

Supporting Information

Highly Efficient Carbon Catalyzed Aerobic Selective Oxidation of Alcohols under Transition-Metal and Hetero- atom Free Conditions

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1. Experimental

All solvents and chemicals were obtained commercially and were used as received.

NMR spectra were measured using a Bruker AVANCE IIIHD spectrometer at 400 MHz (1H). All spectra were recorded in CDCl₃ and d₆-DMSO and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Mass spectra were in general recorded on an HP 6890/5973 GRF-HT-C-MS. Nitrogen adsorption isotherms were recorded with an ASAP2020 adsorption analyzer at 77 K. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. Scanning electron microscopy (SEM) investigations were carried out with a JSM-6701F instrument. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Stoe STADI P automated transmission diffractometer instrument equipped with an incident beam curved germanium monochromator selecting Cu K α 1 radiation. The XRD diffraction patterns were scanned in the 2 θ range of 10-80°. XPS measurements were conducted on a VG ESCALAB 210 instrument provided with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar⁺ ion-gun. All the spectra were recorded using non-monochromatic Mg K α (1253.6 eV) radiation.

2. Representative procedure for the preparation of carbon catalysts.

The carbon materials were prepared through a sol-gel polymerization of resorcinol and formaldehyde with Na₂CO₃ as a catalyst. Typically, resorcinol (R, 2.20 g, 20 mmol), formaldehyde (F, 3.25 g, 40 mmol, 36.5% in water, methanol stabilized) and 9 mL distilled water were added into a 100 mL PTFE autoclave. Subsequently, 22.1 mg Na₂CO₃ (1 mol% to resorcinol) were added into the mixture. After vigorous stirring for 1 h, the autoclave was sealed and treated at 80 °C for one day. Then the autoclave was cooled to room temperature. The wet gels were put into a round-bottom flask and vacuum dried at 130 °C for 3 h. Then, the RF gel and KOH were mixed with a mass ratio of 1 : 1 (1.5 g/1.5 g) and were carbonized at 800 °C for 5 h under nitrogen flow (20 mL/min). The resulted carbon material was ultrasonically washed by distilled water till neutral (100 mL \times 5) and dried in 80 °C for 6 h. Finally, about 730 mg carbon material was obtained and it was denoted as Carbon-1. Several carbon materials were prepared with the same procedure by treating the RF gel with different bases, i.e. NaOH (1.5 g/1.5 g), K₂CO₃ (1.5 g/1.5 g) and Na₂CO₃ (1.5 g/1.5 g), and the carbon materials were denoted as RF-HT-C-2, RF-HT-C-3 and RF-HT-C-4. By varying the amount of KOH to 0.375 g and 1.88 g, and carbon materials RF-HT-C-5 and RF-HT-C-6 were obtained. For comparing, the RF gel itself was also carbonized at 800 °C for 5 h under nitrogen flow (20 mL/min), and the final sample was denoted as RF-HT-C-0.

3. Representative procedures for the selective oxidation of alcohols

3.1. Representative procedure for oxidation of alcohols to aldehydes

All the reactions were performed in a Schlenk tube. 1 mmol benzyl alcohol, 100 mg catalyst, 0.2 mmol KOH and 2 mL toluene were added into the reactor, and reacted at 100 °C for 12 h at 1 atm O₂. After reaction, it was cooled down to room temperature and 1 mmol biphenyl and 10 mL EtOH was added for quantitatively analysis with a GRF-HT-C-FID (Agilent 7890A).

3.2 Representative procedure for oxidation of alcohols to carboxylic acids

All the reactions were performed in a Schlenk tube. 1 mmol benzyl alcohol, 100 mg catalyst, 2 mmol KOH and 2 mL toluene were added into a Schlenk tube, and reacted at 100 °C for 12 h at 1 atm O₂. After reaction, it was cooled down to room temperature. The product is

extracted by separatory funnel using water, ethyl acetate and HCl. After removing the solvent by distillation, the white solid is obtained finally.

Table S1. C_{1s} and O_{1s} XPS spectra of the typical carbon catalysts.

catalysts	Binding energy (eV)	
	C1s	O1s
RF-HT-C-0	284.8	532.1
RF-HT-C-1	284.8	532.1
RF-HT-C-2	284.7	532.9
RF-HT-C-3	284.8	532.3
RF-HT-C-4	284.8	532.2
RF-HT-C-5	284.8	532.7

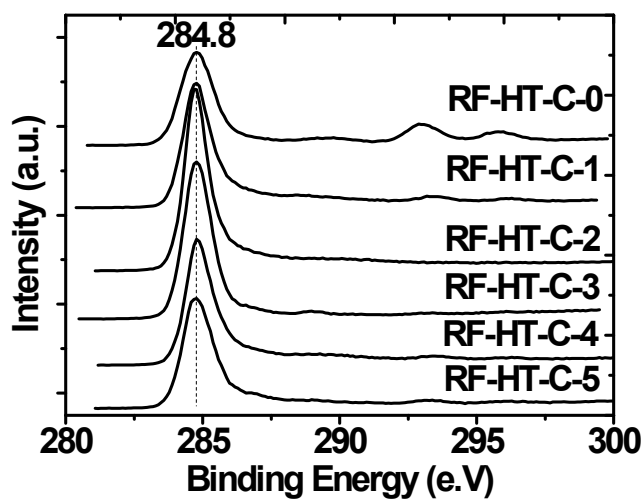


Figure S1. C_{1s} XPS spectra of the carbon materials

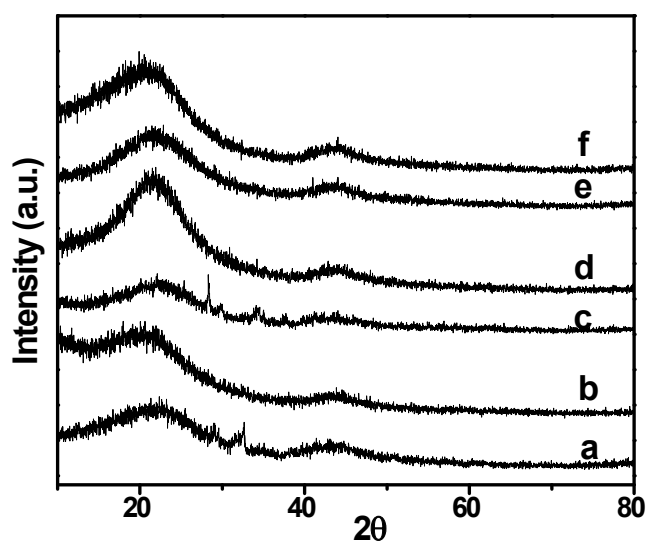
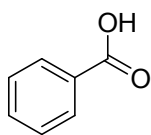
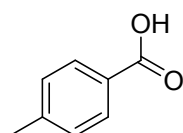


