

# **Aerobic Photooxidative Hydroxylation of Boronic acids catalyzed by Anthraquinone-Containing Polymeric Photosensitizer**

Yang Chen<sup>a</sup>, Jianhua Hu<sup>a,\*</sup>, Aishun Ding<sup>b,\*</sup>

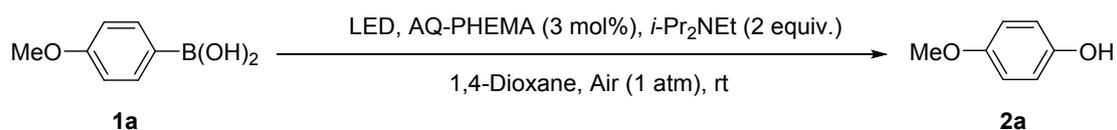
<sup>a</sup> State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, 2005 Songhu Road, Shanghai 200438, PR China. E-mail address: hujh@fudan.edu.cn (J. Hu), Fax: +86-21-31242888, Tel: +86-21-55665280

<sup>b</sup> Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, PR China. E-mail address: shunzi0522@126.com, Fax: +86-21-31249190, Tel: +86-21-31249190

## **Supplementary Information**

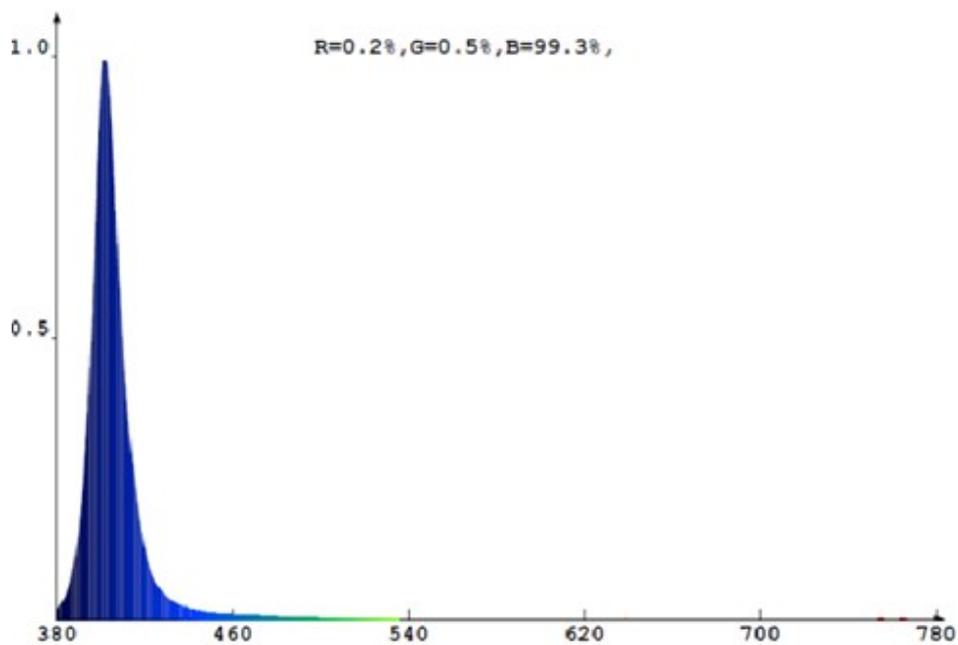
Table S1	S2
Figure S1	S3
Figure S2	S3
Experimental Section	S4
NMR Spectra	S17
References	S33

Table S1. Screening of different LED<sup>a</sup>.

