Supporting Information

Ni@ETS-10-catalyzed carboxylation of aryl and alkyl halides with CO_2 in water: a green strategy for CO_2 utilization

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Supporting Online Material

Content	Page no.
1. Chemicals and Methods	S2
2. Figures and Tables	S6
3. Analytical data	S15
4. References	S26
5. Spectra of these compounds	S27

1. Chemicals and Methods

Chemicals

All aryl and alkenyl halides used in parallel synthesis experiments were commercially available and used without any treatment unless otherwise noted. It is particularly important to note that the substrate for synthesis of **3s** possesses a pungent, offensive odor; therefore, it is mandatory to carry out both the reaction and work-up procedures in a well-ventilated fume hood. The water used as solvent was deionized water prepared in the laboratory. Ethyl acetate employed for extracting the organic phase was distilled prior to use to avoid product contamination. The petroleum ether used was the fraction with a boiling point range of 60–90 °C.

Methods

Prepare of KETS-10, RbETS-10 and CsETS-10 samples: The NaKETS-10 zeolite was synthesized according to our previous work.[S1] The METS-10 (M = K, Rb, and Cs) samples were obtained by cation-exchanged treatment of the as-synthesized NaKETS-10. Typically, 2.0 g as-synthesized ETS-10 was added into an aqueous solution (20 mL, 0.25 mol/L) of the potassium nitrate, rubidium nitrate and cesium nitrate, respectively. The mixture was stirred at 50 °C for 16 h. Then, the suspension was filtrated; the obtained solid was thoroughly washed with deionized water to remove the residual nitrate. The final solid was dried at 100 °C for 8 h, and calcined at 200 °C for 2 h. The resulting materials were named KETS-10, RbETS-10 and CsETS-10, respectively.

Prepare of Ni@ETS-10 catalyst: The target catalyst was prepared using the impregnation method. The typical procedure is as follows: an appropriate amount of $Ni(NO_3)_2{\cdot}6H_2O$ was weighed and dissolved in 1.15 g of deionized water. After thorough shaking to ensure complete dissolution, the solution was slowly dropped into a 25 mL beaker containing 1.0 g of ETS-10 zeolite. Upon completion of the addition, the beaker was gently swirled to uniformly wet the zeolite powder. The mixture was allowed to stand at room temperature for 10 h, followed by placement in an oven at 100

°C for 12 h. After removal from the oven, the sample was thoroughly ground using a mortar. The ground powder was then transferred into a ceramic boat and placed in a muffle furnace for calcination. The temperature was raised from room temperature to 450 °C with a heating rate of 2 °C/min, and held at 450 °C for 2.5 h.

Analysis of products: The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (60~90 °C) and ethyl acetate as eluents. Compounds described in the literature were characterized by comparing their ^{1}H spectra with the reported data. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Advance III (300 MHz, and 500 MHz) instruments at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform ($CDCl_3$) (0 ppm) unless otherwise stated. Data for ^{1}H NMR were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextet, m = multiplet, ovrlp = overlap), coupling constants (*J*, in Hz), and integration. All GC analyses were performed on an Agilent Technologies 7890B GC system with an FID detector.

SS **NMR, and IR experiments**

SS NMR experiment: The solid-state NMR spectroscopy (SS NMR) of the 3-methoxybenzyl chloride (**moc**) adsorbed catalyst samples were collected on Bruker AVANCE III 400-WB spectrometer. Pre-analyzed zeolite sample was outgassed at 400 °C for 4 h under dynamic vacuum up to a final pressure of 10^{-3} Pa. Then, the sample was cooling down to 100°C (reaction temperature), and it was exposed to **moc** vapor for 5 min. Subsequently, maintain in an oxygen atmosphere for 1.5 h to promote the activation process of **moc** on the active sites, and then evacuated at 60 °C for 2 h to eliminate physisorbed **moc**. The **moc** chemisorbed samples were noted as Ni@NaKETS-10-**moc**. The evacuated sample was immediately transferred into the rotors in a glove box. Then ^{1}H SS NMR and ^{13}C SS NMR spectra were recorded at 399.9 MHz under room temperature, using a VT CP-MAS Varian probe with 5 mm silicon nitride rotors spinning at 13 kHz. The p/2 rad pulses of 6 ms and a recycle delay of 5 s were used.

IR experiment: IR spectra of the 3-methoxybenzyl chloride (**moc**) chemisorbed Ni@NaKETS-10 sample (Ni@NaKETS-10-**moc**) were obtained on a Bruker TENSOR 27 infrared spectroscope equipped with a reactor cell. Prior to measurement, the Ni@NaKETS-10-**moc** sample was evacuated to 10^{-2} Pa at 320 ºC for 4 h, and then the temperature was decreased to 100 ºC (reaction temperature). The **moc** was introduced into the reactor cell by He flow (20 mL/min) for 10 s, and maintain in an oxygen atmosphere for 1.5 h to promote the activation process of moc on the active sites. Immediately, the spectrum (Ni@NaKETS-10-moc-0 min) was obtained in the absorbance mode and was shown after subtraction of a background spectrum for the Ni@NaKETS-10 sample, which was also obtained at 100 °C. After the Ni@NaKETS-10-moc sample was treated at 100 °C for 30 min, the spectrum of Ni@NaKETS-10-moc-30 min was obtained.

Activity test: The typical experimental procedure for the carboxylation of aryl and alkyl halides was as follows: Under O_2 stream, catalyst (10 mg), halide **1** (0.3 mmol), and deionized water (1.0 mL) were placed into a sealed tube (10 mL). The sealed tube was connected to two balloons, one filled with O_2 at 1 atm and the other with CO_2 at 1 atm. The mixture was heated to 80 °C and kept for 5 h with stirring (300 rpm) by a stir bar. The reaction temperature and stirring rate in the sealed tube were controlled using an IKA stirrer (model of RTC BS025). When the system was finished and cooled to room temperature, the reaction mixture was extracted four times with 5 mL of distilled ethyl acetate each time. The combined organic phases were evaporated to dryness, and the residue was purified by column chromatography. The isolated yield of the system was then calculated. The catalyst was finally separated by centrifugation and filtration from the solvent of water.

Scale-up synthesis of 2a, 3a: The scale-up experiment was carried out in a 50 mL three necked round-bottom flask. Under a flow of O_2, the halide, catalyst of 150 mg, magnetic stir bar, and water of 35 mL were added to the flask. Two Balloons filled with (O_2, 1 atm) and nitrogen (N_2, 1 atm) were attached to the two side necks. The flask was placed in an oil bath preheated to the designated temperature and allowed to react for 27 h (**2a**, at 80 °C) and 48 h (**3a**, at 100 °C), respectively. After the reaction, the product was isolated and purified following the same procedure as described in the activity test, and the isolated yield was then calculated. To minimize product loss during purification, the obtained reaction mixture was evenly divided into five portions, and each portion was purified separately.

Catalyst recycle test: After the reaction completion (Table 2, entry **2a**), the catalyst was collected carefully from the reaction mixture by filtration and washed with EA, and then kept at 80 °C for 5 h. After that, the catalyst was properly stored prior to the next cycle. And, any catalyst lost during the recycle process was replenished with fresh catalyst to maintain a total catalyst amount of 10 mg.

2. Figures and Tables

Figures

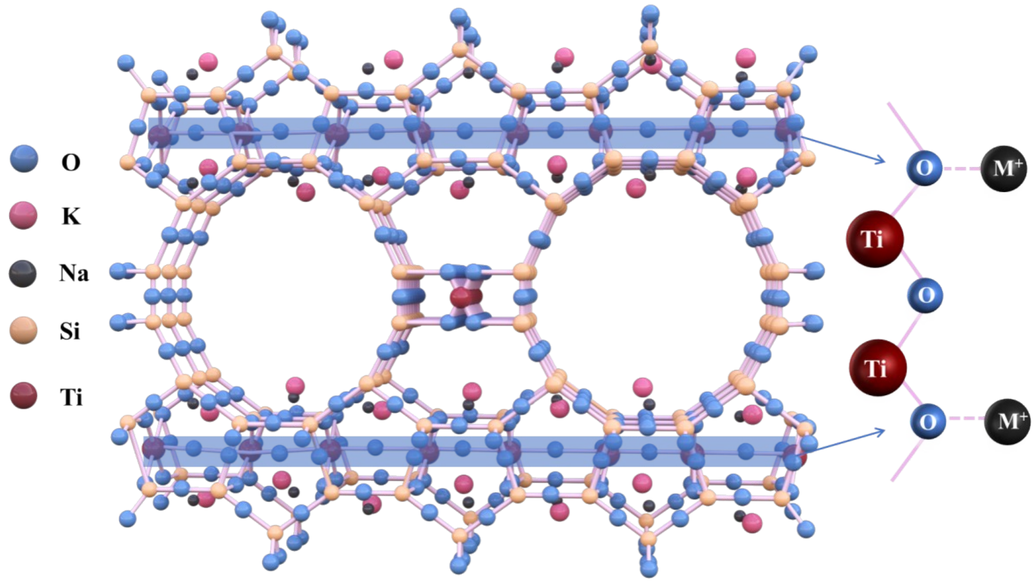


Fig. S1 The framework structure of NaKETS-10 zeolite.

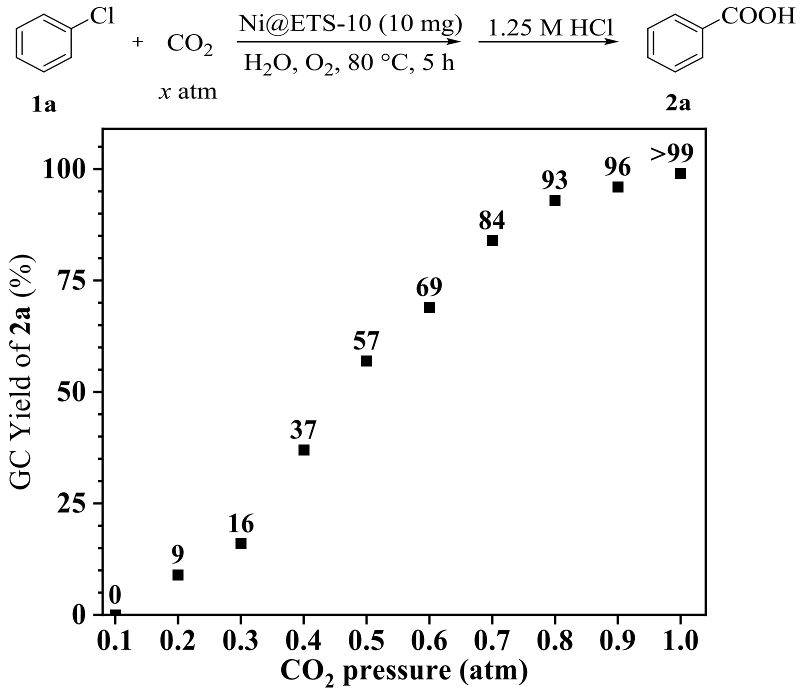


Fig. S2 Yield of **2a** as a function of CO_2 pressure (**1a** of 0.3 mmol, H_2O of 1 mL, O_2 of 1 atm).

Discussion: We employed the carboxylation of chlorobenzene **1a** with industrial-grade CO_2 (99.5% purity, purchased from Hefei Zhongyi Chemical Products Co., Ltd.) as a model reaction to investigate the effective CO_2 partial pressure range for this Ni@ETS-10 catalytic strategy. As shown in Fig. S2, when the CO_2 partial pressure in the reaction system is below 0.1 atm, the carboxylation reaction hardly occurs, indicating that the CO_2 fixation is difficult. With a gradual increase in CO_2 partial pressure, the GC yield of **2a** steadily increases, reaching > 99% when the partial pressure of CO_2 reaches 1.0 atm. These preliminary results suggest that for CO_2 fixation via the Ni@ETS-10-catalyzed carboxylation of halides with CO_2, the effective CO_2 partial pressure range is above 0.1 atm. To ensure product yield, all experiments in this work were carried out under a CO_2 partial pressure of 1 atm.

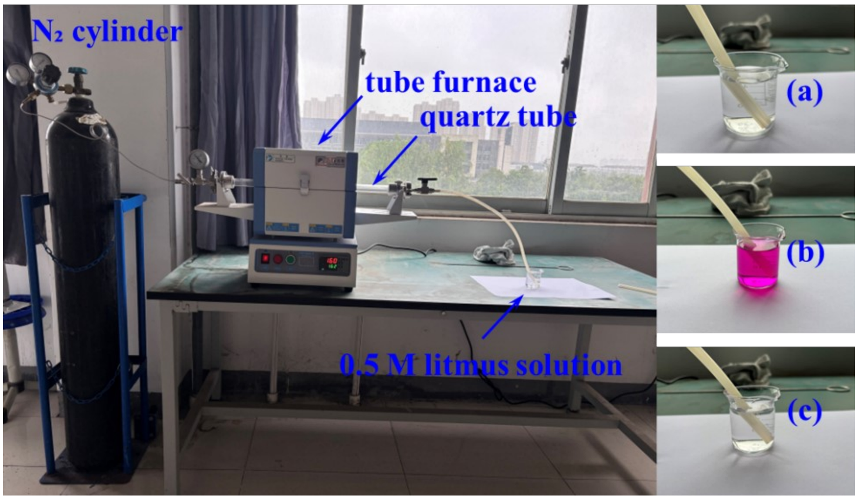
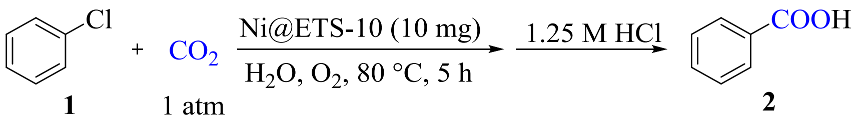


Fig. S3 The color-changing test of litmus solution.

Discussion: The litmus solution test was performed in a tube furnace equipped with a N_2 cylinder and tail gas collection apparatus. To better monitor the color change of the litmus solution, the catalysts from five parallel carboxylation runs of **1a** under standard conditions were collected. From the start of heating, the tail gas was directed through a plastic tube into a beaker containing 0.5 M litmus solution. During the calcination process, the colorless litmus solution (a) gradually turned red (b), indicating that the Cl atoms adsorbed on the surface of Ni oxide were removed in the form of Cl_2 gas. Notably, the red litmus solution rapidly bleached to colorless (c) after persisting for about 10 minutes, which is attributed to the strong oxidizing nature of the generated HClO.

Tables

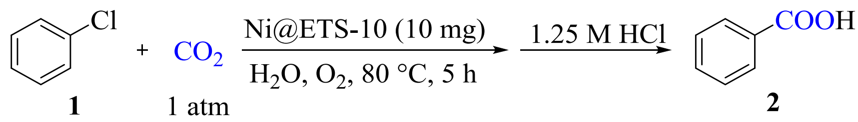
Table S1. Additive screening. [a]



Entry	Base	Yield (%) [b]	reference
1	no	97	this work
2	$MnCl_2$	39	S2
3	LiCl	34	S2, S3
4	$B(OPh)_3$	16	S2
5	LiBr	43	S2
6	$LiBF_4$	19	S2
7	Et_4NBr	39	S3
8	LiOAc	< 1	S3
9	NaOAc	59	S3
10	KOAc	17	S3
11	Li_2CO_3	31	S3
12	Et_4NCl	27	S3
13	Et_4NI	31	S3
14	PPh_3	22	S4
15	$P(4\text{-}MeOC_6H_4)_3$	17	S4

[a] Reaction conditions: **1** (0.3 mmol), solvent (1.0 mL), additive (2.0 equiv.), O_2 (1 atm). [b] isolated yield.

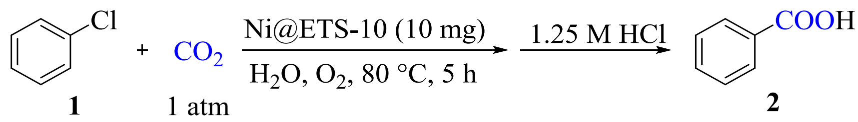
Table S2. Reductant screening. [a]



Entry	Reductant	Yield (%) [b]	reference
1	no	97	this work
2	DMAP-OED	< 1	S2
3	Cp^*_2Co	59	S2
4	Mn powder	37	S2, S3, S4
5	Zn powder	31	S2, S3, S4
6	Mg powder	15	S4
7	Mn-Zn powder	29	

[a] Reaction conditions: **1** (0.3 mmol), solvent (1.0 mL), reductant (1.5 equiv.), O_2 (1 atm). [b] isolated yield.

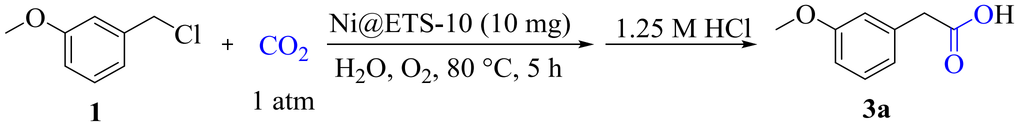
Table S3. Reductant and additive screening. [a]



Entry	Reductant	Additive	Yield (%) [b]
1	no	no	97
2	DMAP-OED	$MnCl_2$	trace
3	$Cp^*{}_2Co$	$MnCl_2$	15
4	Mn powder	$P(4\text{-}MeOC_6H_4)_3$	11
5	Zn powder	$P(4\text{-}MeOC_6H_4)_3$	9
6	Mg powder	Li_2CO_3	33
7	Mn-Zn powder	Li_2CO_3	37

[a] Reaction conditions: **1** (0.3 mmol), solvent (1.0 mL), reductant (1.5 equiv.), O_2 (1 atm). [b] isolated yield.

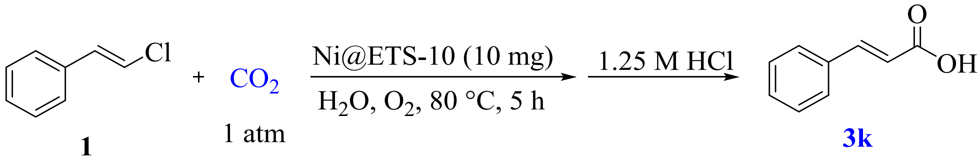
Table S4. The condition reoptimization of alkyl halide carboxylation reaction.



Entry	Alteration	Yield (%) [b]
1	no	37
2	reaction for 10 h	45
3	increasing the amount of catalyst to 20 mg	39
4	raising the reaction temperature to 90 °C	51
5	raising the reaction temperature to 100 °C	63
6	at 100 °C for 8 h	74
7	at 100 °C for 10 h	82
8	at 100 °C for 12 h	83

[a] Reaction conditions: **1** (0.3 mmol), solvent (1.0 mL), catalyst (10 mg), O_2 (1 atm). [b] isolated yield.

Table S5. The condition reoptimization of vinyl halide carboxylation reaction.



Entry	Alteration	Yield (%) [b]
1	no	29
2	reaction for 10 h	36
3	increasing the amount of catalyst to 20 mg	41
4	raising the reaction temperature to 90 °C	52
5	raising the reaction temperature to 100 °C	59
6	at 100 °C for 8 h	77
7	at 100 °C for 10 h	81
8	at 100 °C for 12 h	79

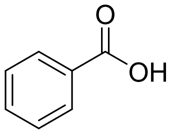
[a] Reaction conditions: **1** (0.3 mmol), solvent (1.0 mL), catalyst (10 mg), O_2 (1 atm). [b] isolated yield.

Table S6 The results of ICP-OES analysis.