Figure S2. XRD diffraction patterns of carbon materials RF-HT-C-0 (a), RF-HT-C-1(b), RF-HT-C-2 (c), RF-HT-C-3 (d), RF-HT-C-4 (e) and RF-HT-C-5 (f)

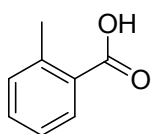
Characterization of compounds and NMR spectra



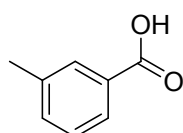
Benzoic acid: (table 3, entry 1) According to representative procedure 3.2, benzyl alcohol (108 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (112.3 mg, 92%); ¹H NMR (400 MHz, CDCl₃): δ=2.32 (s, 1H), 8.55-8.01 (m, 2H), 7.64 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H).



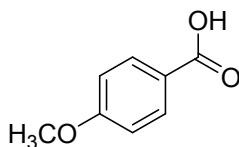
4-methylbenzoic acid: (table 3, entry 2) According to representative procedure 3.2, 4-methylbenzyl alcohol (122 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (134.6 mg, 99%); ¹H NMR (400 MHz, DMSO): δ=12.80 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H).



2-methylbenzoic acid: (table 3, entry 3) According to representative procedure 3.2, 2-methylbenzyl alcohol (122 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (113.0 mg, 83%); ¹H NMR (400 MHz, DMSO): δ=12.88 (s, 1H), 7.95-7.69 (m, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.29 (t, *J* = 8.2 Hz, 2H), 2.52 (s, 3H).

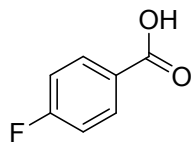


3-methylbenzoic acid: (table 3, entry 4) According to representative procedure 3.2, 3-methylbenzyl alcohol (122 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (115.6 mg, 85%); ¹H NMR (400 MHz, DMSO): δ=12.89 (s, 1H), 7.90-7.62 (m, 2H), 7.41 (dt, *J* = 15.0, 7.5 Hz, 2H), 2.37 (s, 3H).

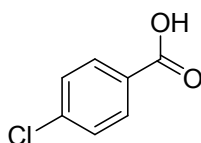


4-methoxybenzoic acid: (table 3, entry 5) According to representative procedure 3.2, 3-methylbenzyl alcohol (138 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate

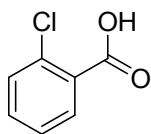
after neutralization with hydrochloric acid (146.0 mg, 96%); ^1H NMR (400 MHz, DMSO) δ = 12.63 (s, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H).



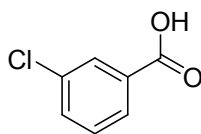
4-fluorobenzoic acid: (table 3, entry 6) According to representative procedure 3.2, 4-chlorobenzyl alcohol (126 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (119.0 mg, 85%); ^1H NMR (400MHz,DMSO) δ =12.98 (s, 1H), 8.01 (dd, J = 8.9, 5.6 Hz, 2H), 7.33 (t, J = 8.9 Hz, 2H)..



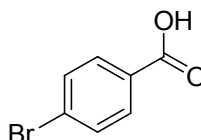
4-chlorobenzoic acid: (table 3, entry 7) According to representative procedure 3.2, 4-chlorobenzyl alcohol (142 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (153.0 mg, 98%); ^1H NMR (400 MHz, DMSO) δ = 13.20 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H).



2-chlorobenzoic acid: (table 3, entry 8) According to representative procedure 3.2, 2-chlorobenzyl alcohol (142 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (124.8 mg, 80%); ^1H NMR (400 MHz, DMSO): δ =13.38 (s, 1H), 7.87-7.66 (m, 1H), 7.66 -7.04 (m, 3H).

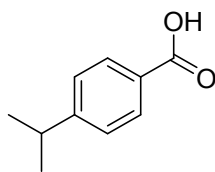


3-chlorobenzoic acid: (table 3, entry 9) According to representative procedure 3.2, 3-chlorobenzyl alcohol (142 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (143.5 mg, 92%); ^1H NMR (400 MHz, DMSO): δ =13.35 (s, 1H), 7.99-7.84 (m, 2H), 7.77-7.66 (m, 1H), 7.55 (t, J = 8.1 Hz, 1H).

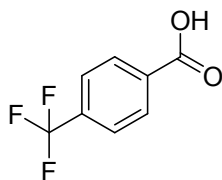


4-bromobenzoic acid: (table 3, entry 10) According to representative procedure 3.2, 4-bromobenzyl alcohol (186 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title

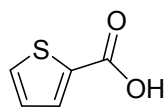
compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (171.1 mg, 92%); $^1\text{H NMR}$ (400 MHz, DMSO): $\delta=13.19$ (s, 1H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.5$ Hz, 2H).



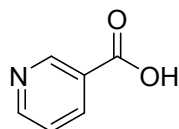
4-isopropylbenzoic acid: (table 3, entry 11) According to representative procedure 3.2, 4-isopropyl benzyl alcohol (150 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (155.6 mg, 91%); $^1\text{H NMR}$ (400 MHz, DMSO): $\delta=12.81$ (s, 1H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 2.96 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.22 (d, $J = 6.9$ Hz, 6H).