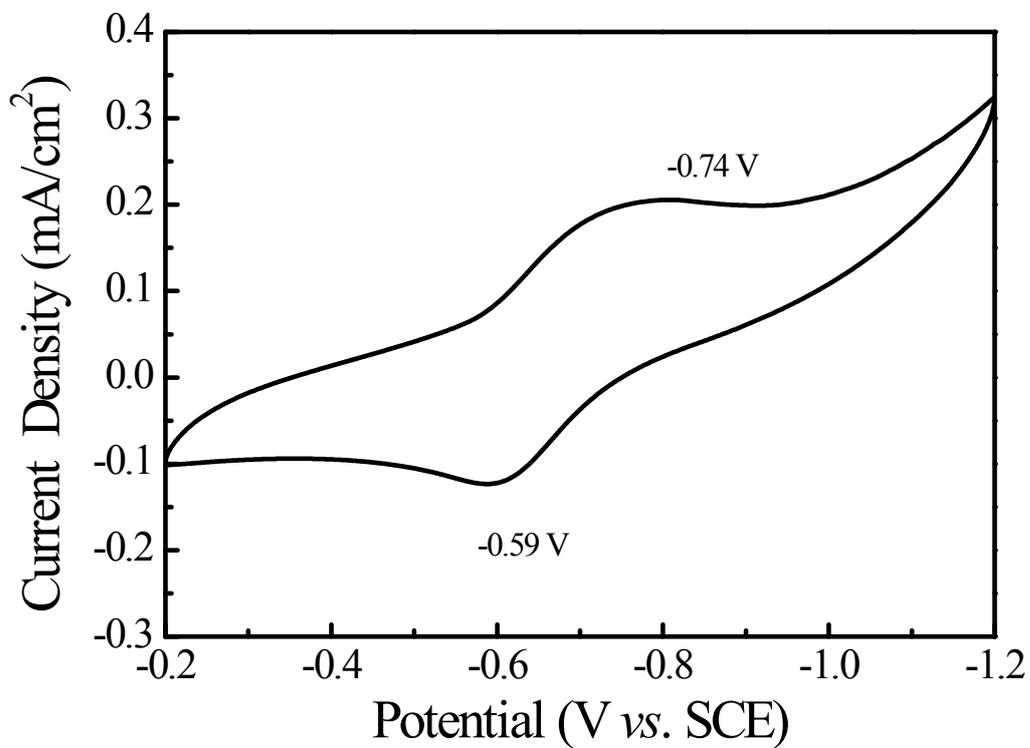


Entry	LED	Time (h)	Yield (%) <sup>b</sup>
1	Red	27	8(90) <sup>c</sup>
2	Yellow	27	10(89) <sup>c</sup>
3	Blue	27	11(87) <sup>c</sup>
4	White	27	9(89) <sup>c</sup>

<sup>a</sup> The reaction were carried out using **1a** (1 mmol), AQ-PHEMA( 3 mol%), *i*-Pr<sub>2</sub>NEt (2 equiv) in 1,4-dioxane (5 mL), irradiated by LED under air atmosphere at rt. (Based on AQ anchored on PHEMA, the mass of 3 mol% AQ-PHEMA is 10 mg.) <sup>b</sup> Yield determined by <sup>1</sup>H NMR analysis using CH<sub>2</sub>Br<sub>2</sub> (1 mmol) as internal standard. <sup>c</sup> Recovered yield of **1a** determined by <sup>1</sup>H NMR analysis using CH<sub>2</sub>Br<sub>2</sub> (1 mmol) as internal standard.



**Figure S1.** Emission spectra of purple LED



**Figure S2.** CV of AQ-PHEMA coated on GC electrode, 0.05 mol/L KCl electrolyte solutions at the scan rates at 100 mV/s.