Cycle number	Ni loading (%)		solvent after catalysis (μg/L)
	catalyst after catalysis	fresh catalyst	
1	2.35	2.47	0.31
2	2.45		0.29
3	2.34		0.33
4	2.33		0.37
5	2.38		0.22
6	2.41		0.13
7	2.34		0.29
8	2.35		0.37
9	2.38		0.31
10	2.37		0.12

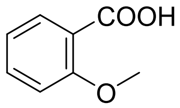
Discussion: The ICP results showing values of catalyst and solvent after catalysis, and fresh catalyst have been summarized in Table S6. The similar Ni loading of the catalyst before and after the reaction, together with the extremely low Ni concentration detected in the solvent after catalysis (0.12–0.37 μg/L), indicates that metal leaching was almost negligible during the process.

3. Analytical data



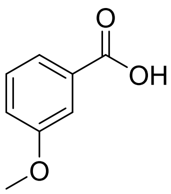
(2a) benzoic acid: yellow solid was obtained in 97% (from chloride) and 98% (from bromide) isolated yields, 122-123°C;[S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 12.29 (s, 1H), δ 8.13 (dd, J = 8.4, 1.3 Hz, 2H), δ 7.62 (tt, J = 7.5, 1.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H).



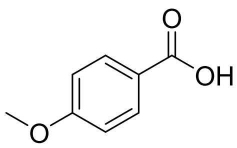
(2b) 2-methoxybenzoic acid: white solid was obtained in 98% (from chloride) and 97% (from bromide) isolated yields, 102-103°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 10.80 (s, 1H), δ 8.18 (dd, J = 7.8, 1.7 Hz, 1H), 7.59 (td, J = 7.9, 1.7 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 4.09 (s, 3H).



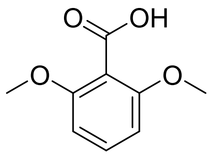
(2c) 3-methoxybenzoic acid: light yellow powder was obtained in 95% (from chloride) and 97% (from bromide) isolated yields, 106-107°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 (dt, J = 7.7, 1.3 Hz, 1H), 7.63 (dd, J = 2.7, 1.5 Hz, 1H), 7.39 (t, J = 7.9Hz, 1H), 7.17 (ddd, J = 8.3, 2.7, 1.0 Hz, 1H), 3.88 (s, 3H).



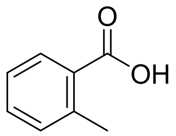
(2d) 4-methoxybenzoic acid: white powder was obtained in 94% (from chloride) and 96% (from bromide) isolated yields, 183-184°C; [S3]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.03 (m, 2H), 7.00 – 6.89 (m, 2H), 3.88 (s, 3H).



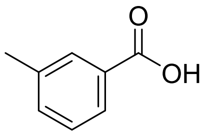
(2e) 2,6-dimethoxybenzoic acid: white crystal was obtained in 95% (from chloride) and 97% (from bromide) isolated yields, 186-187°C; [S4]

¹H NMR (300 MHz, Chloroform-d) δ 7.26 (t, J = 8.4 Hz, 1H), 6.53 (d, J = 8.4 Hz, 2H), 3.81 (s, 6H).



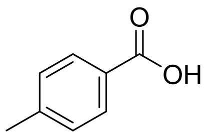
(2f) 2-methylbenzoic acid: light yellow crystal was obtained in 95% (from chloride) and 98% (from bromide) isolated yields, 103-104°C; [S3]

¹H NMR (400 MHz, Chloroform-d) δ 8.08 (dd, J = 8.3, 1.2 Hz, 1H), 7.46 (td, J = 7.4, 1.3 Hz, 1H), 7.29 (t, J = 7.3 Hz, 2H), 2.67 (s, 3H).



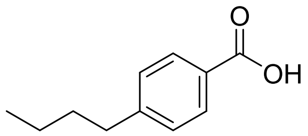
(2g) 3-methylbenzoic acid: light yellow crystal was obtained in 98% (from chloride) and 98% (from bromide) isolated yields, 109-112°C; [S3]

¹H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 7.7 Hz, 2H), 7.42 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 2.42 (s, 3H).



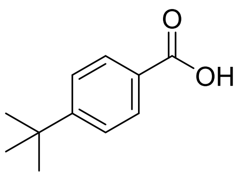
(2h) 4-methylbenzoic acid: light yellow powder was obtained in 98% (from chloride) and 98% (from bromide) isolated yields, 177-179°C; [S3]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).



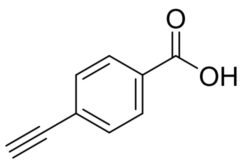
(2i) 4-butylbenzoic acid: white solid was obtained in 96% (from chloride) and 95% (from bromide) isolated yields, 102-103°C; [S4]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 1.63 (p, J = 7.7 Hz, 2H), 1.37 (h, J = 7.2 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).



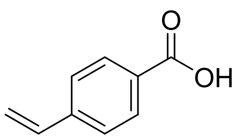
(2j) 4-(tert-butyl)benzoic acid: white solid was obtained in 97% (from chloride) and 98% (from bromide) isolated yields, 162-163°C; [S4]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 1.35 (s, 9H).



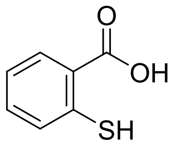
(2k) 4-ethynylbenzoic acid: light yellow crystal was obtained in 98% (from chloride) and 96% (from bromide) isolated yields, 199-200°C; [S5]

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.90 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 4.19 (s, 1H).



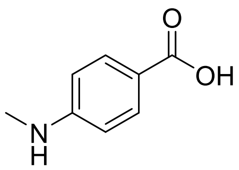
(2l) 4-vinylbenzoic acid: white solid was obtained in 96% (from chloride) and 97% (from bromide) isolated yields, 143-144°C; [S5]

^{1}H NMR (300 MHz, Chloroform-d) δ 8.00 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 5.33 (d, J = 10.9 Hz, 1H).



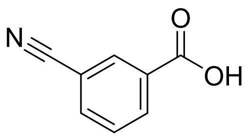
(2m) 2-mercaptobenzoic acid: light yellow crystal was obtained in 97% (from chloride) and 98% (from bromide) isolated yields, 163-165°C; [S6]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.14 (ddd, *J* = 8.0, 6.8, 1.6 Hz, 1H), 4.55 (s, 1H).



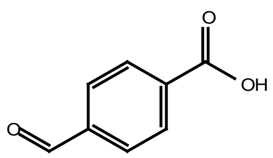
(2n) 4-(methylamino)benzoic acid: light gray solid was obtained in 94% (from chloride) and 94% (from bromide) isolated yields, 162-163°C; [S4]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.7 Hz, 1H), 6.50 (d, *J* = 8.9 Hz, 1H), 2.84 (s, 2H).



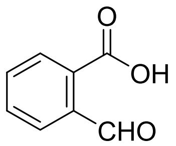
(2o) 3-cyanobenzoic acid: white solid was obtained in 79% (from chloride) and 82% (from bromide) isolated yields, 223-224°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.40 (s, 1H), 8.34 (d, J = 7.9 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H).



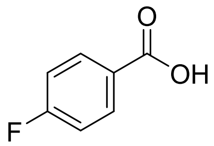
(2p) 4-formylbenzoic acid: yellow solid was obtained in 80% (from chloride) and 85% (from bromide) isolated yields, 245-247°C; [S5]

^{1}H NMR (400 MHz, Chloroform-d) δ 10.13 (s, 1H), 8.27 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H).



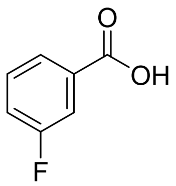
(2q) 2-formylbenzoic acid: white crystal was obtained in 76% (from chloride) and 81% (from bromide) isolated yields, 95-97°C; [S5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 5.53 (s, 1H).



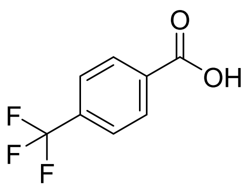
(2r) 4-fluorobenzoic acid： light yellow liquid was obtained in 84% (from chloride) and 83% (from bromide) isolated yields; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 – 8.07 (m, 2H), 7.21 – 7.10 (m, 2H).



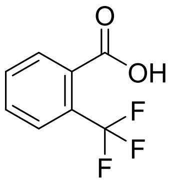
(2s) 3-fluorobenzoic acid： light yellow crystal was obtained in 81% (from chloride) and 79% (from bromide) isolated yields, 123-124°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (dt, J = 7.7, 1.3 Hz, 1H), 7.80 (ddd, J = 9.2, 2.7, 1.5 Hz, 1H), 7.47 (td, J = 8.0, 5.5 Hz, 1H), 7.33 (tdd, J = 8.3, 2.6, 0.9 Hz, 1H).



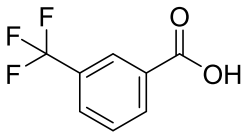
(2t) 4-(trifluoromethyl)benzoic acid: light gray crystal was obtained in 82% (from chloride) and 85% (from bromide) isolated yields, 219-220°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.23 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H).



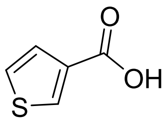
(2u) 2-(trifluoromethyl)benzoic acid: light yellow crystal was obtained in 83% (from chloride) and 83% (from bromide) isolated yields, 109-110°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 11.29 (s, 1H), 8.06 – 7.93 (m, 1H), 7.85 – 7.75 (m, 1H), 7.73 – 7.60 (m, 2H).



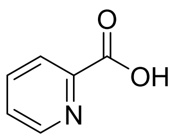
(2v) 3-(trifluoromethyl)benzoic acid: white crystal was obtained in 85% (from chloride) and 82% (from bromide) isolated yields, 105-106°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 11.27 (s, 1H), 8.40 (s, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H).



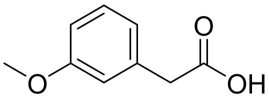
(2w) thiophene-3-carboxylic acid: white crystal was obtained in 98% (from chloride) and 97% (from bromide) isolated yields, 138-141°C; [S3]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.25 (dd, J = 3.0, 1.1 Hz, 1H), 7.58 (dd, J = 5.1, 1.1 Hz, 1H), 7.34 (dd, J = 5.1, 3.1 Hz, 1H).



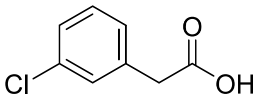
(2x) picolinic acid: white crystal was obtained in 96% isolated yields, 139-141°C; [S5]

^{1}H NMR (400 MHz, Chloroform-d) δ 12.13 (s, 1H), 9.02 – 8.68 (m, 1H), 8.30 (d, J = 7.8 Hz, 1H), 8.01 (td, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.77 – 7.45 (m, 1H).



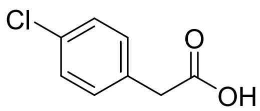
(3a) 2-(3-methoxyphenyl)acetic acid: white crystal was obtained in 82% (from chloride) and 78% (from bromide) isolated yields, 68-69°C; [S6]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 – 7.13 (m, 1H), 6.79 (d, J = 7.7 Hz, 1H), 6.78 – 6.73 (m, 2H), 3.72 (s, 3H), 3.55 (s, 2H).



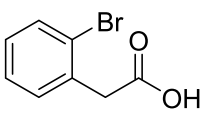
(3b) 2-(3-chlorophenyl)acetic acid： white crystal was obtained in 79% (from chloride) and 83% (from bromide) isolated yields, 78-79°C; [S6]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.17 (m, 3H), 7.12 – 7.06 (m, 1H), 3.56 (s, 2H).



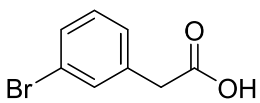
(3c) 2-(4-chlorophenyl)acetic acid: white powder was obtained in 74% (from chloride) and 76% (from bromide) isolated yields, 104-105°C; [S6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.2 Hz, 3H), 7.14 (d, *J* = 8.2 Hz, 3H), 3.54 (s, 3H).



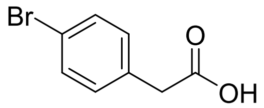
(3d) 2-(2-bromophenyl)acetic acid： white powder was obtained in 79% (from chloride) and 79% (from bromide) isolated yields, 104-105°C; [S6]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 (d, J = 7.9 Hz, 1H), 7.22 (dd, J = 5.0, 0.9 Hz, 2H), 7.13 – 7.05 (m, 1H), 3.77 (s, 2H).



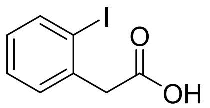
(3e) 2-(3-bromophenyl)acetic acid: white powder was obtained in 78% (from chloride) and 81% (from bromide) isolated yields, 101-102°C; [S6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 - 7.30 (m, 2H), δ 7.17 - 7.11 (m, 2H), 3.55 (s, 2H).



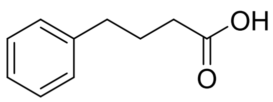
(3f) 2-(4-bromophenyl)acetic acid: light yellow powder was obtained in 86% (from chloride) and 85% (from bromide) isolated yields, 115-116°C; [S6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.01 Hz, 2H), 3.53 (s, 2H).



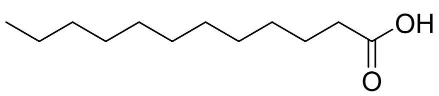
(3g) 2-(2-iodophenyl)acetic acid: light yellow powder was obtained in 72% (from chloride) and 75% (from bromide) isolated yields, 118-119°C; [S6]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (dd, J = 7.9, 1.0 Hz, 1H), 7.29 – 7.20 (m, 2H), 6.91 (ddd, J = 7.9, 6.9, 2.1 Hz, 1H), 3.78 (s, 2H).



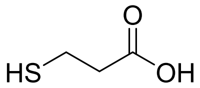
(**3h**) **4-phenylbutanoic acid**: white powder was obtained in 94% (from chloride) and 97% (from bromide) isolated yields, 50-51°C; [S5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 2H), 7.17 – 7.08 (m, 3H), 2.66 – 2.54 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.90 (p, *J* = 7.5 Hz, 2H).



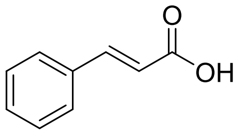
(3i) dodecanoic acid: white solid was obtained in 55% (from chloride) and 51% (from bromide) isolated yields, 44-45°C; [S5]

^{1}H NMR (300 MHz, Chloroform-d) δ 2.28 (t, J = 7.5 Hz, 2H), 1.56 (p, J = 7.1 Hz, 2H), 1.35 – 1.09 (d, J = 11.7 Hz, 16H), 0.81 (t, J = 6.3 Hz, 3H).



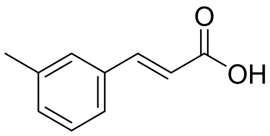
(3j) 3-mercaptopropanoic acid： colorless liquid was obtained in 52% (from chloride) and 47% (from bromide) isolated yields; [S5]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.80 - 2.57 (m, 4H), 1.61 (t, *J* = 7.8 Hz, 1H).



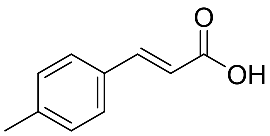
(3k) cinnamic acid: white powder was obtained in 81% (from chloride) and 83% (from bromide) isolated yields, 132-133°C; [S6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.76 (s, 1H), 7.73 (d, *J* = 15.8 Hz, 1H), 6.49 - 5.84 (m, 5H), 6.39 (d, *J* = 15.9 Hz, 1H).



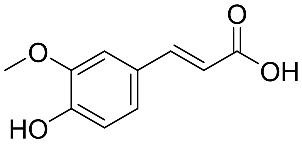
(3l) (E)-3-(m-tolyl)acrylic acid: white powder was obtained in 84% (from chloride) and 84% (from bromide) isolated yields, 115-116°C; [S6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.37 – 7.07 (m, 4H), 6.37 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 3H).



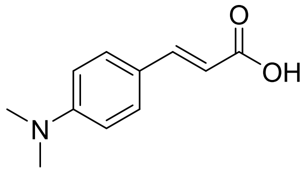
(3m) (E)-3-(p-tolyl)acrylic acid: white powder was obtained in 87% (from chloride) and 89% (from bromide) isolated yields, 197-198°C; [S6]

^{1}H NMR (300 MHz, Chloroform-d) δ 7.70 (d, J = 15.9 Hz, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 2.31 (s, 3H).



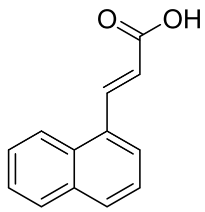
(3n) (E)-3-(4-hydroxy-3-methoxyphenyl)acrylic acid: light yellow powder was obtained in 67% (from chloride) and 70% (from bromide) isolated yields, 170-172°C; [S6]

^{1}H NMR (300 MHz, Chloroform-d) δ 7.64 (d, J = 15.9 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.99 (s, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.23 (d, J = 15.9 Hz, 1H), 5.83 (s, 1H), 3.88 (s, 3H).



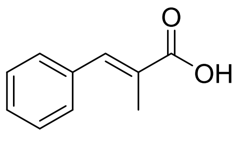
(3o) (E)-3-(4-(dimethylamino)phenyl)acrylic acid: yellow powder was obtained in 74% (from chloride) and 73% (from bromide) isolated yields, 224-226°C; [S6]

^{1}H NMR (300 MHz, Chloroform-d) δ 7.64 (d, J = 15.7 Hz, 1H), 7.38 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 8.5 Hz, 2H), 6.15 (d, J = 15.8 Hz, 1H), 2.96 (s, 5H).



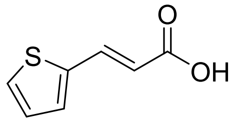
(3p) 3-(naphthalen-1-yl)acrylic acid: light yellow powder was obtained in 61% (from chloride) and 67% (from bromide) isolated yields, 211-212°C; [S6]

^{1}H NMR (300 MHz, Chloroform-d) δ 8.59 (d, J = 15.7 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.92 – 7.78 (m, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.59 – 7.41 (m, 3H), 6.51 (d, J = 15.7 Hz, 1H).



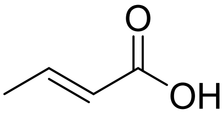
(3q) 2-methyl-3-phenylacrylic acid: light yellow powder was obtained in 72% (from chloride) and 72% (from bromide) isolated yields, 80-81°C; [S6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.43 – 7.21 (m, 5H), 2.08 (s, 3H).



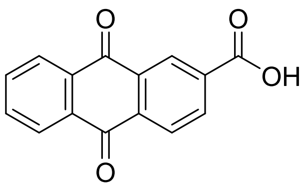
(3r) (E)-3-(thiophen-2-yl)acrylic acid: light yellow solid was obtained in 73% (from chloride) and 79% (from bromide) isolated yields, 147-148°C;[S6]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (d, J = 15.6 Hz, 1H), 7.36 (d, J = 5.1 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.01 (dd, J = 5.1, 3.6 Hz, 1H), 6.17 (d, J = 15.6 Hz, 1H).



(3s) (E)-but-2-enoic acid: white solid was obtained in 53% (from chloride) and 49% (from bromide) isolated yields, 71-72°C;[S5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.78 (dq, *J* = 15.5, 1.6 Hz, 1H), 1.85 (d, *J* = 8.4 Hz, 3H).



(5a) Anthraquinone-2-carboxylic Acid: white powder was obtained in 93% (from chloride) isolated yields, 287-288°C; [S7]

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.66 (s, 1H), 8.38 (d, *J* = 7.9 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.24 – 8.19 (m, 2H), 7.99 - 7.90 (m, 2H).

4. References

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[S2] D. J. Charboneau, G. W. Brudvig, N. Hazari, H. M. C. Lant and A. K. Saydjari, *ACS Catal*., 2019, **9**, 3228−3241.

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[S4] T. Fujihara, K. Nogi, T. H. Xu, J. Terao and Y. Tsuji, *J. Am. Chem. Soc*., 2012, **134**, 9106−9109.

[S5] G. Q. Sun, W. Zhang, L. L. Liao, L. Li, Z. H. Nie, J. G. Wu, Z. Zhang and D. G. Yu, *Nat. Commun*., 2021, **12**, 7086−7095.