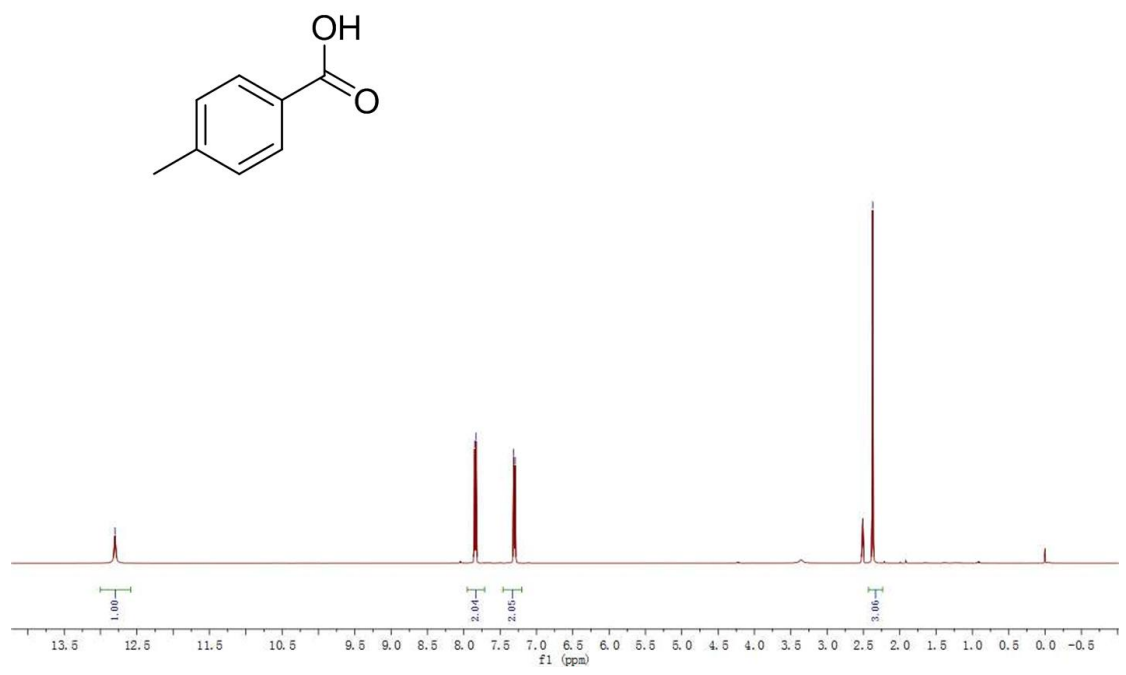
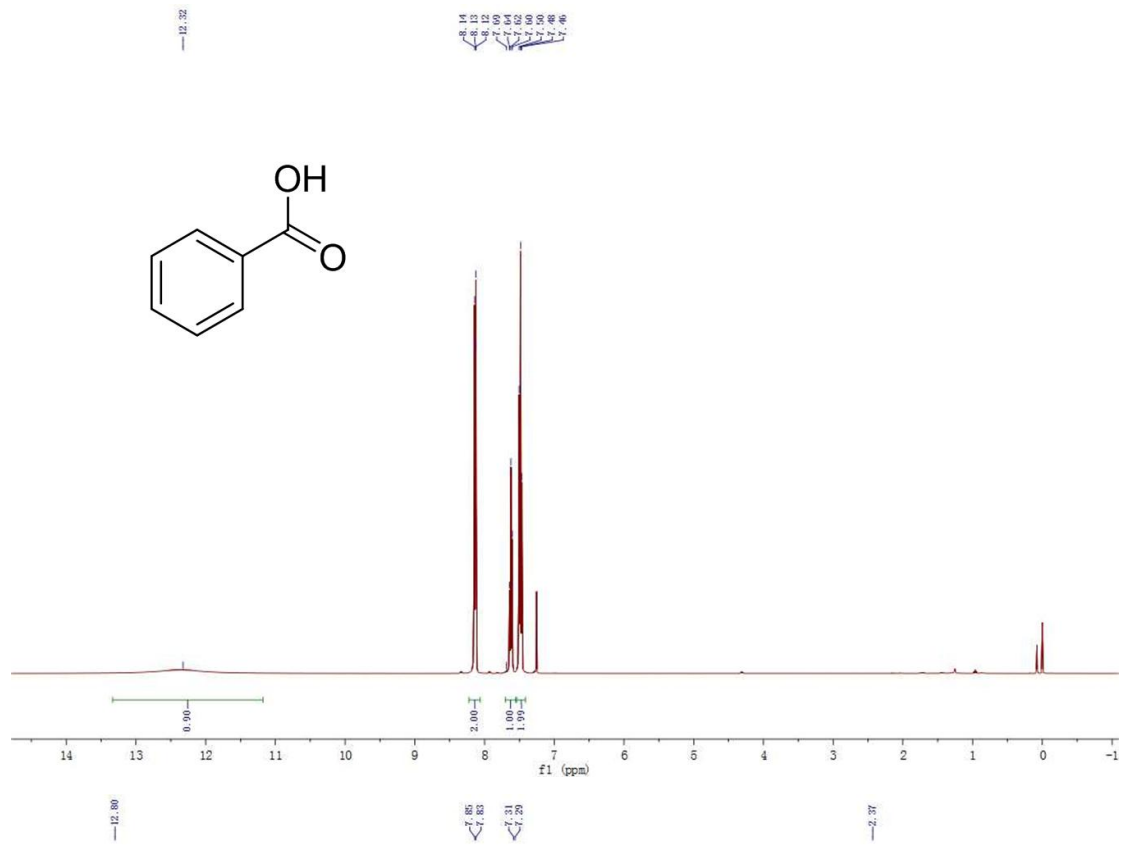
4-(trifluoromethyl)benzoic acid: (table 3, entry 12) According to representative procedure 3.2, 4-trifluoromethylbenzyl alcohol (176 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (171 mg, 90%); $^1\text{H NMR}$ (400 MHz, DMSO): $\delta = 3.46$ (s, 1H), 8.14 (d, $J = 8.1$ Hz, 2H), 7.88 (d, $J = 8.3$ Hz, 2H).

