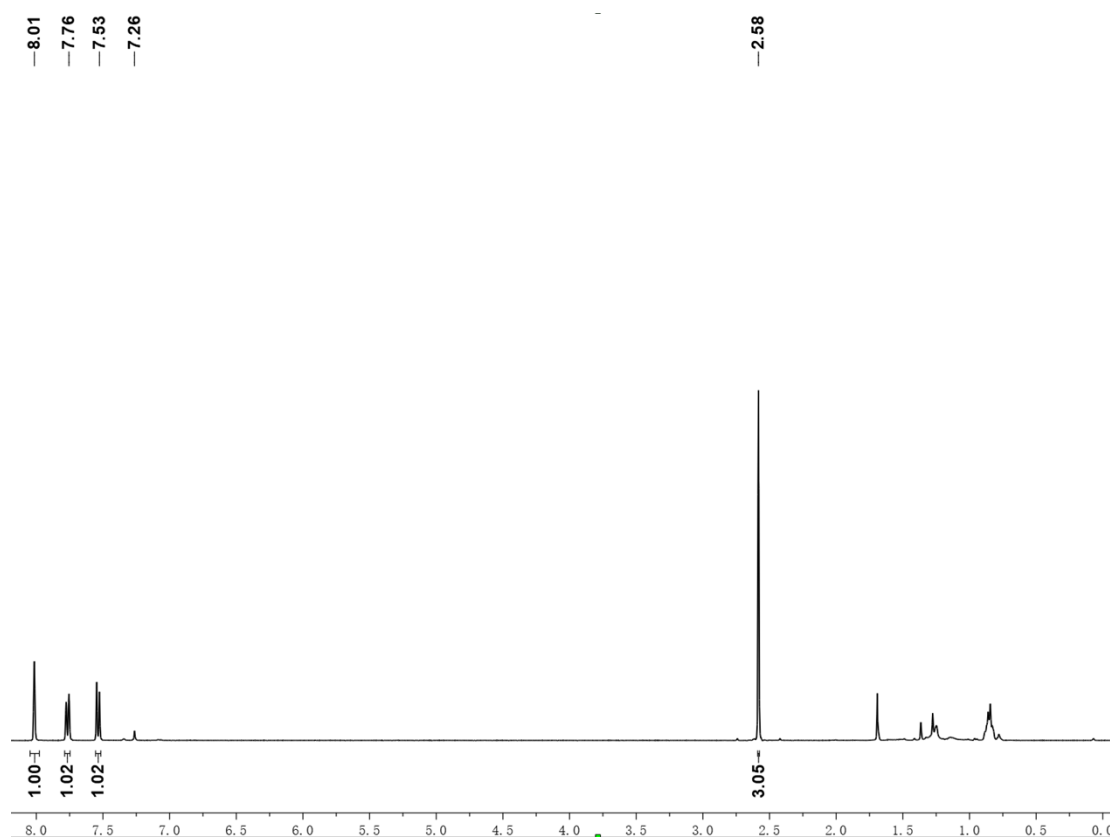


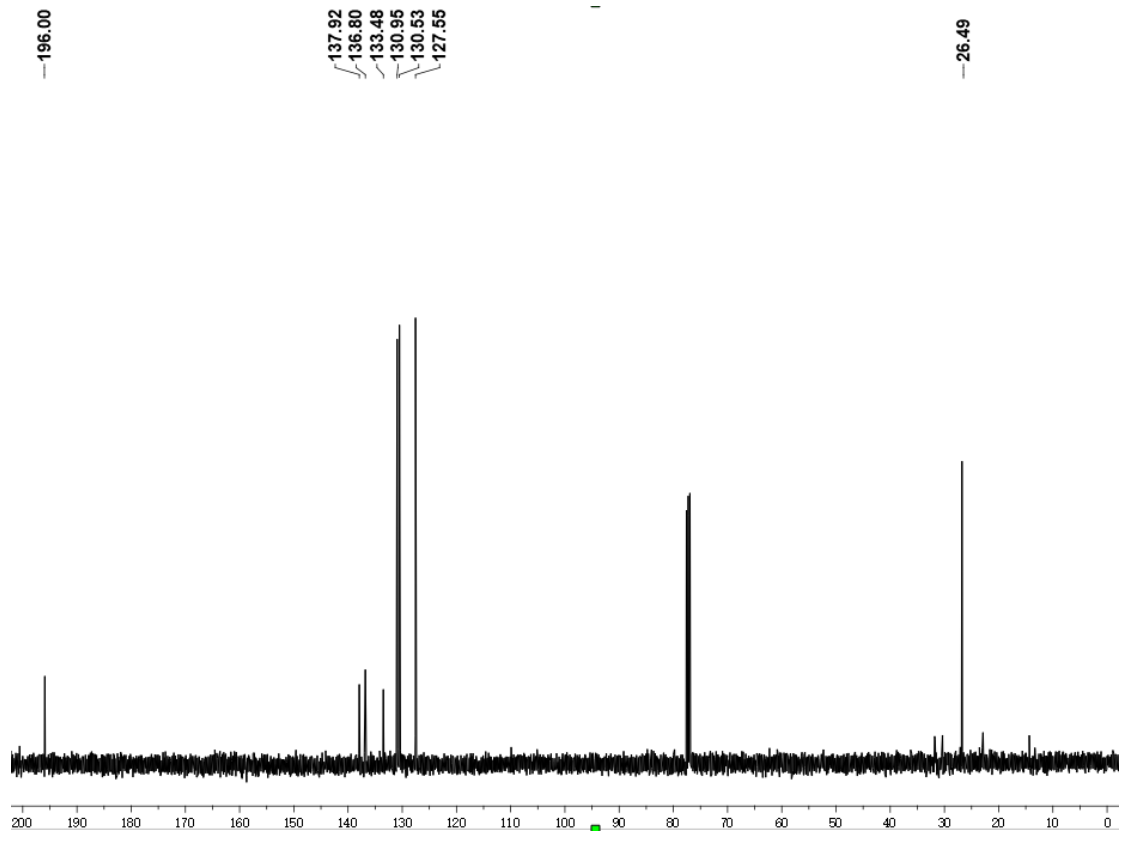


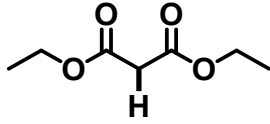
1-(3,4-dichlorophenyl)ethan-1-one:

^1H NMR (CDCl_3 , 400 MHz): δ 8.01 (d, 1H), 7.76 (dd, $J=4.0$ Hz, 1H), 7.53 (dd, $J=4.0$ Hz, 1H), 2.58 (s, 3H).

^{13}C NMR (CDCl_3 , 400 MHz): δ 196.0, 137.9, 136.8, 133.5, 130.9, 130.5, 127.5, 26.5.







Diethyl malonate:

^1H NMR (CDCl_3 , 400 MHz): δ 4.18-4.14 (q, 2H), 3.28 (s, 1H), 1.20 (q, 3H)

^{13}C NMR (CDCl_3 , 400 MHz): δ 166.7, 61.5, 41.8, 14.2.