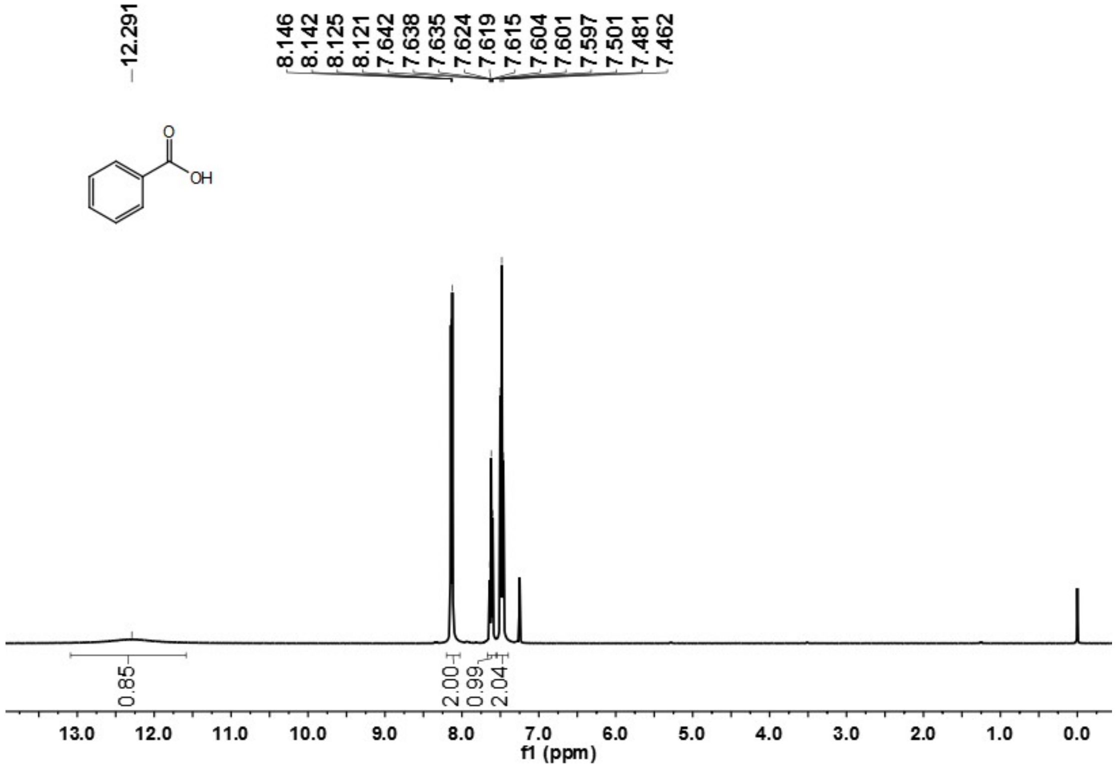
[S6] S. Chen, Z. Shao, Z. Fang, Q. Chen, T. Tang, W. Fu and T. Tang, *J. Catal*., 2016, **338**, 38-46.

[S7] B. S. Park, H. K. Lee, S. E. Lee, X. L. Piao, G. R. Takeoka, R. Y. Wong, Y. Rosalind, Y. J. Ahn, J. H. Kim, *J. Agric. Food Chem*., 2005, 4, 1152−1157.