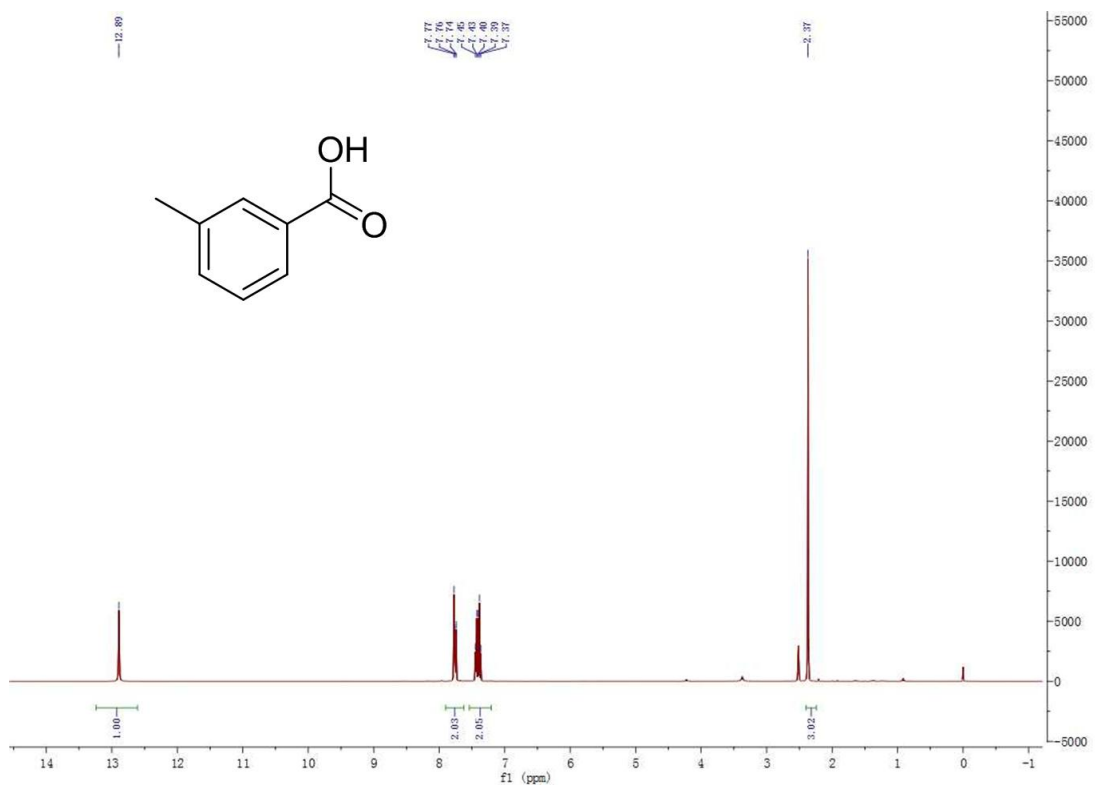
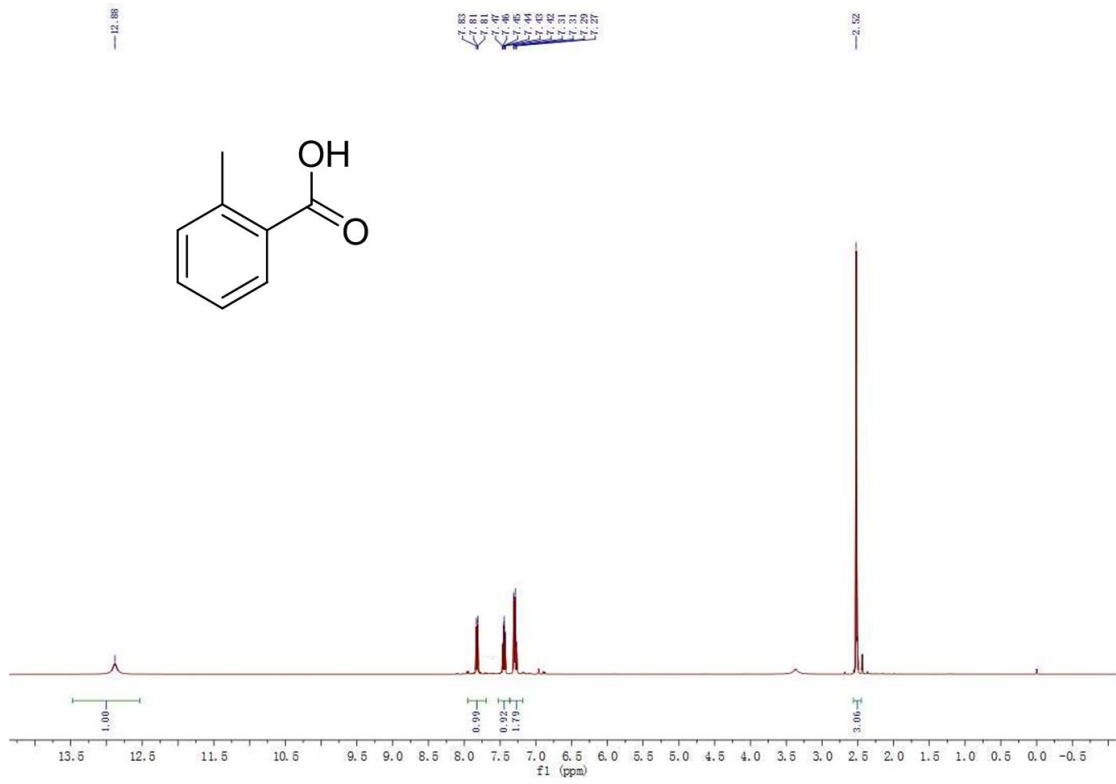