5. Spectra of these compounds

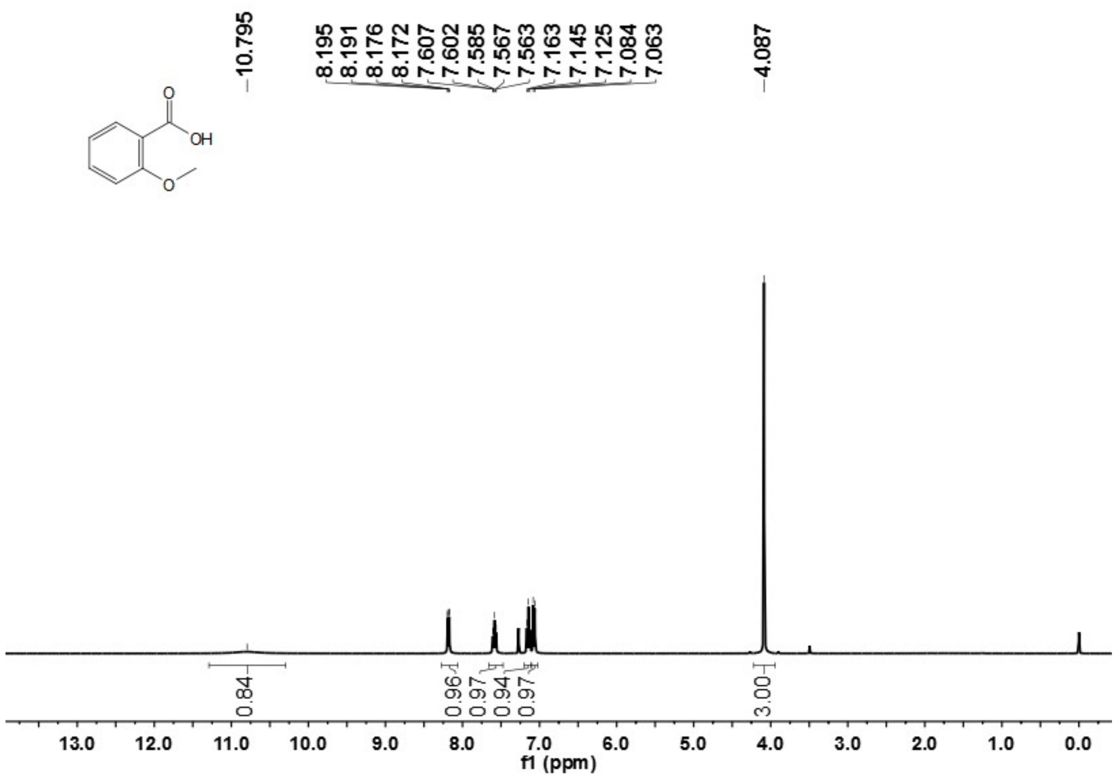
2a

^{1}H NMR



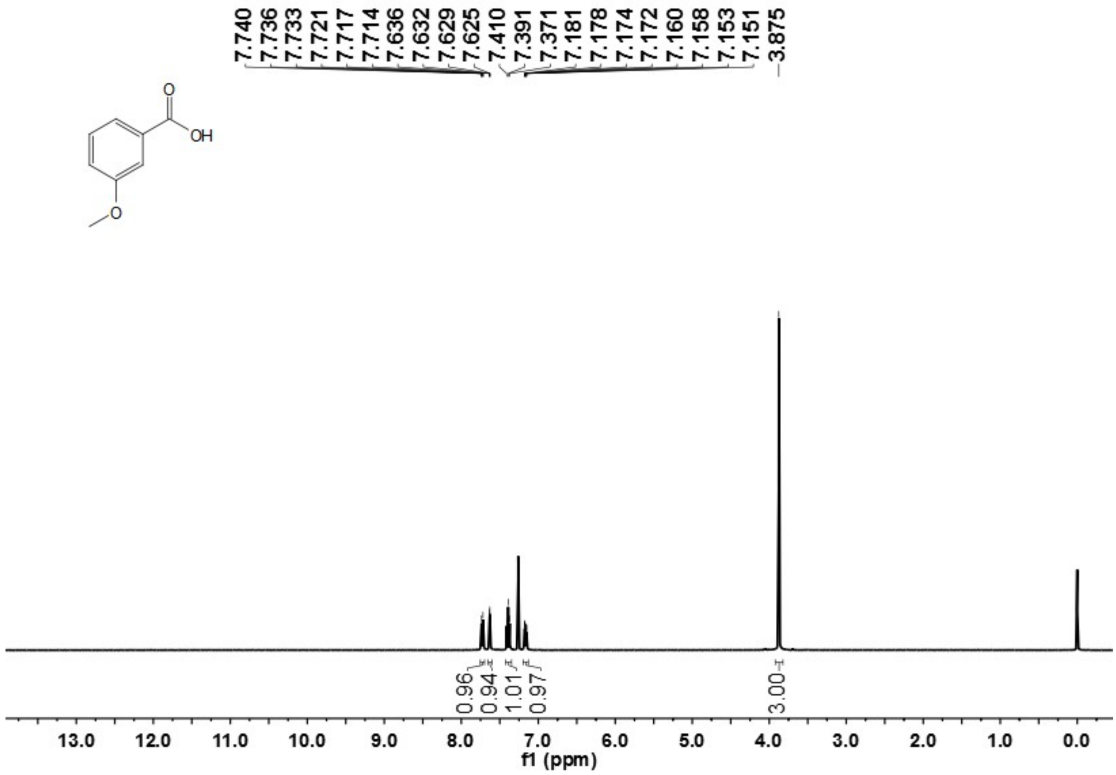
2b

^{1}H NMR



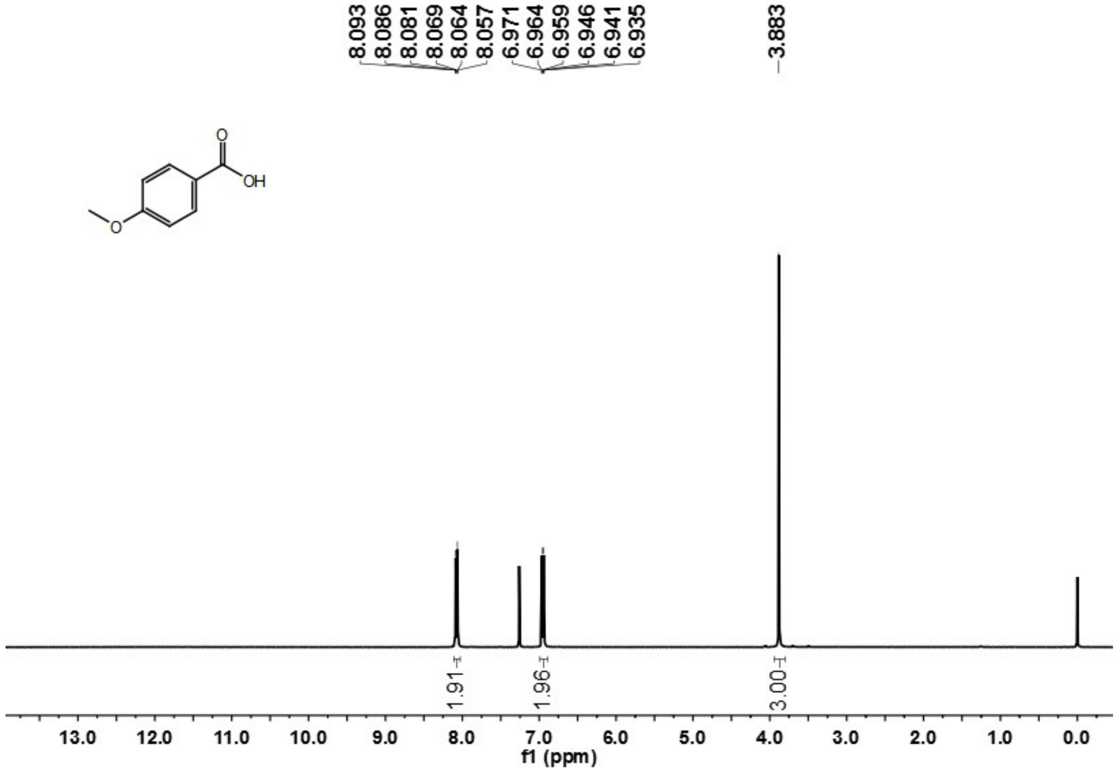
2c

[1]H NMR



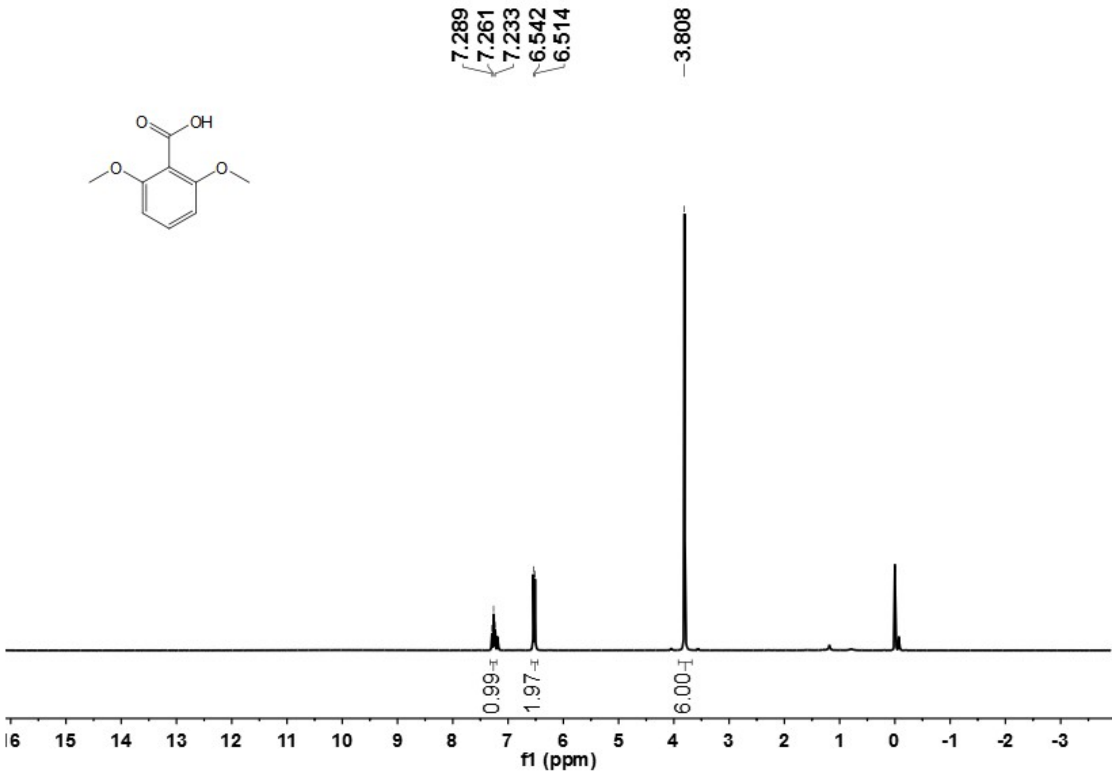
2d

1H NMR



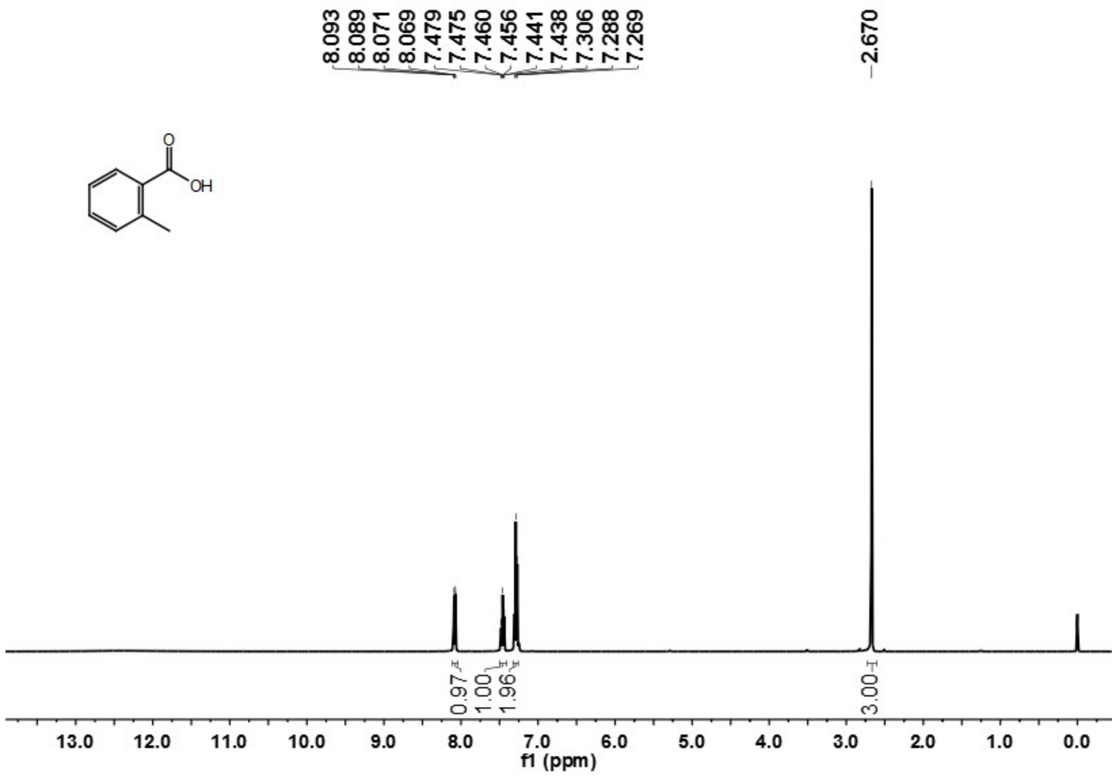
2e

^{1}H NMR



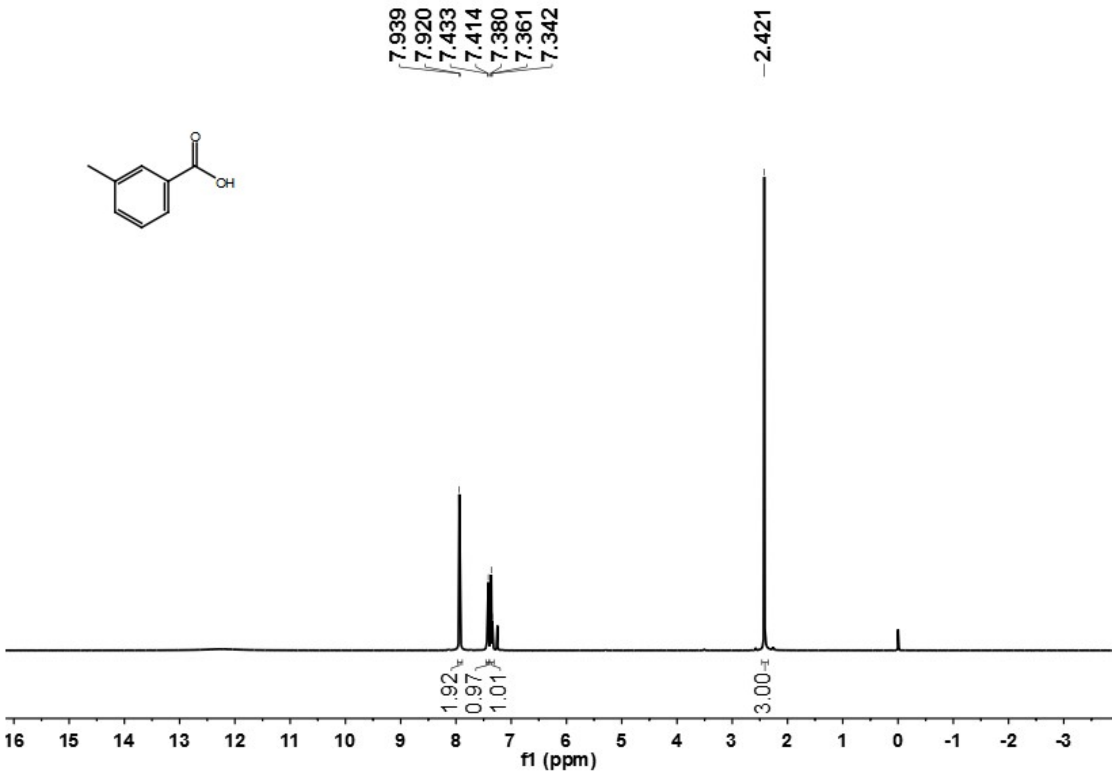
2f

^{1}H NMR



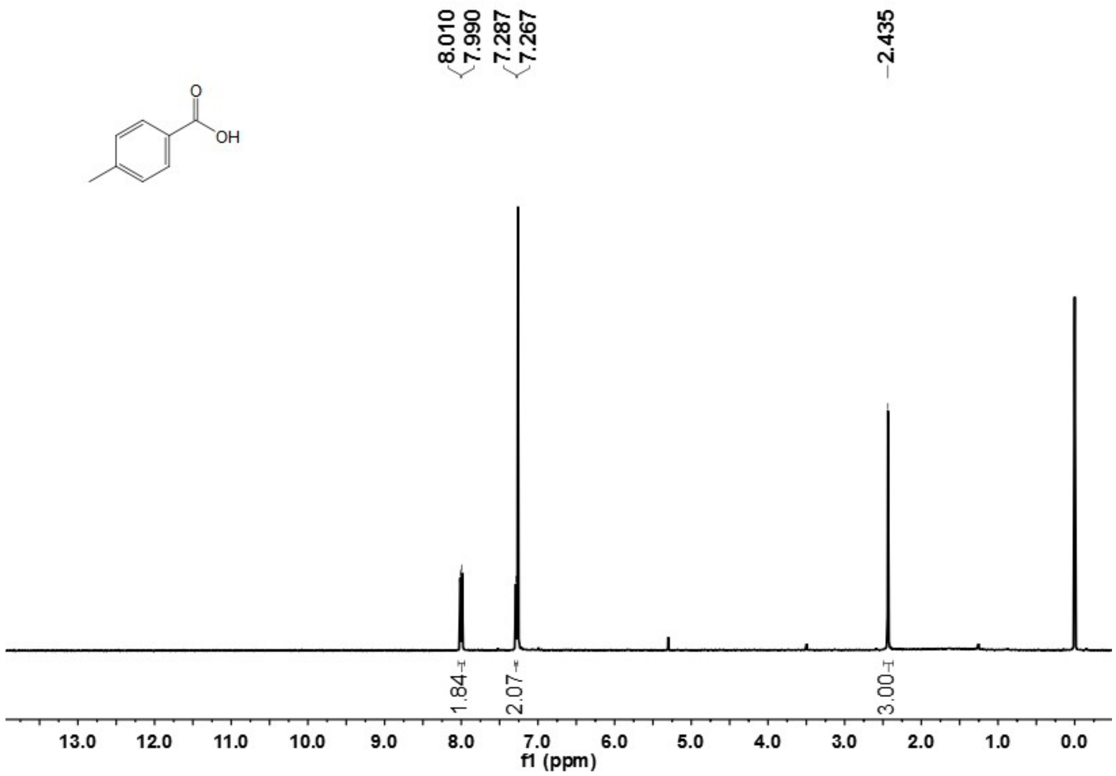
2g

[1]H NMR



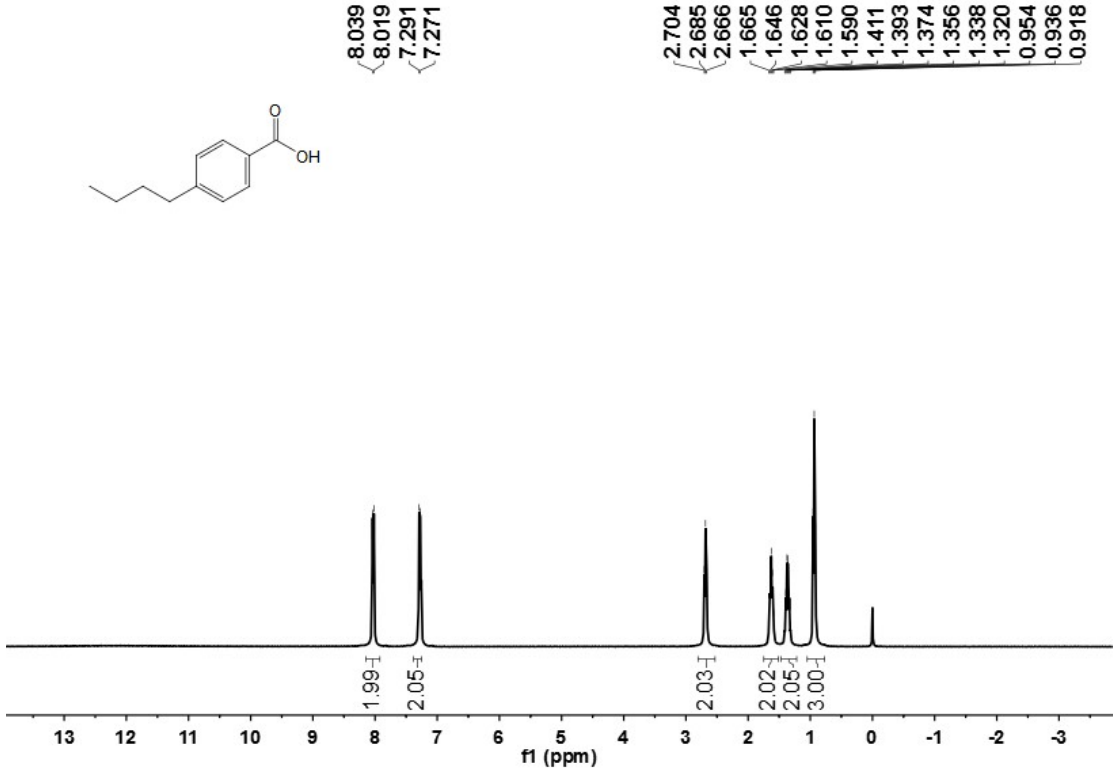
2h

[1]H NMR