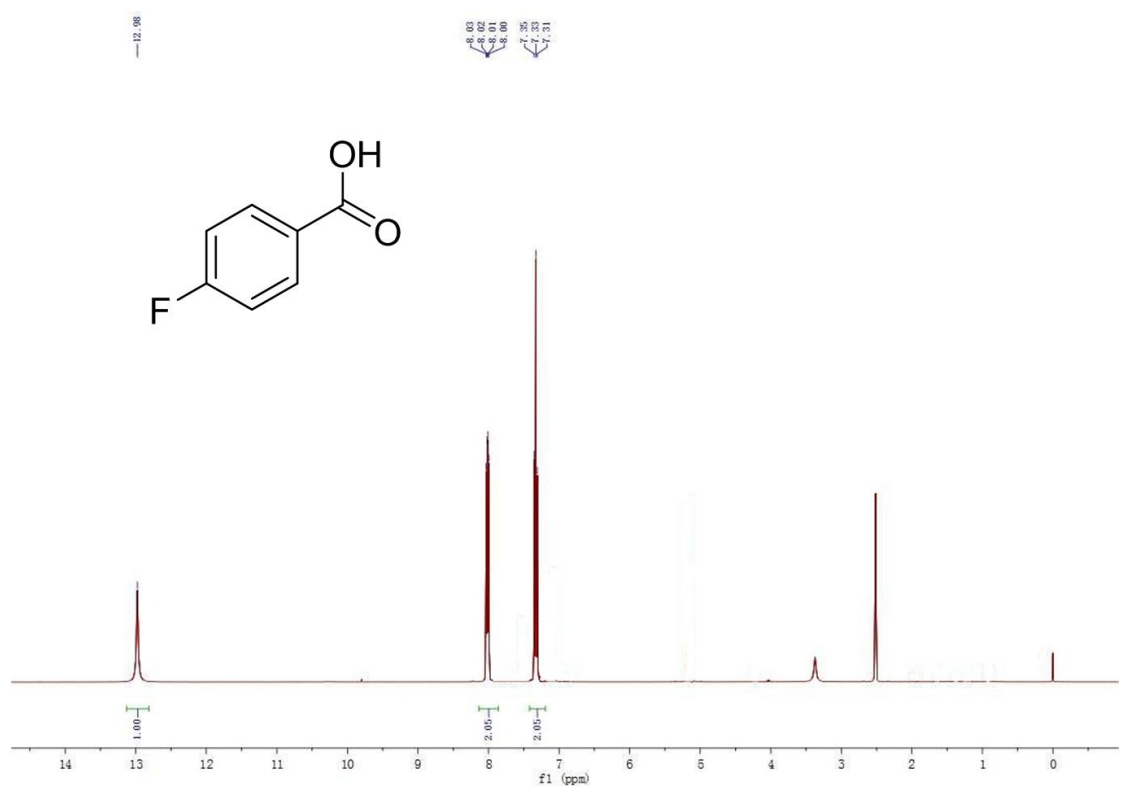
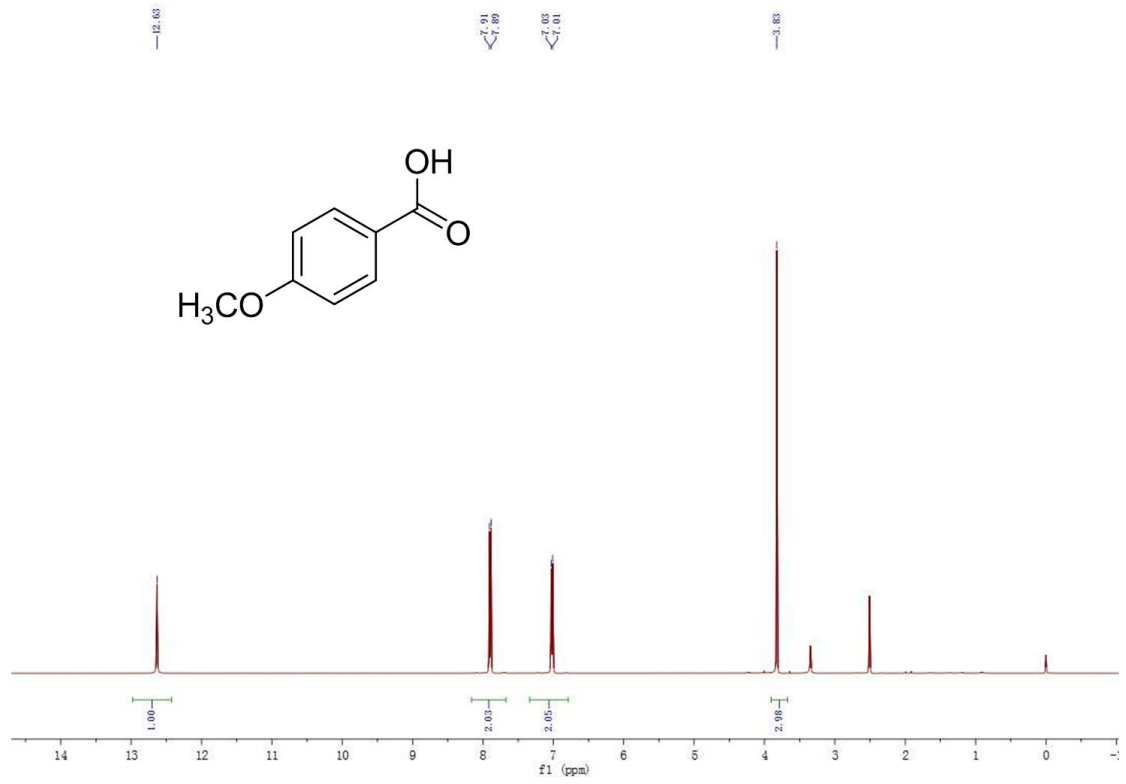
thiophene-2-carboxylic acid: (table 3, entry 13) According to representative procedure 3.2, thiophen-2-ylmethanol (114.6 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (109 mg, 85%); $^1\text{H NMR}$ (400 MHz, DMSO): δ 13.05 (s, 1H), 8.51-7.44 (m, 2H), 7.29-7.04 (m, 1H).