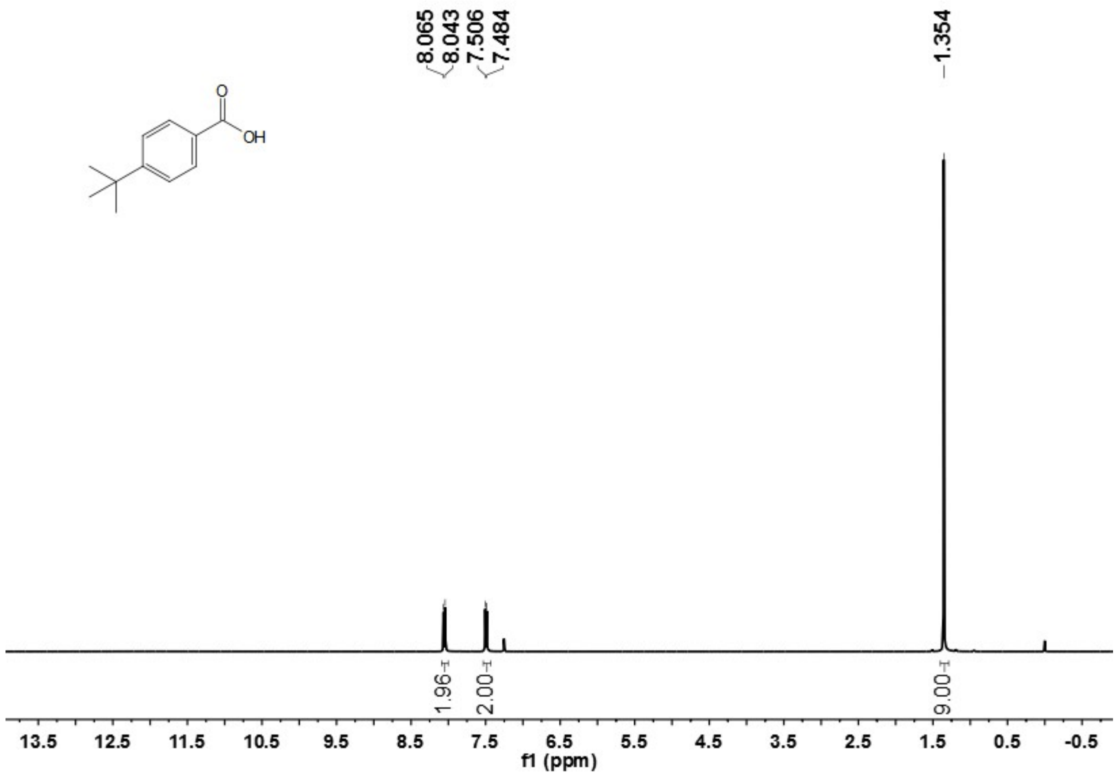
2i

[1]H NMR



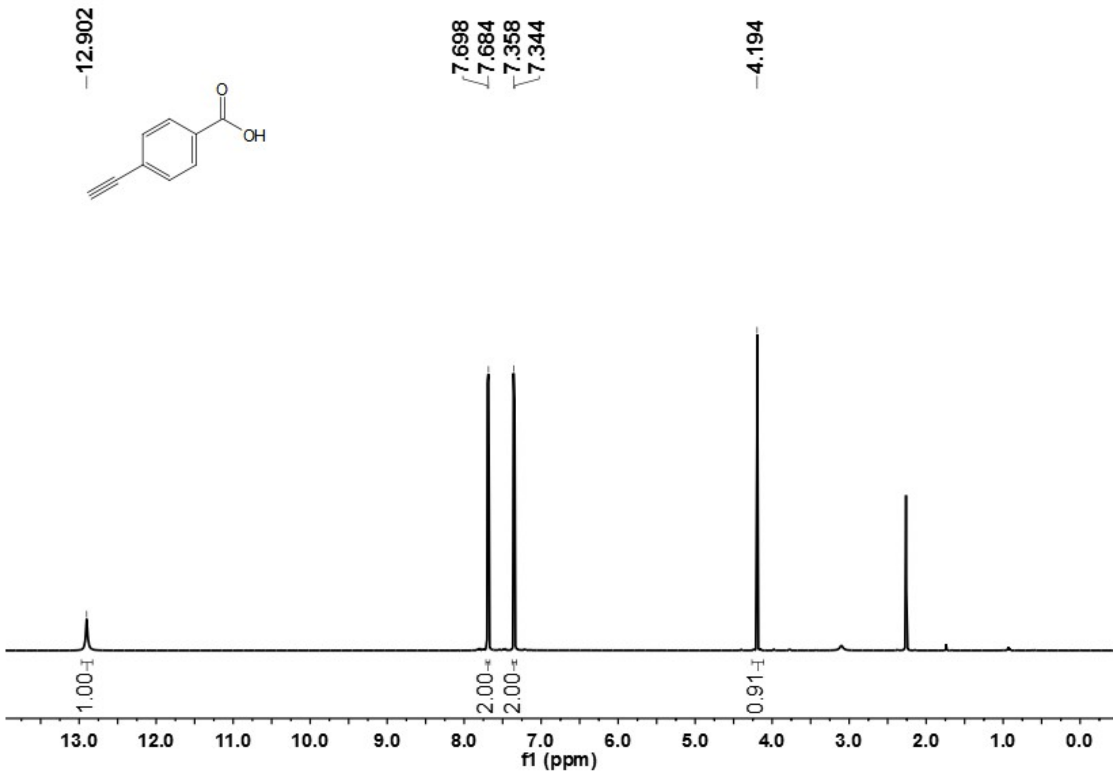
2j

[1]H NMR



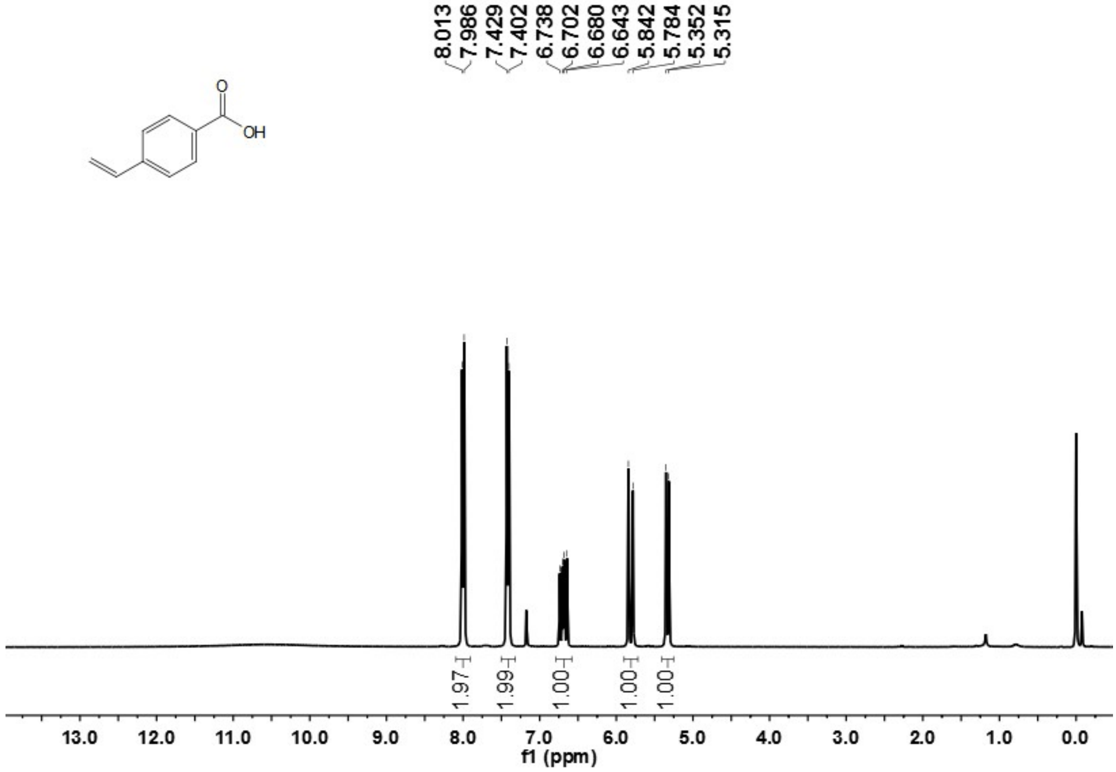
2k

^{1}H NMR



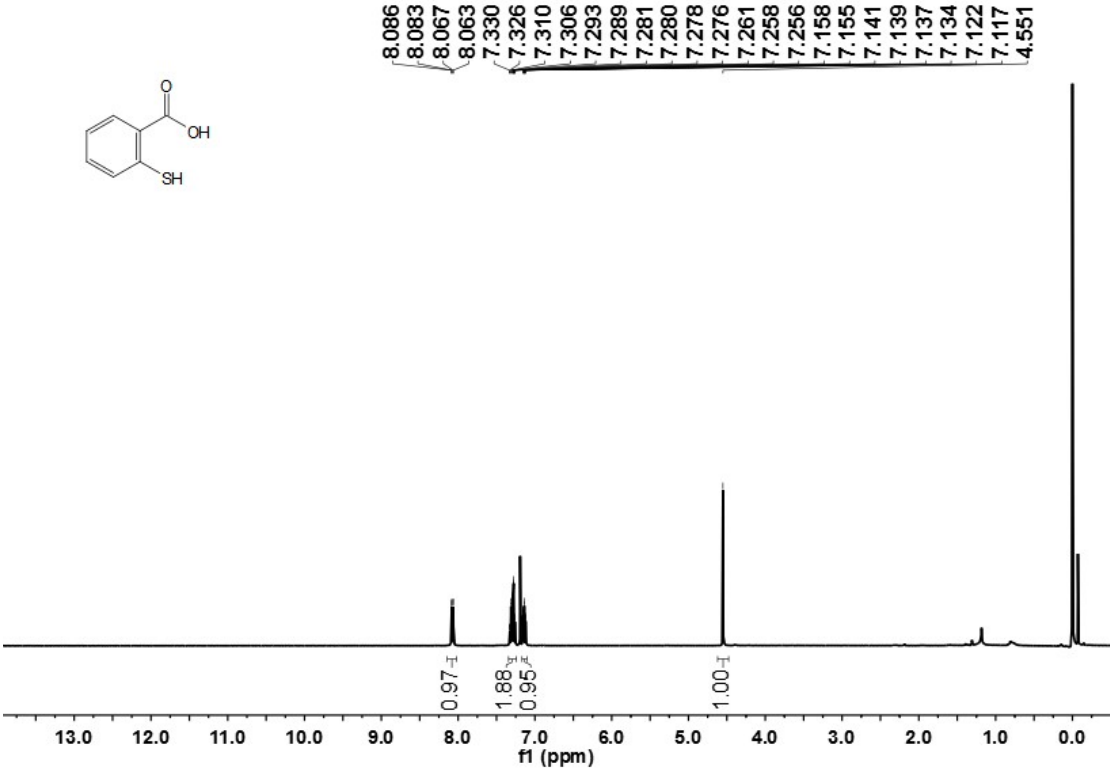
2l

^{1}H NMR



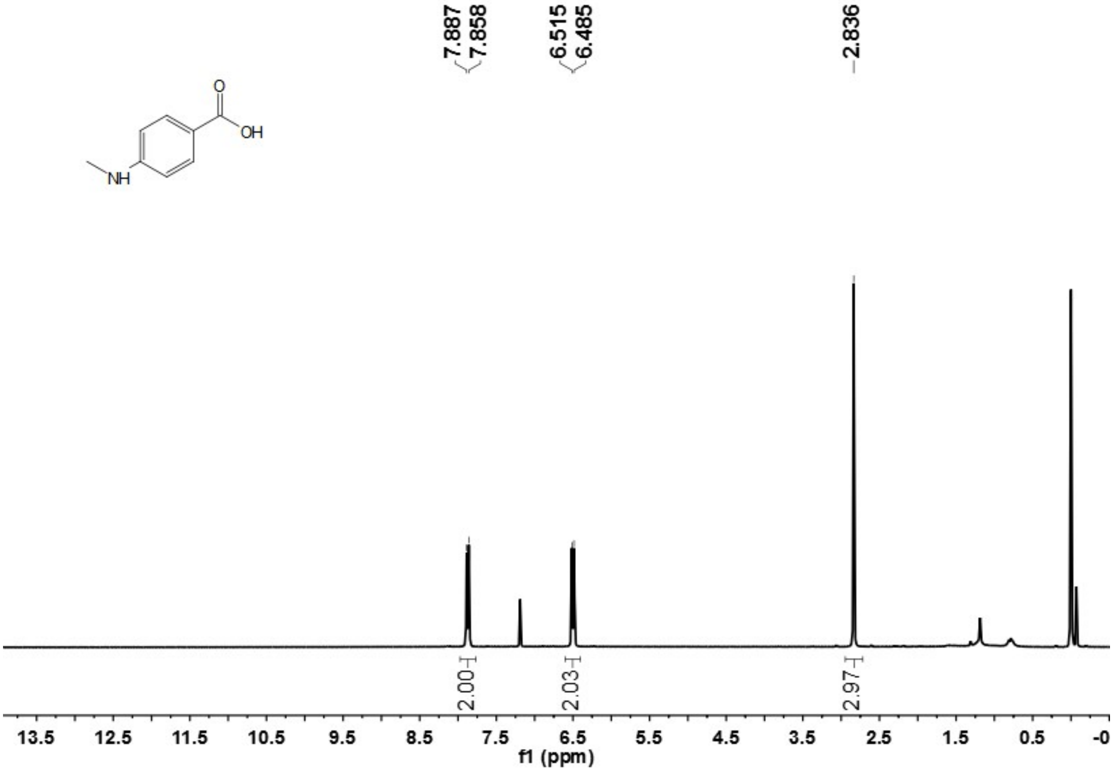
2m

^{1}H NMR



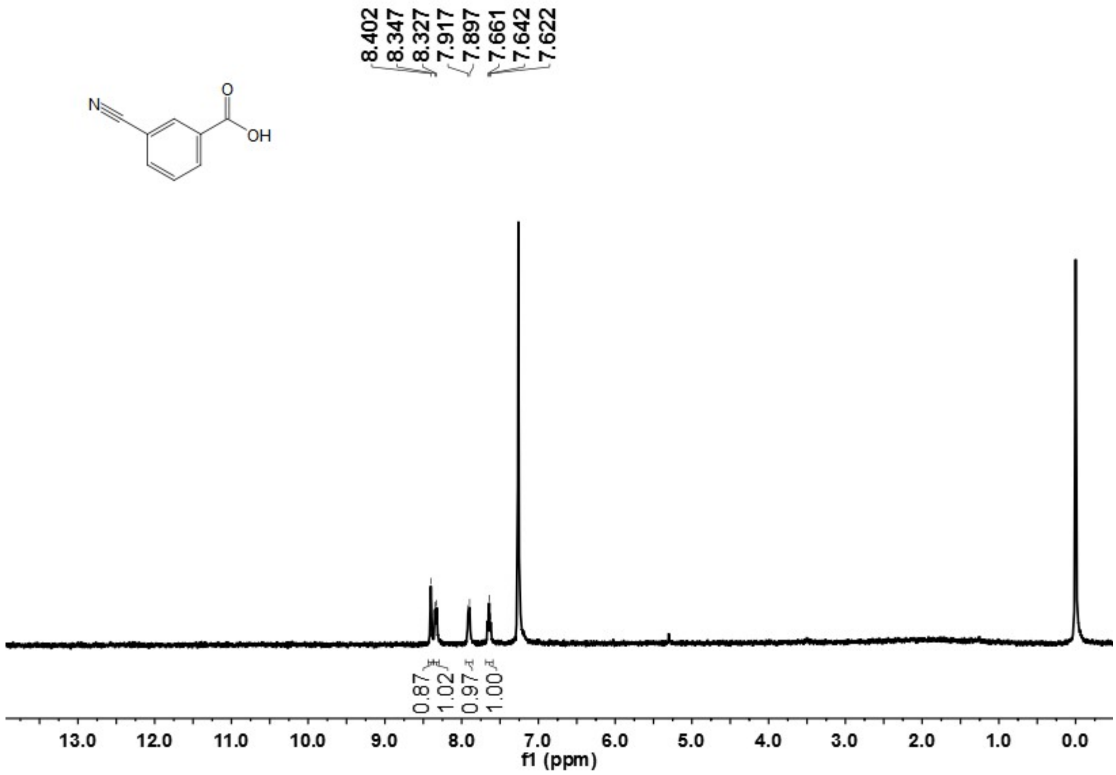
2n

^{1}H NMR



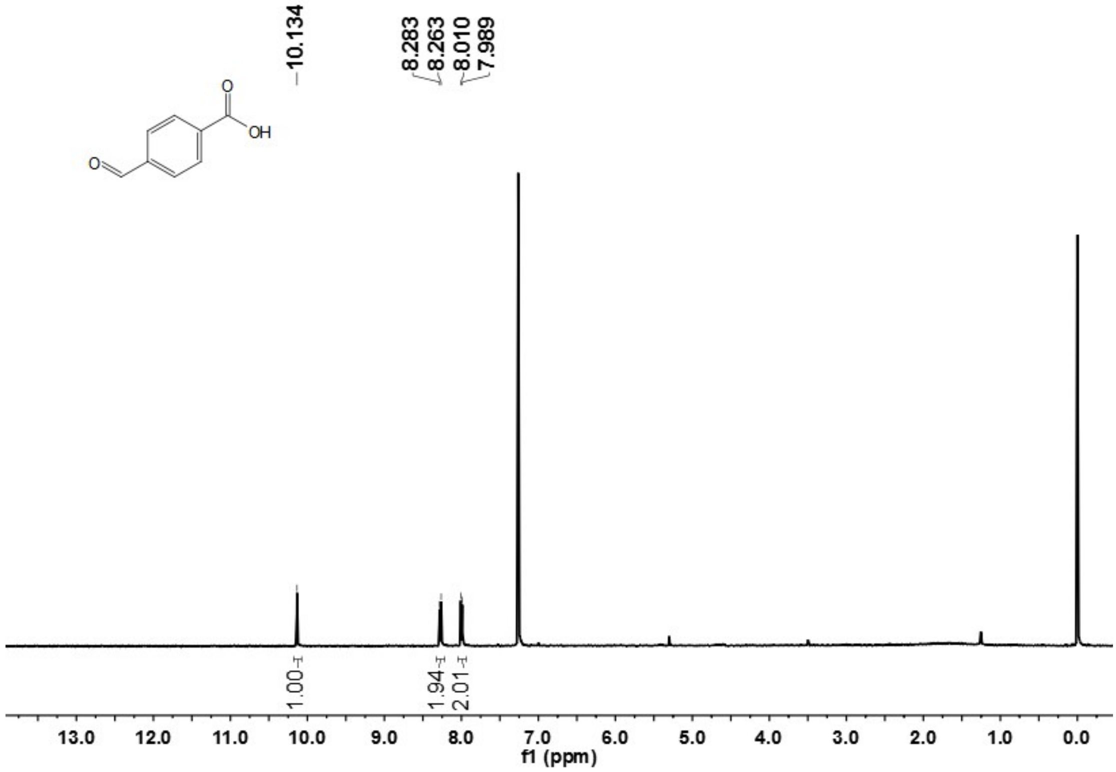
2o

^{1}H NMR



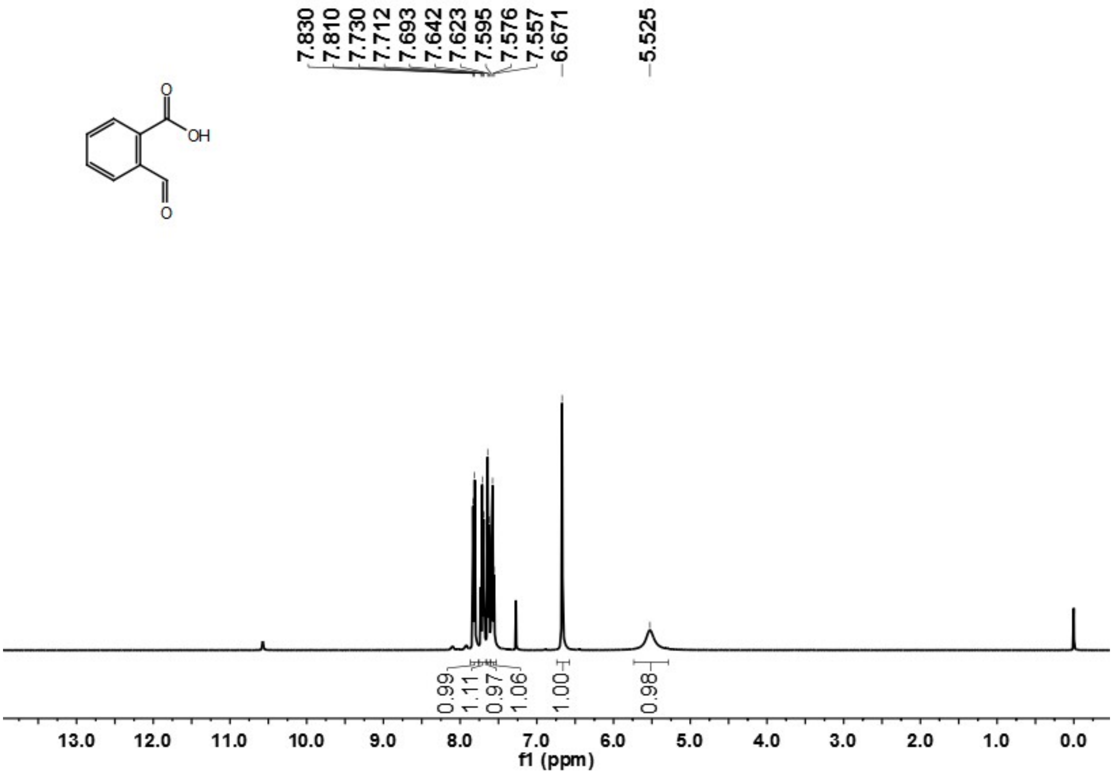
2p

^{1}H NMR



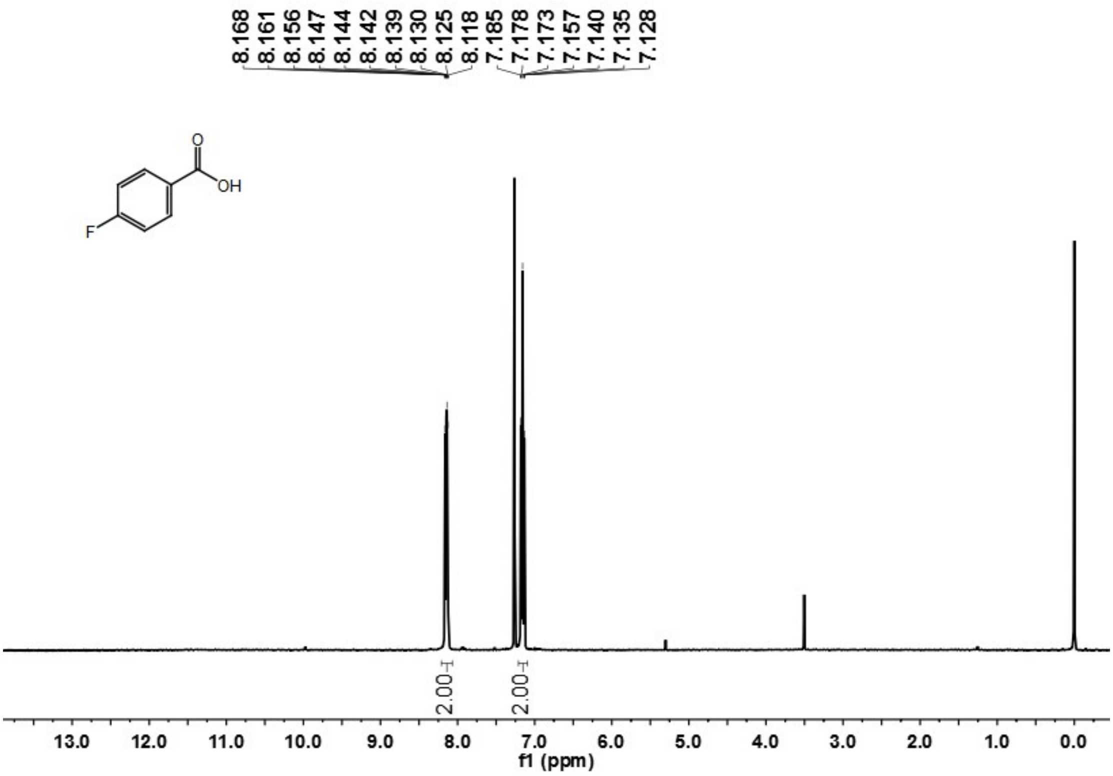
2q

^{1}H NMR



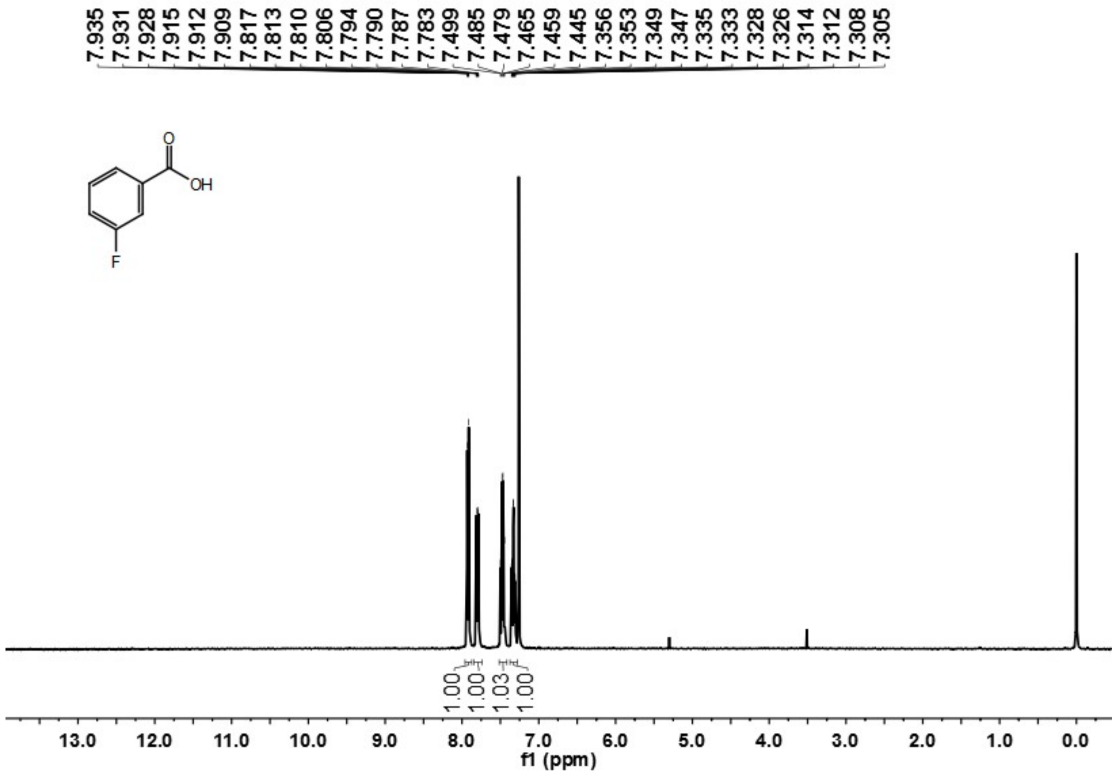
2r

^{1}H NMR



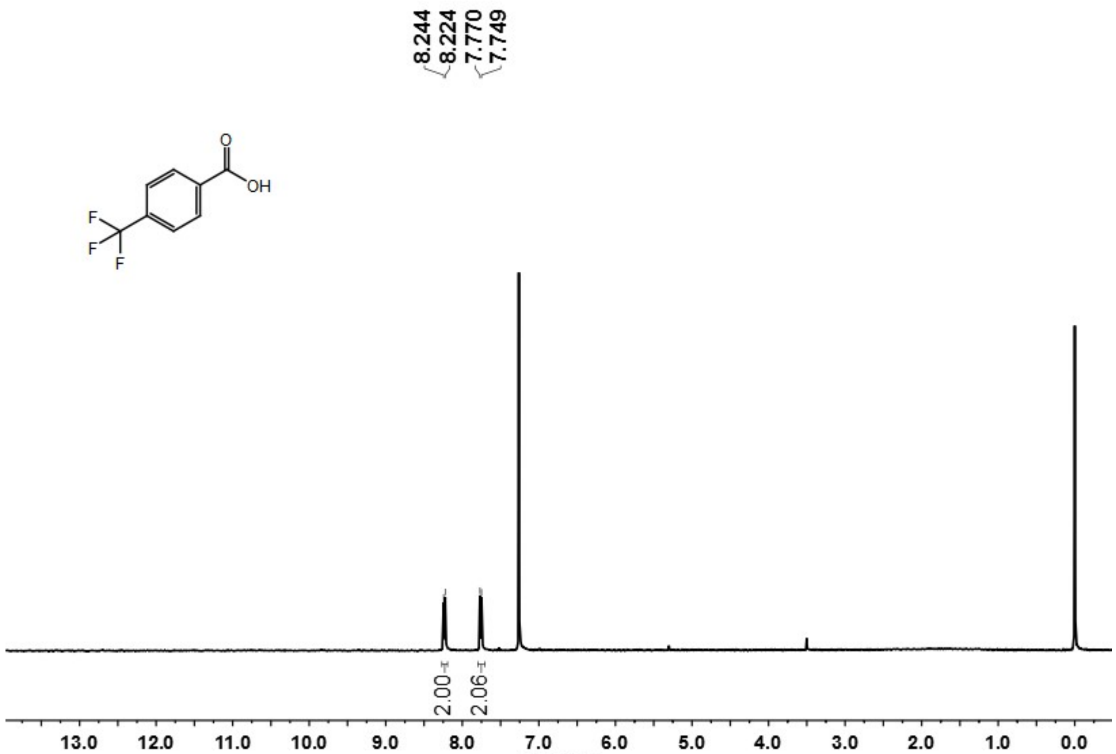
2s

^{1}H NMR



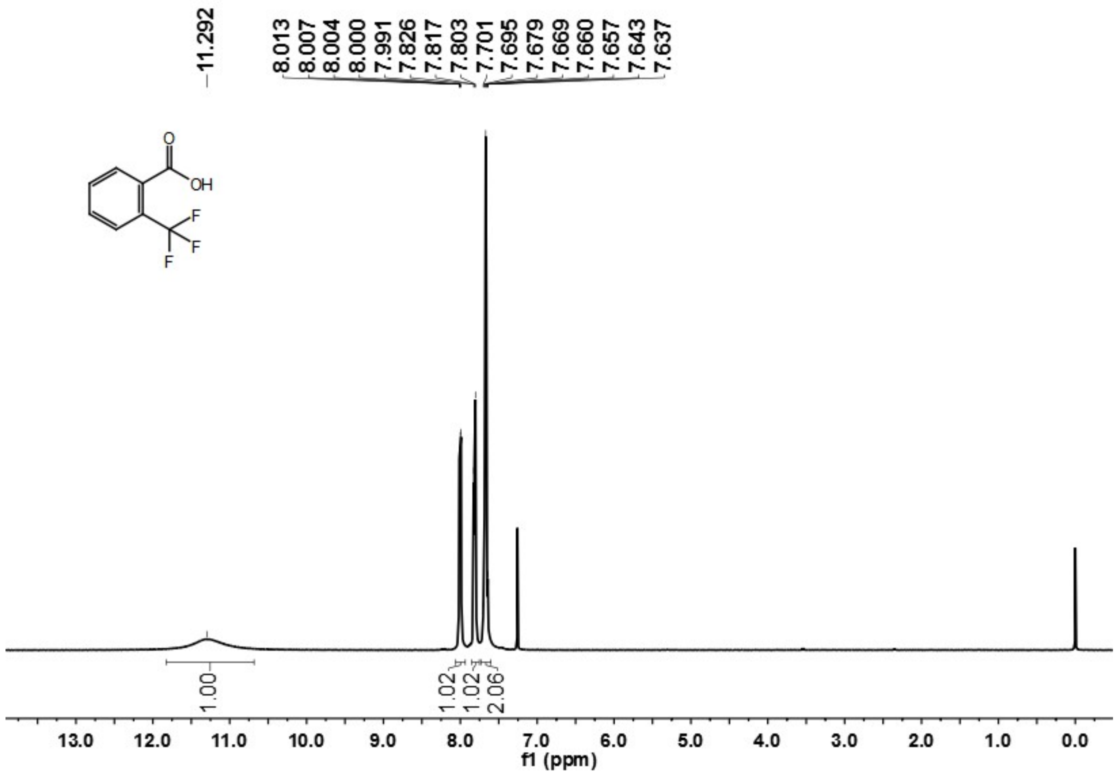
2t

^{1}H NMR



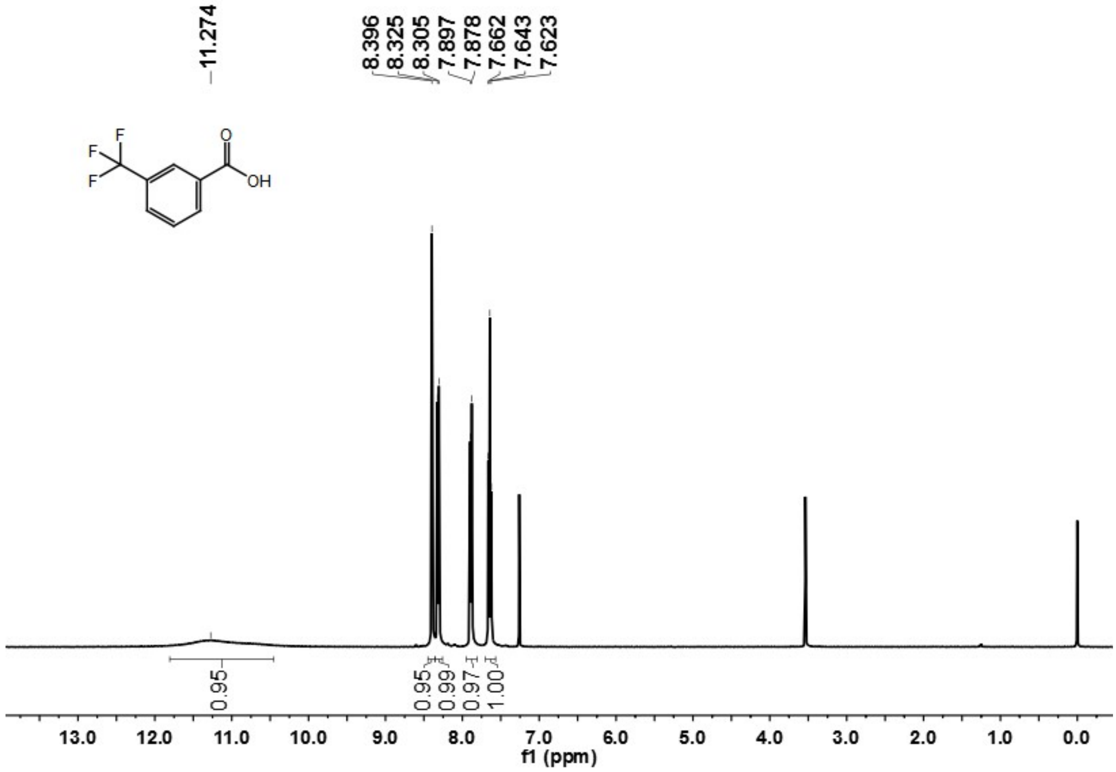
2u

^{1}H NMR



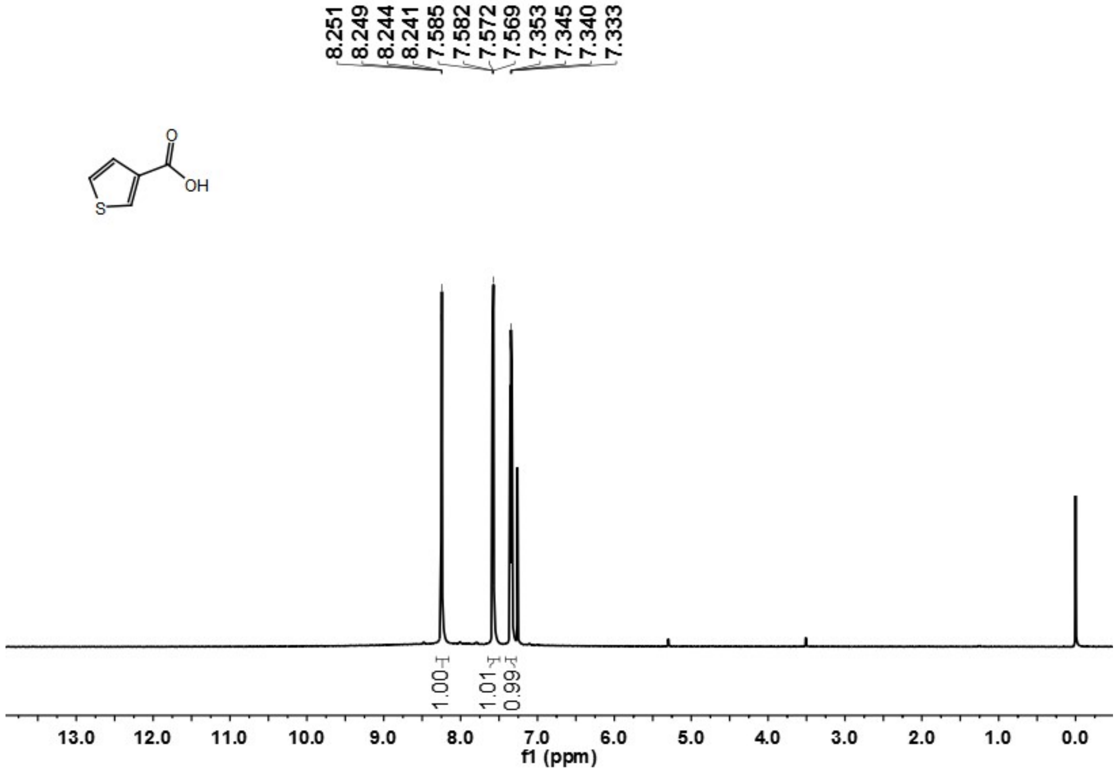
2v

^{1}H NMR



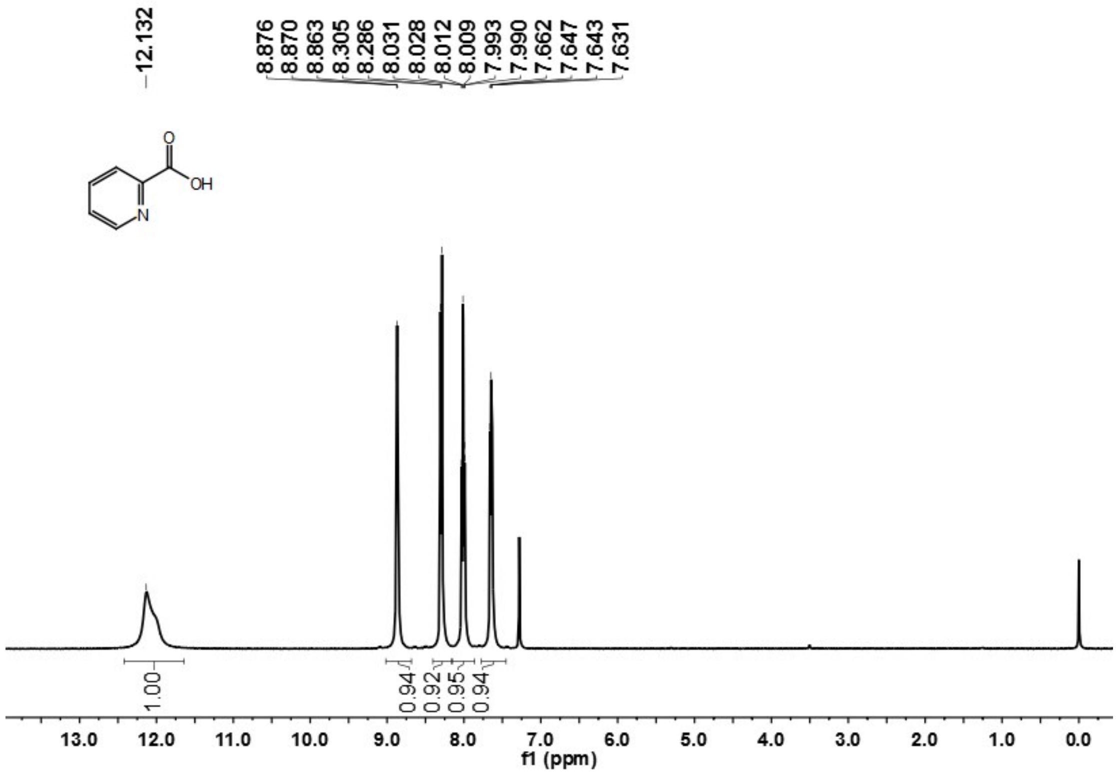
2w

^{1}H NMR



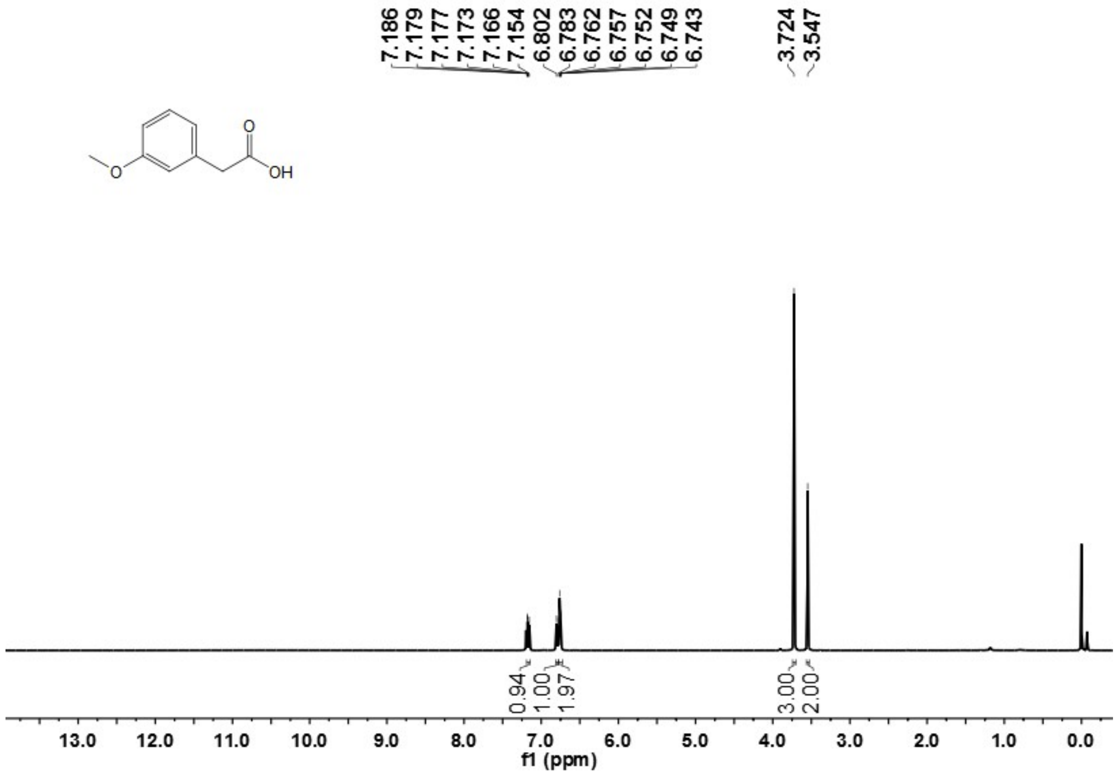
2x

^{1}H NMR



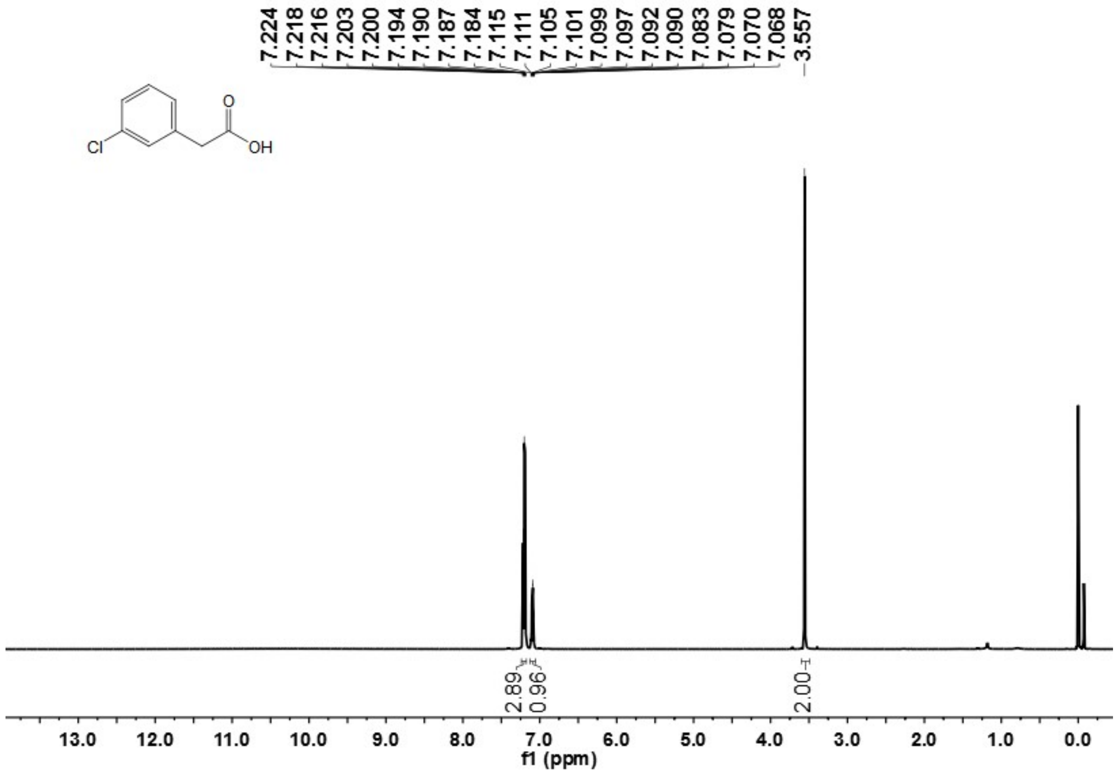
3a

^{1}H NMR