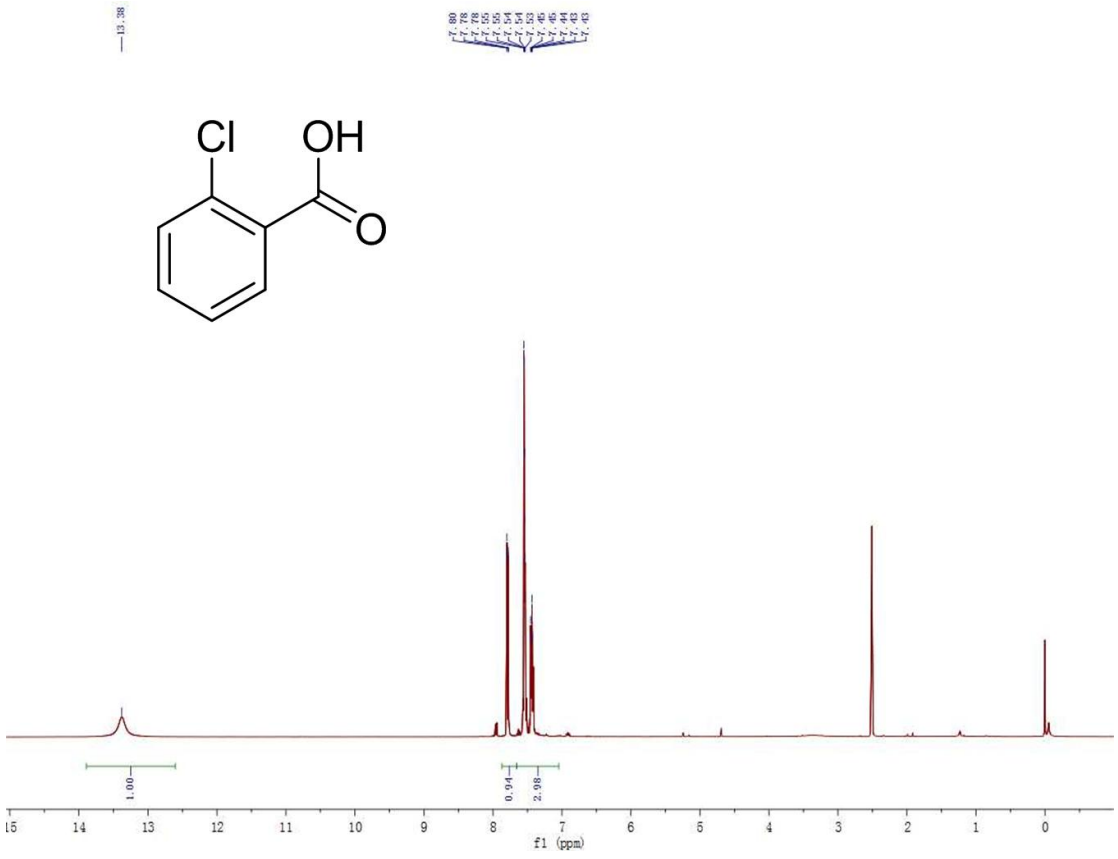
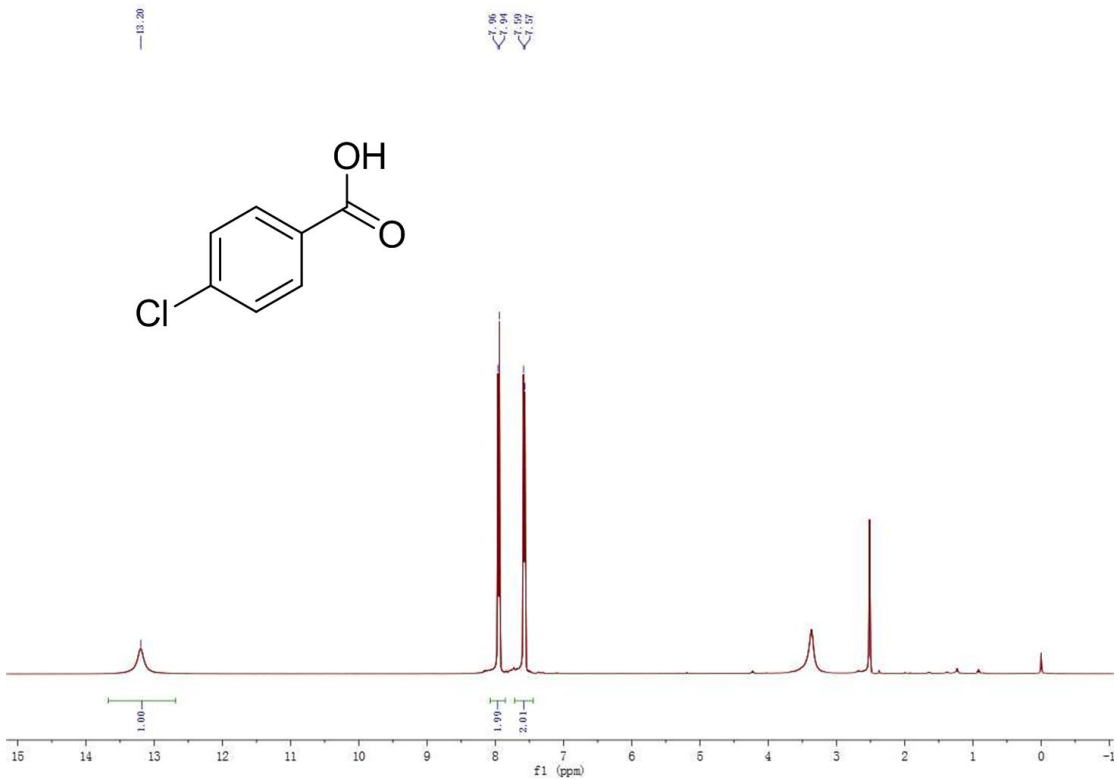