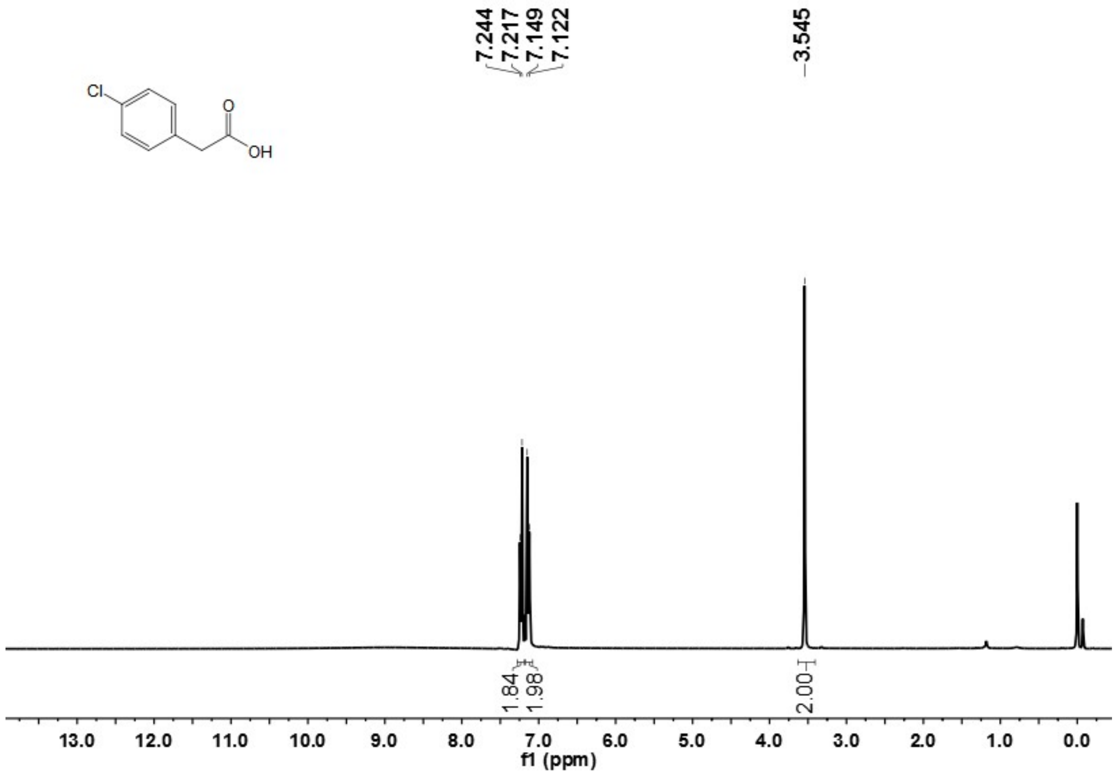
3b

^{1}H NMR



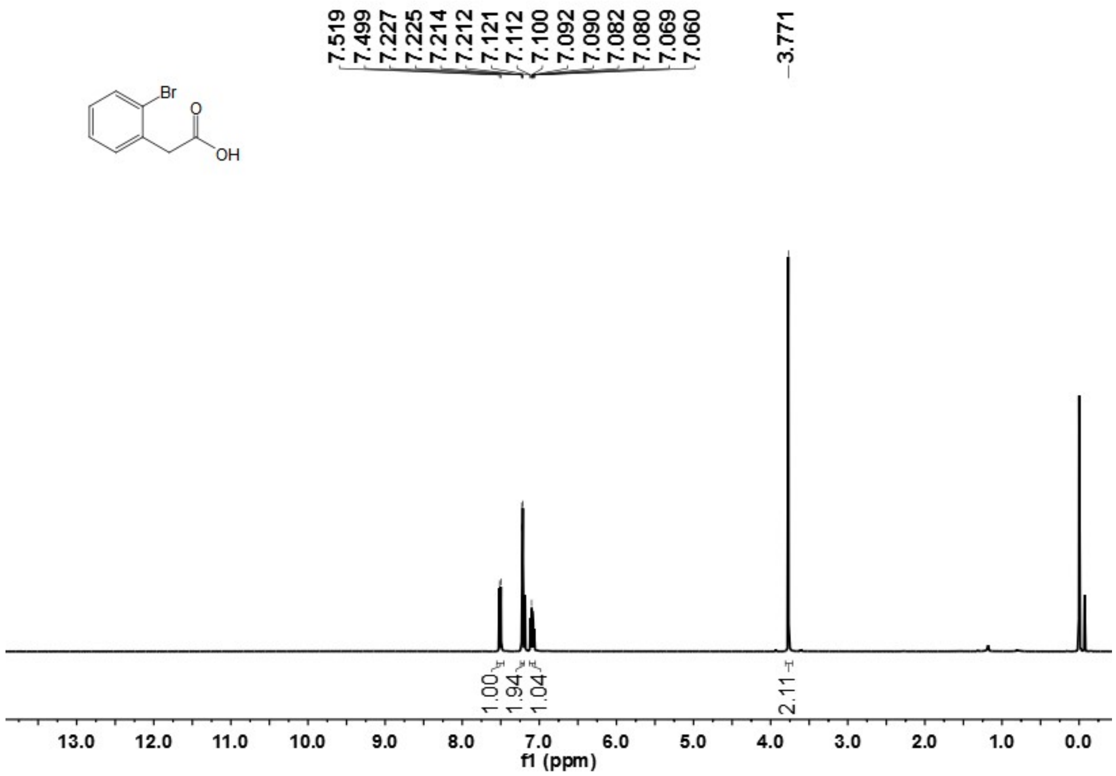
3c

^{1}H NMR



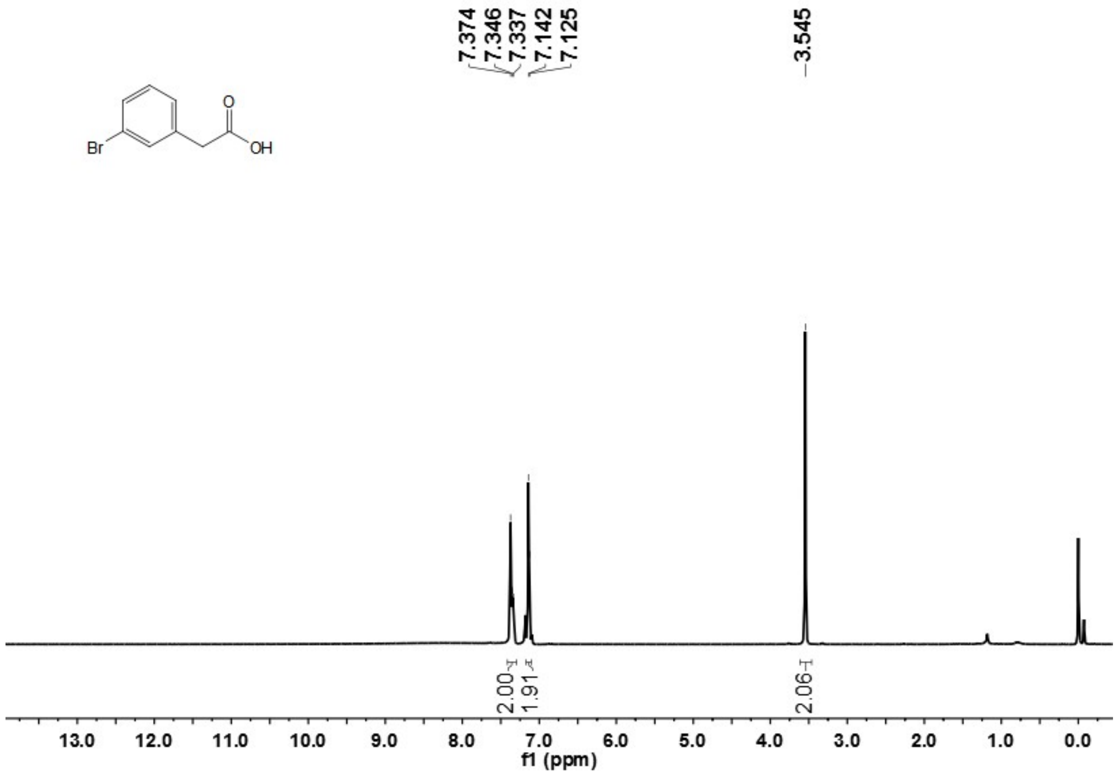
3d

^{1}H NMR



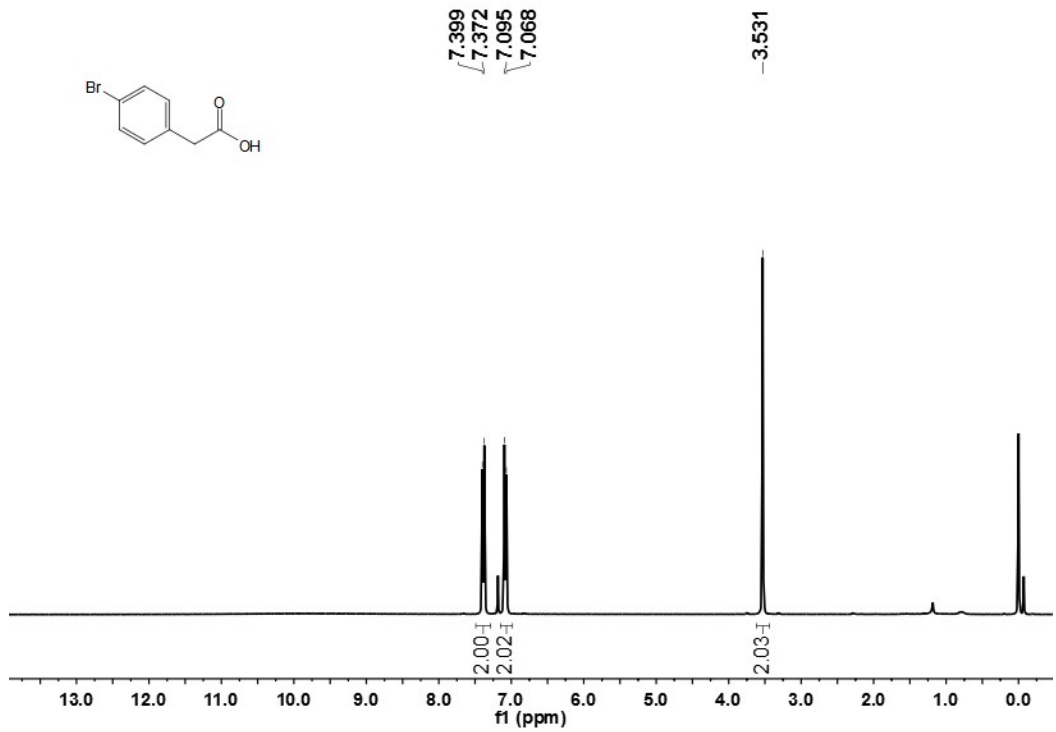
3e

¹H NMR



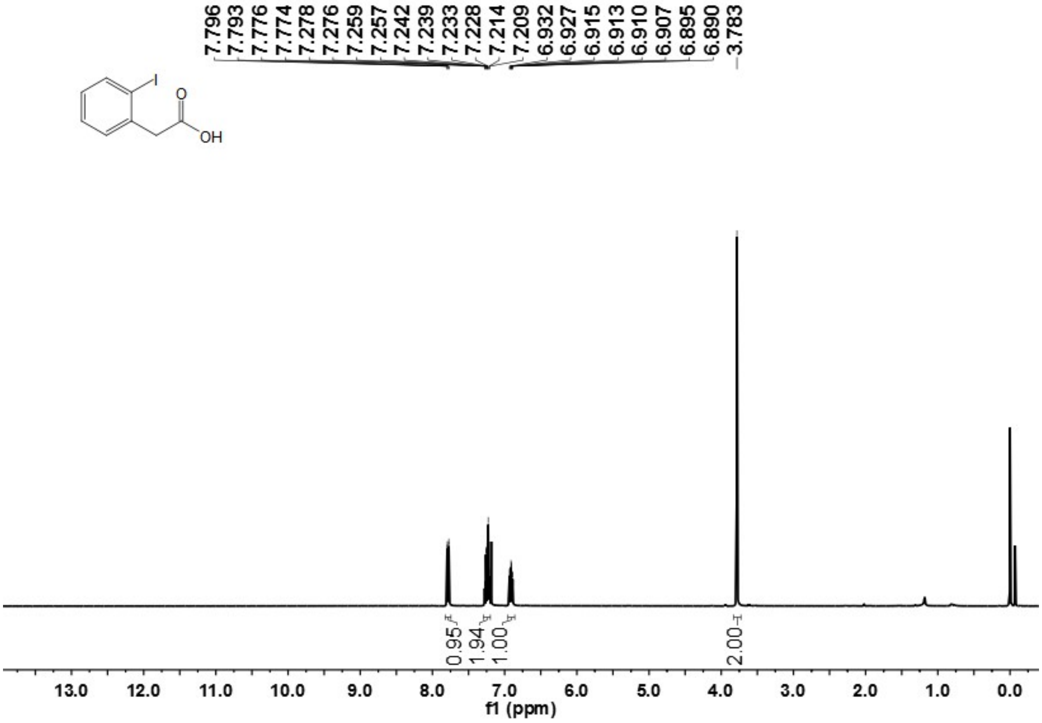
3f

¹H NMR



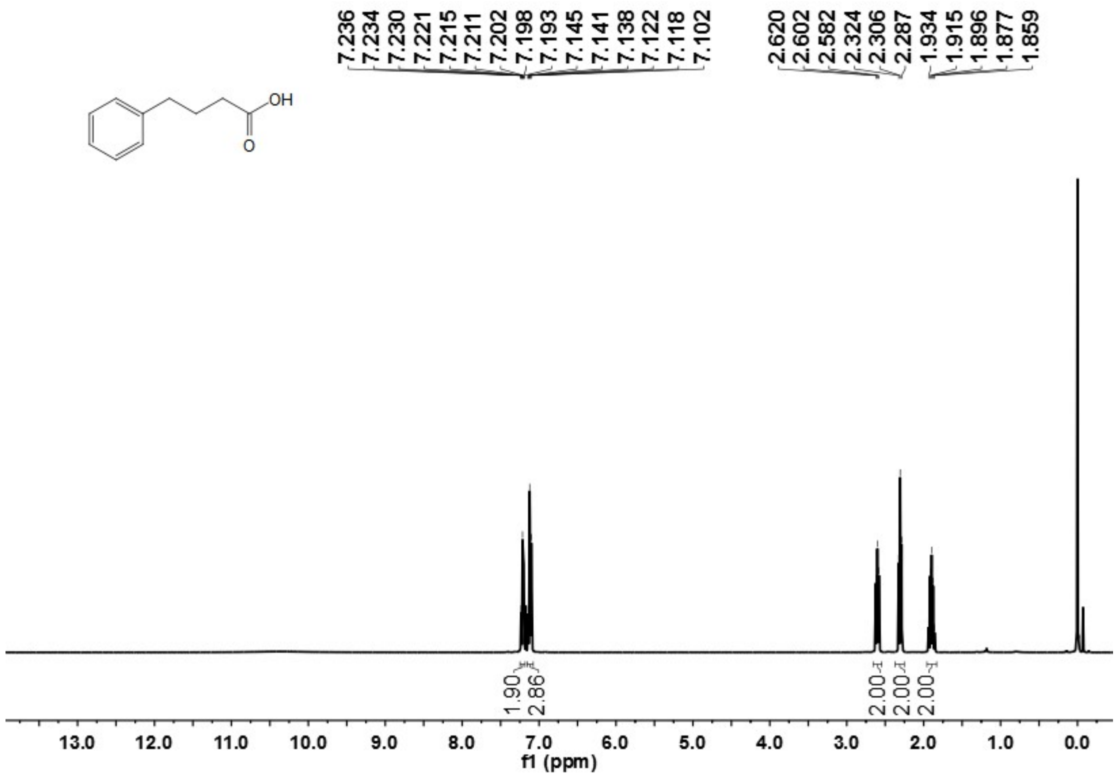
3g

^{1}H NMR



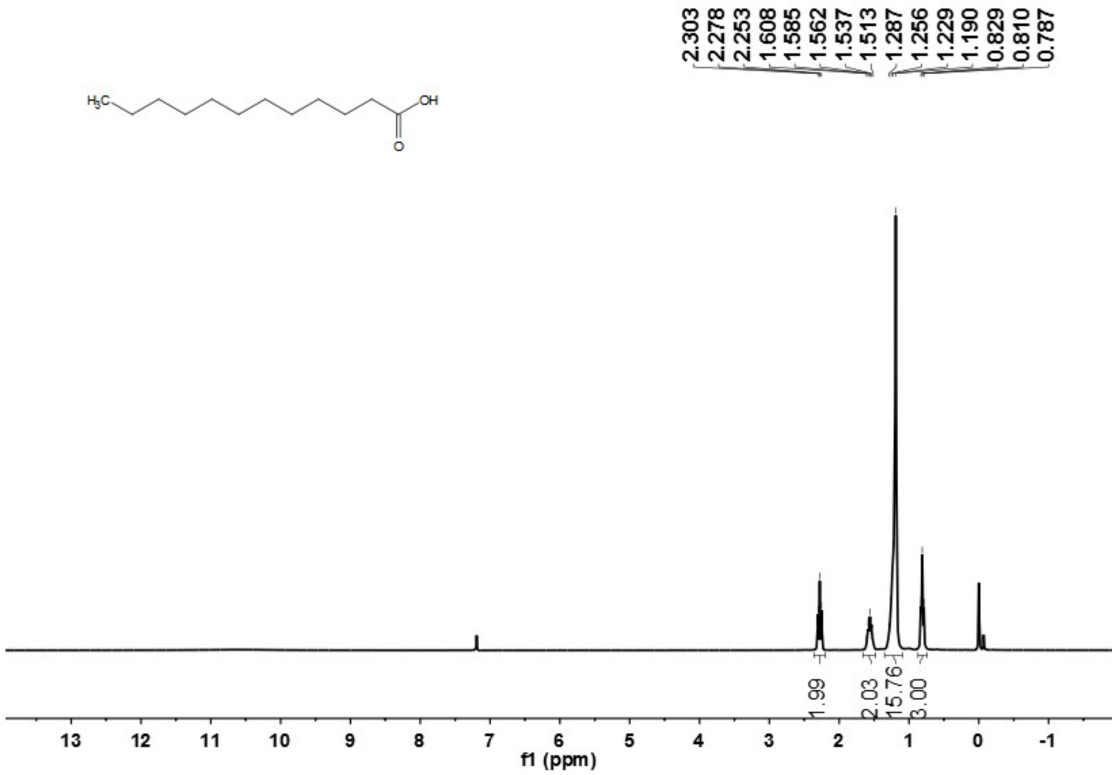
3h

^{1}H NMR



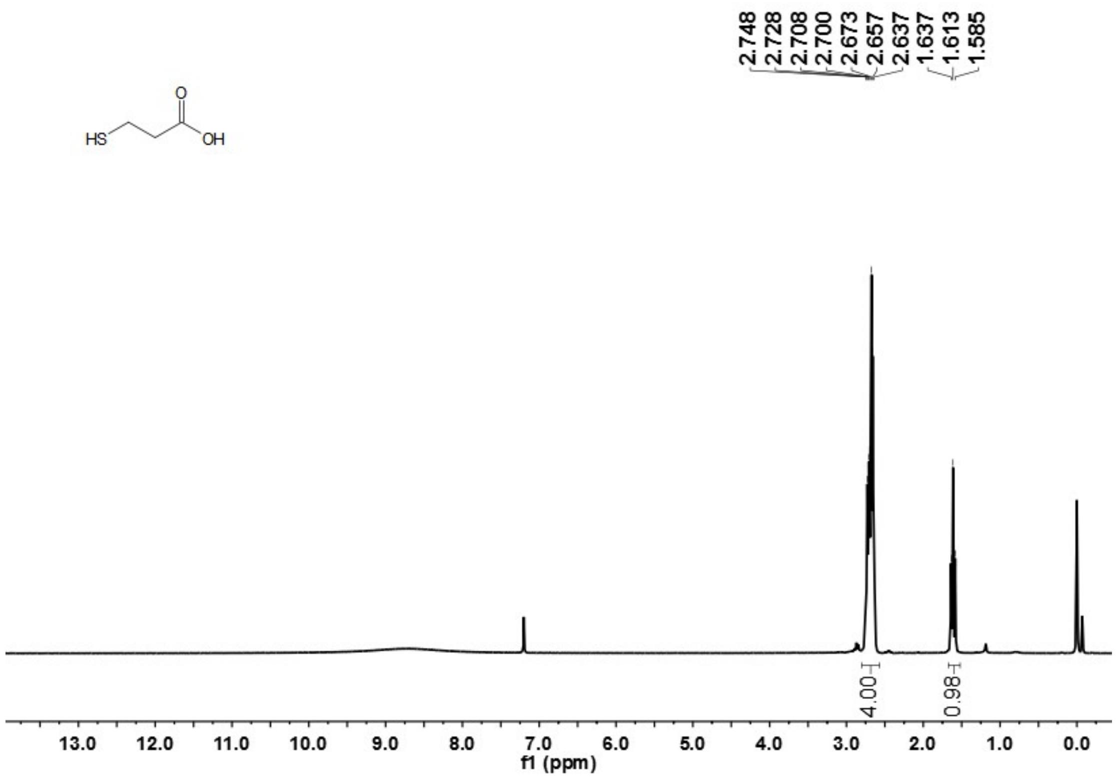
3i

^{1}H NMR



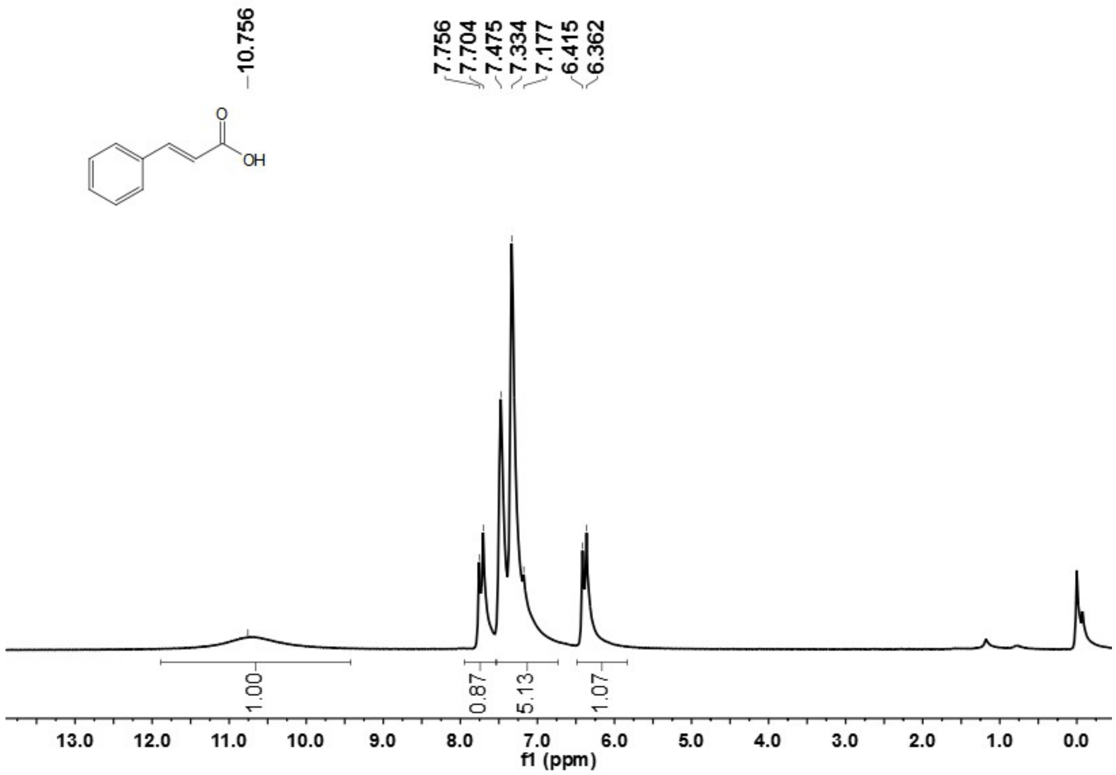
3j

^{1}H NMR



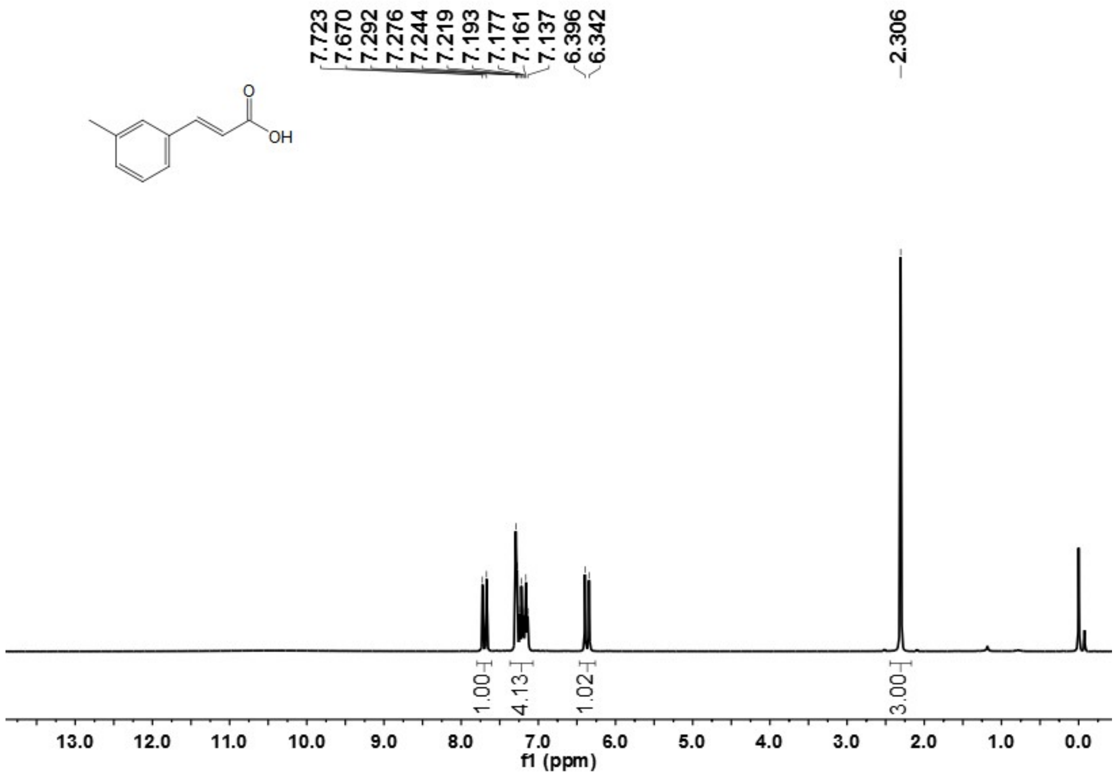
3k

^{1}H NMR



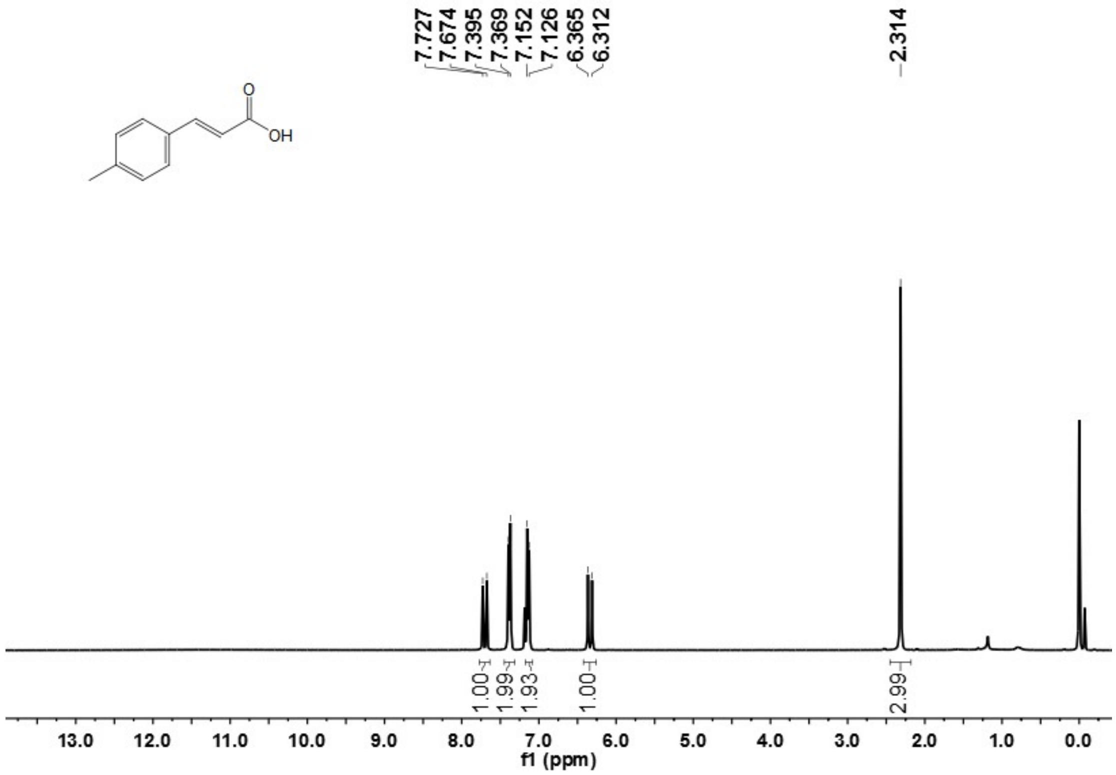
3l

^{1}H NMR



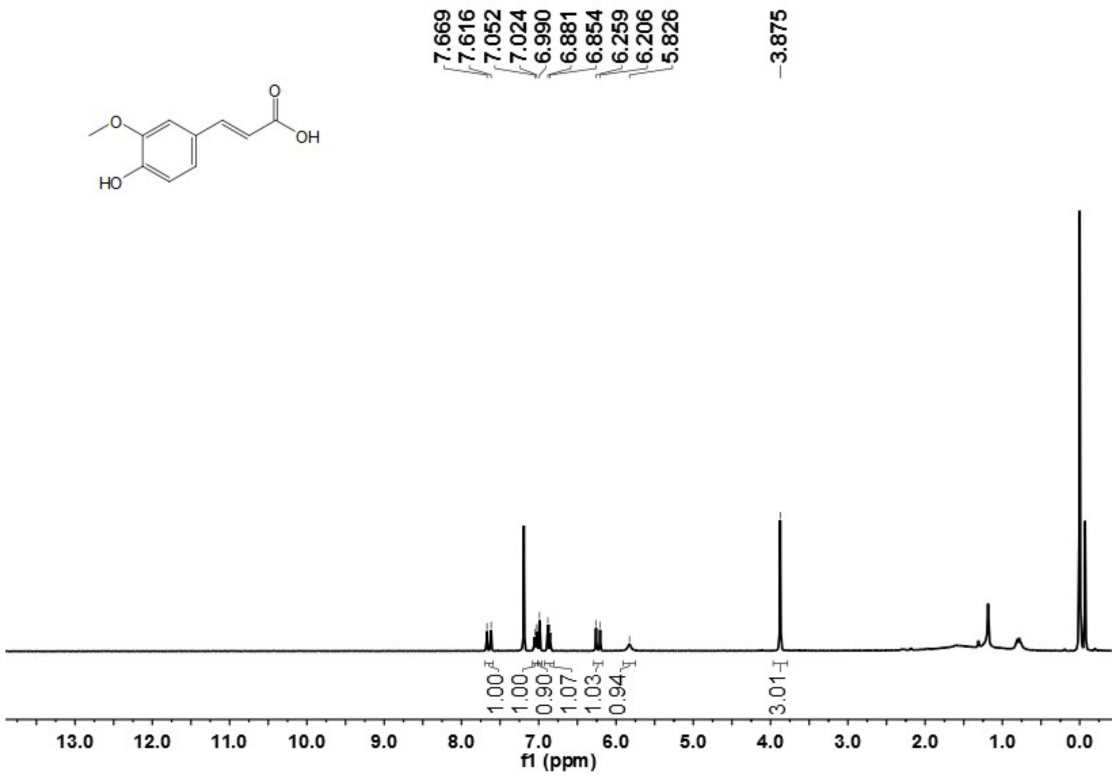
3m

[1]H NMR



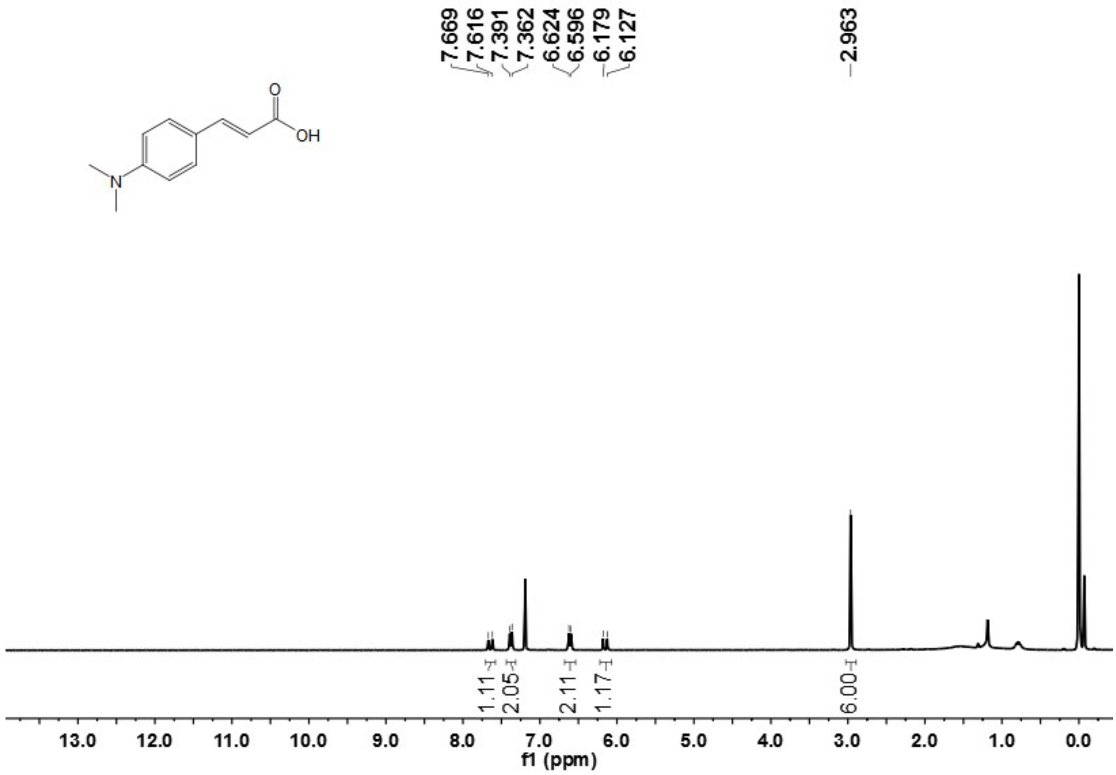
3n

[1]H NMR



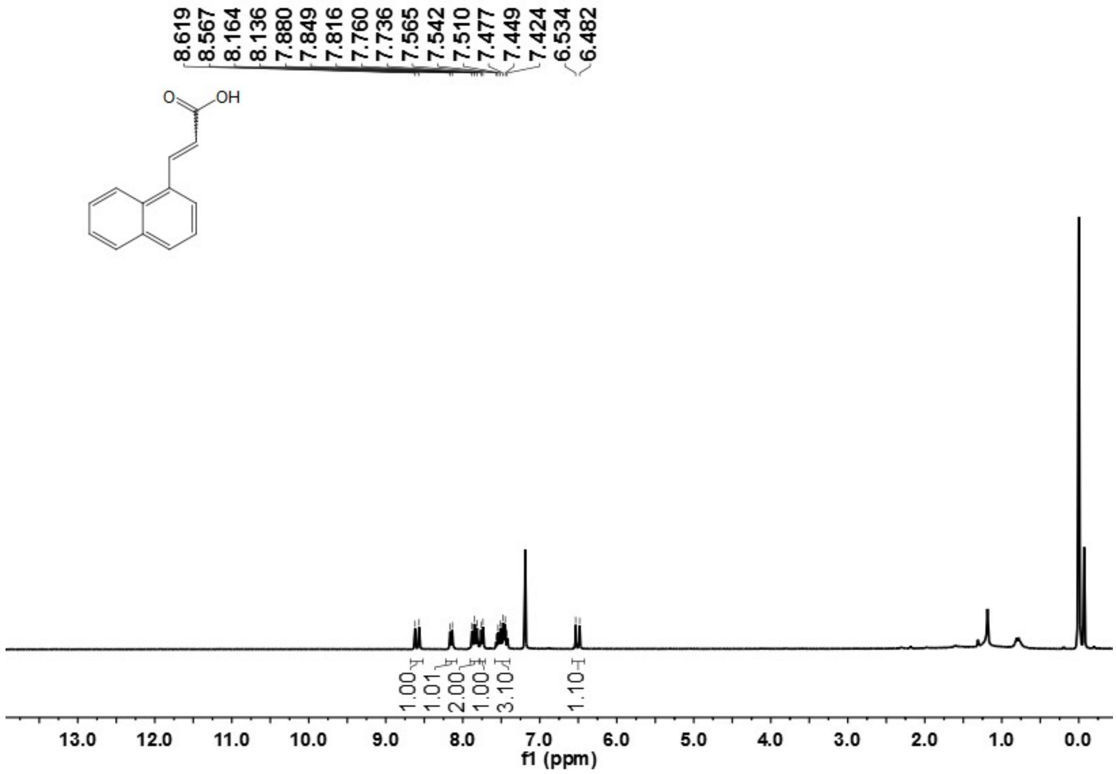
3o

^{1}H NMR



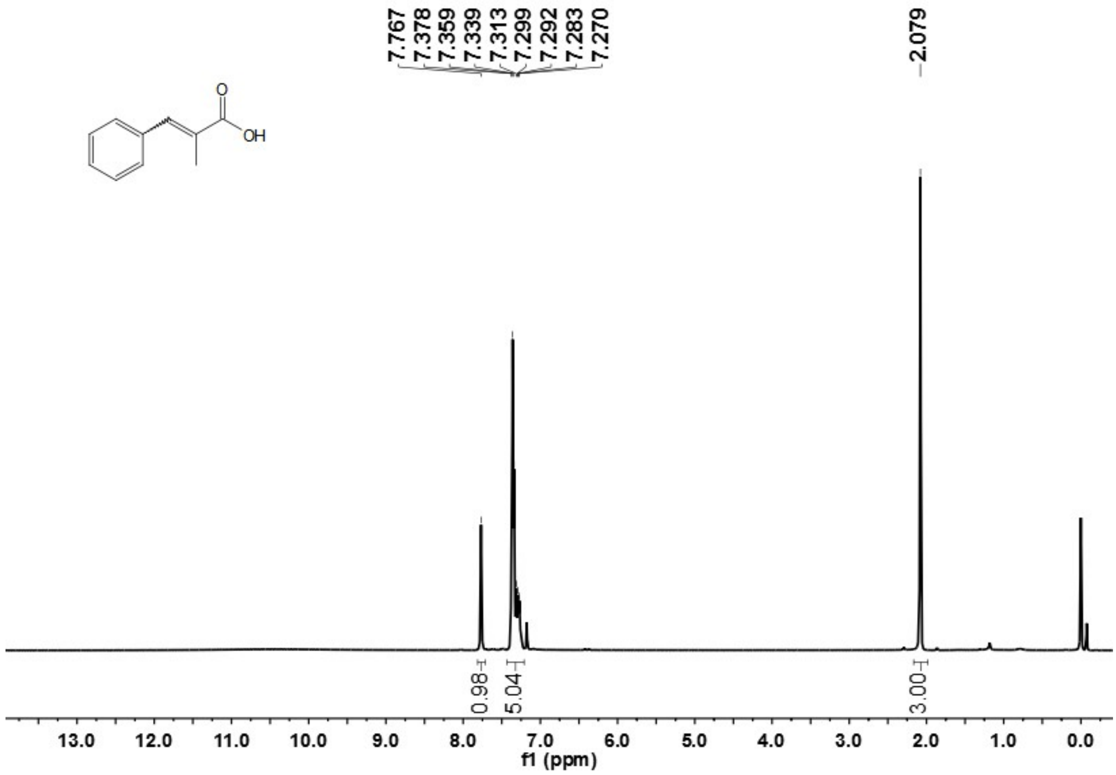
3p

^{1}H NMR



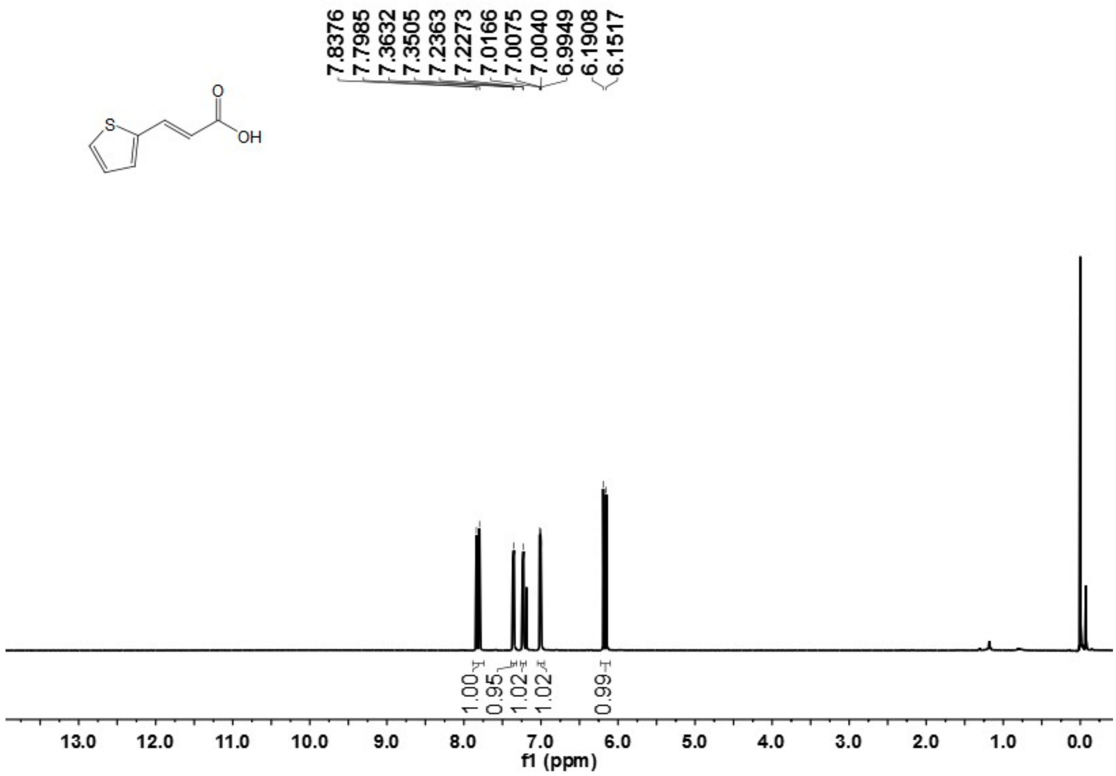
3q

^{1}H NMR



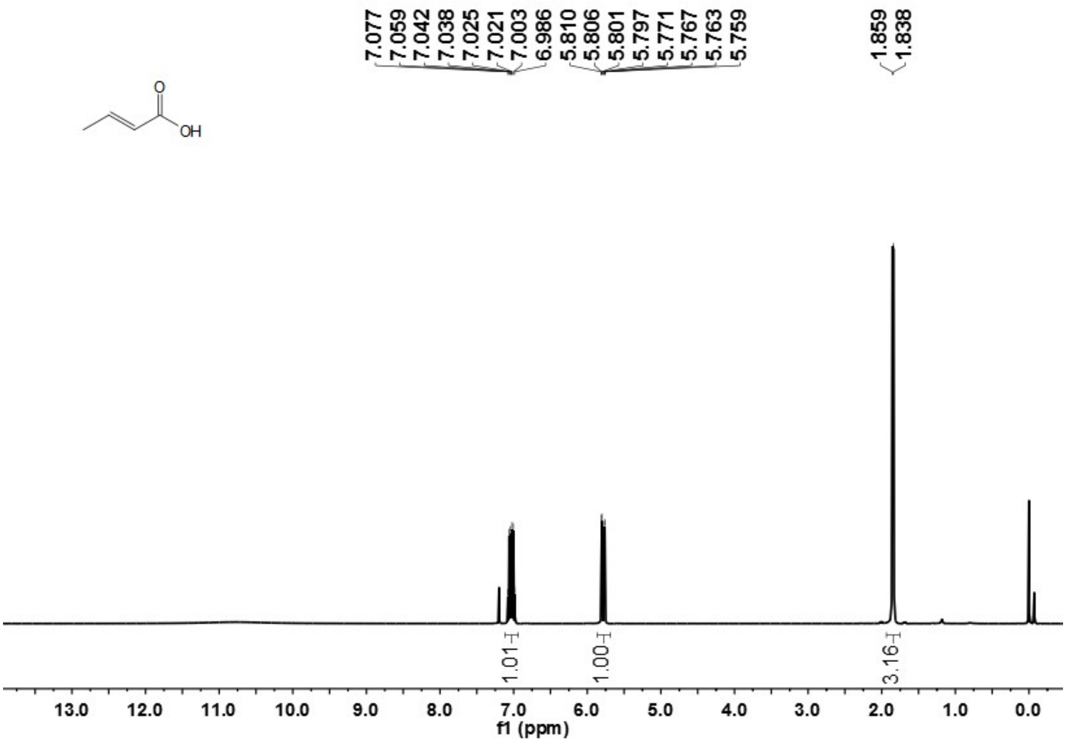
3r

^{1}H NMR



3s

^{1}H NMR



5a

^{1}H NMR