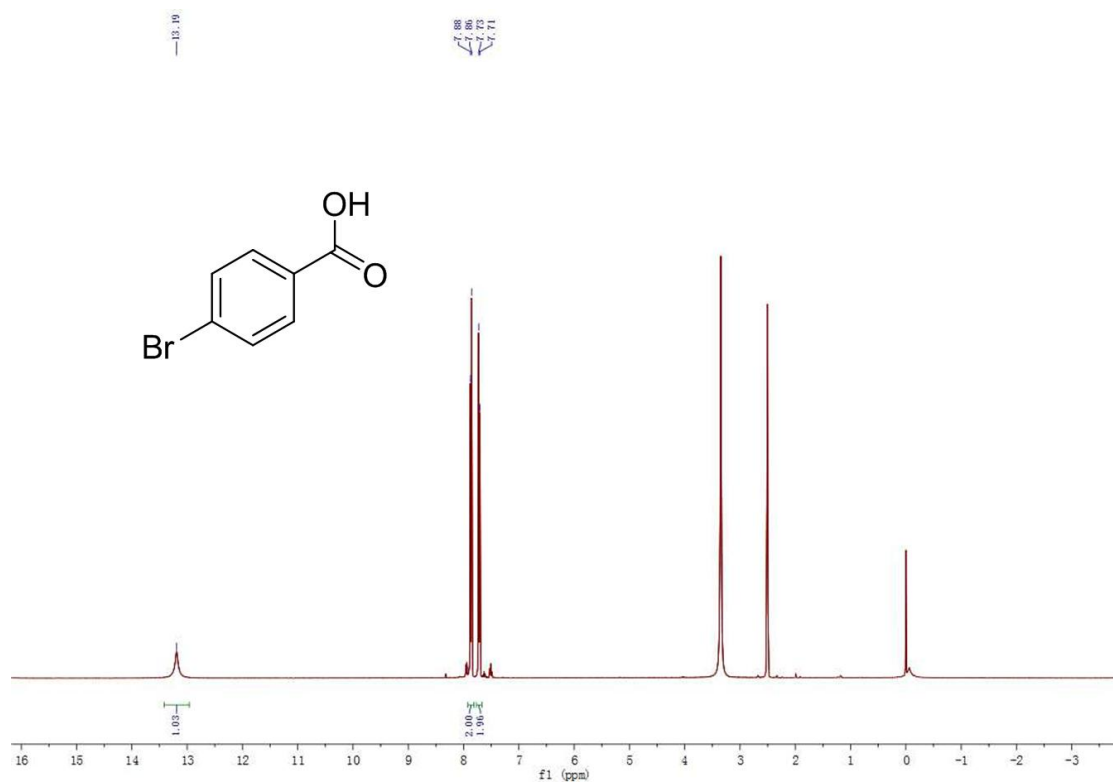
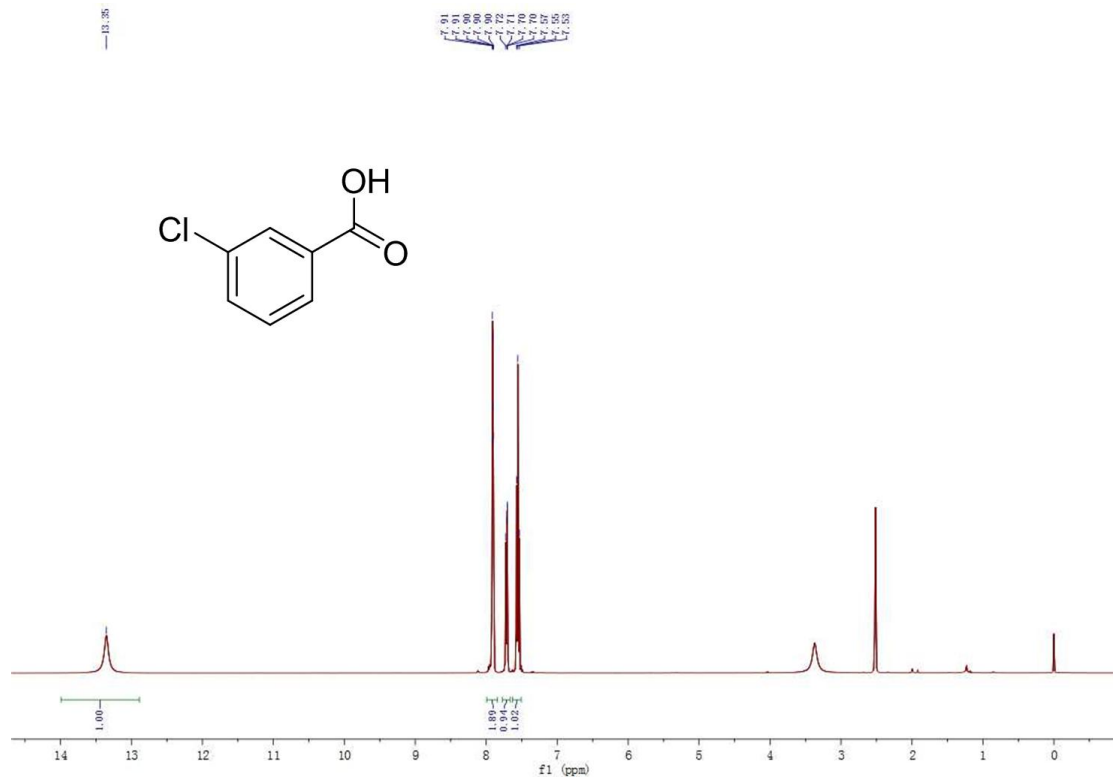
nicotinic acid: (table 3, entry 14) According to representative procedure 3.2, pyridin-3-ylmethanol (109 mg, 1 mmol), 100 mg RF-HT-C-1 and 2.0 mmol KOH were added into a 50 mL reaction tube and reacted at 100 °C under oxygen atmosphere for 12 h, the title compound was obtained and purified by extraction using water and ethyl acetate after neutralization with hydrochloric acid (109 mg, 85%); $^1\text{H NMR}$ (400 MHz, DMSO): δ 13.05 (s, 1H), 8.51-7.44 (m, 2H), 7.29-7.04 (m, 1H).

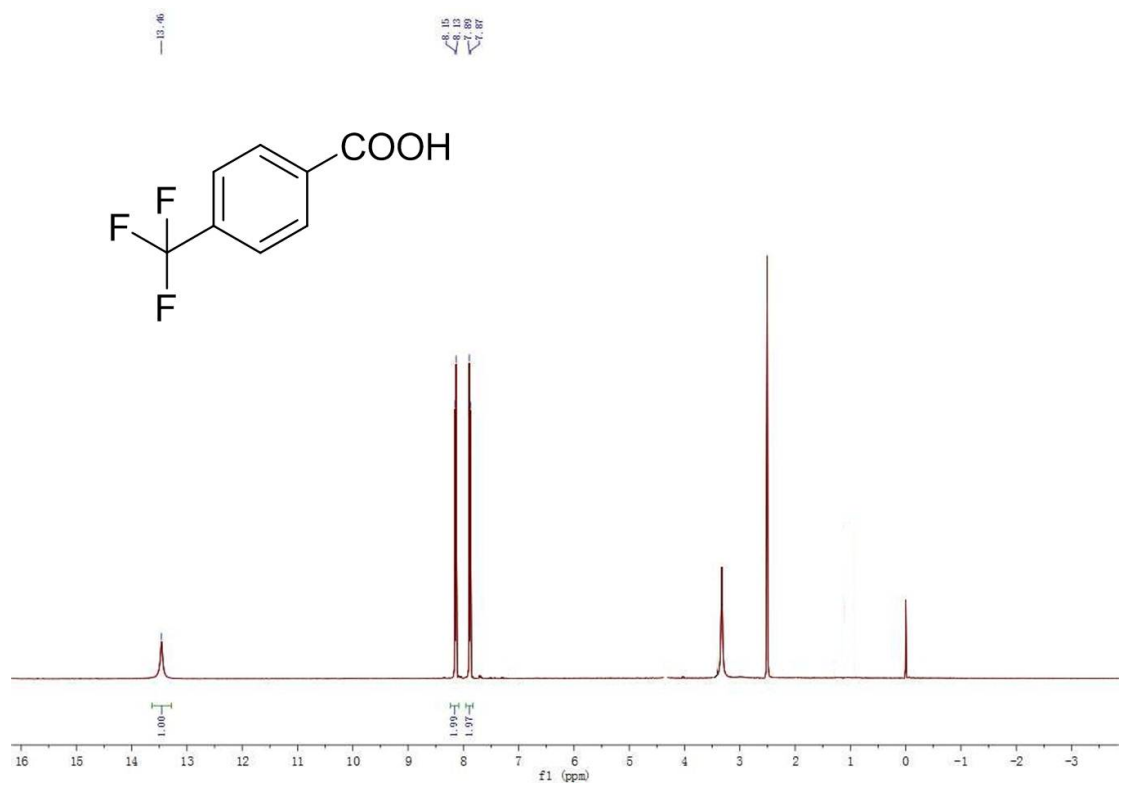
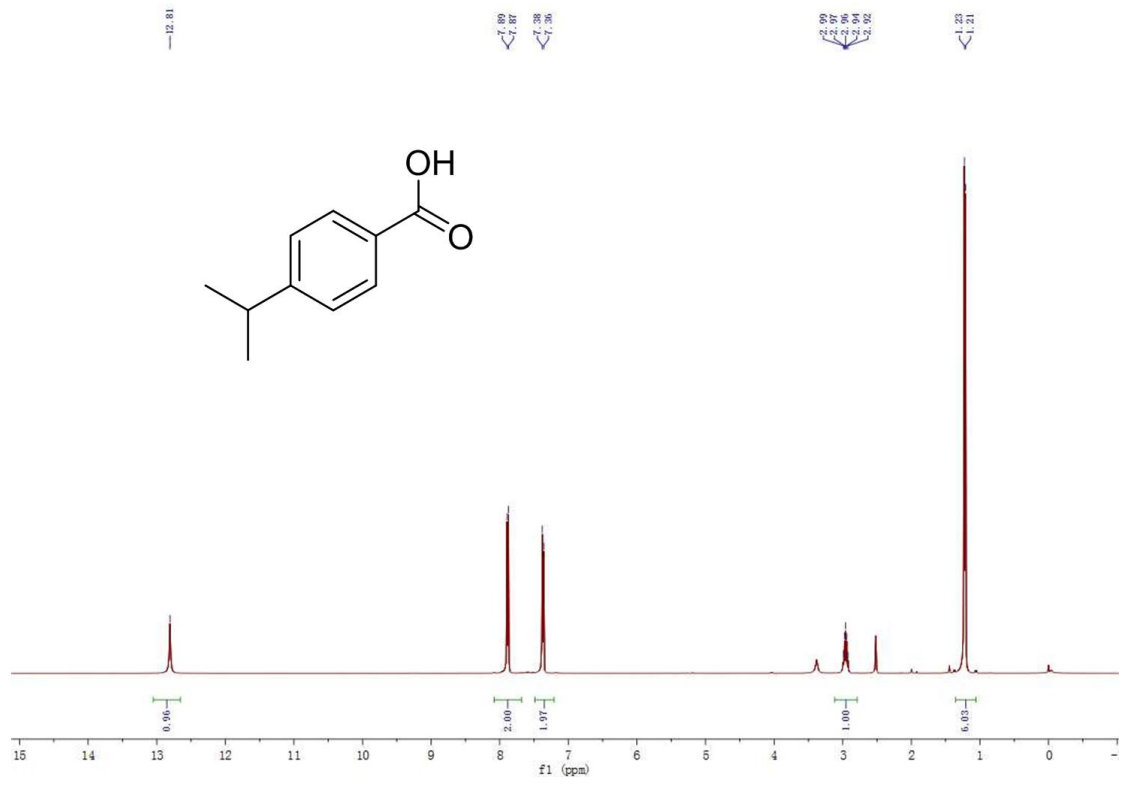












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