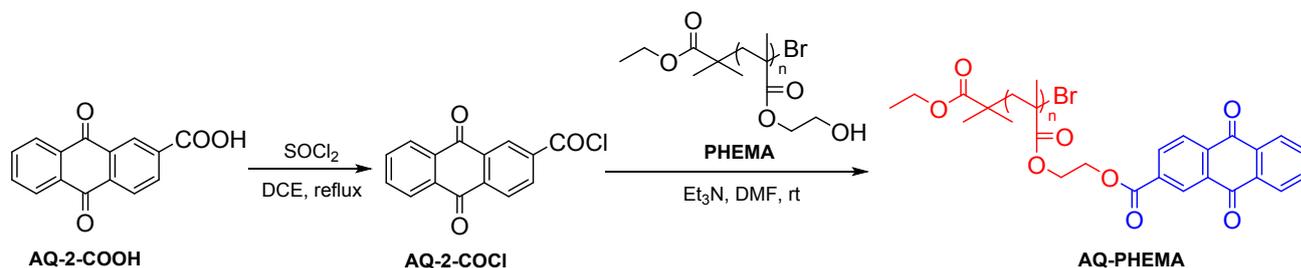
## Experimental Section

All the substrates and reagents were commercial available from Sann Chemical Technology (Shanghai) Co. Ltd. All the photo reactions were carried out using purple LED (1 m strip  $\times$  2, Greethink 5050, 12 V/m) at a distance of 8-10 cm at rt under air atmosphere unless stated otherwise. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. UV-Vis spectroscopies were recorded on an Evolution 220 UV-Visible spectrophotometer. Cyclic voltammogram (CV) was measured by using an electrochemical analyser (CHI 660E, Chenhua, Shanghai, China). A Pt wire and Hg/Hg<sub>2</sub>Cl<sub>2</sub> (SCE) electrode were used as the auxiliary and reference electrodes, respectively. In the 0.05 mol/L KCl as the electrolyte. An initial potential of  $-0.2$  V was applied for 2 s, and subsequently cyclic scans to a final potential of  $-1.2$  V were done for 10 cycles. The CV curves and data reported in the present work were the 10<sup>th</sup> cycle. <sup>1</sup>H (400 MHz) NMR spectra of samples in CDCl<sub>3</sub> or *d*<sub>6</sub>-DMSO at 298 K were recorded on an AVANCE III 400 spectrometer. The apparent molecular weight (*M<sub>w</sub>*) and molecular weight distribution (*M<sub>w</sub>/M<sub>n</sub>*) of polymers were analyzed by size exclusion chromatography (SEC) measurement, which was performed in LiBr-added *N,N*-dimethylformamide (DMF) ([LiBr] = 14 mM) at 55 °C with an elution rate of 1.0 mL/min on an Agilent 1260 equipped with a G1310B pump, a G1362A refractive index detector, and a G1314F variable wavelength detector. Two 5  $\mu$ m LP gel columns (500 Å, molecular range 500-1.2  $\times$  10<sup>5</sup> Da and 200-1.0  $\times$  10<sup>6</sup> Da) were calibrated using poly (methyl methacrylate) (PMMA) standards.

### ***Synthesis and characterization of AQ-PHEMA***

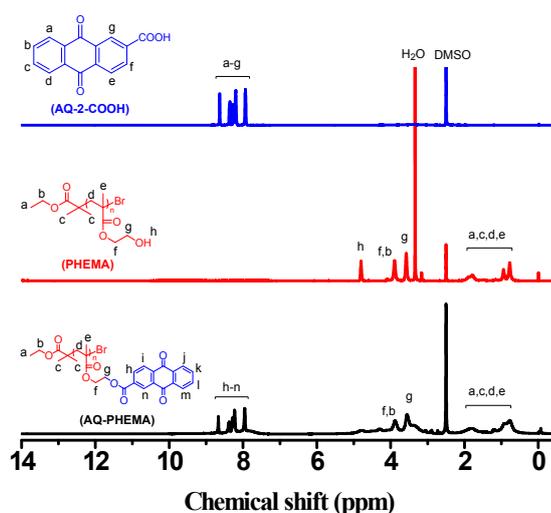
The AQ-PHEMA was prepared by reaction of PHEMA with AQ-2-COCl (**Scheme S1**). At first, AQ-2-COCl was synthesized as the following procedure. In a dry 250 mL of Schlenk flask, under argon atmosphere, AQ-2-COOH (2.704 g, 10.7 mmol) was refluxed with SOCl<sub>2</sub> (2.5 mL) in anhydrous dichloroethane (20 mL). After 4 hours, the mixture was concentrated under vacuum and the residue was stripped twice with anhydrous dichloroethane (10 mL  $\times$  2). Subsequently, the residue was dissolved in anhydrous DMF (20 mL) and transferred into another dry 100 mL of Schlenk flask containing precursor PHEMA (2.792 g) which was previously dried by azeotropic distillation with toluene (100 mL). After that, anhydrous DMF (20 mL) was added. Anhydrous Et<sub>3</sub>N (16 mL) as acid-binding agent was syringed into the flask. The mixture was stirred for 62 hours at rt. The mixture was precipitated with water (500 mL) twice and methanol (500 mL) once. The obtained AQ-PHEMA was further dried under vacuum at 60 °C to a constant weight. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ , ppm,

TMS): 1.00-0.65 (m,  $-\text{CH}_2\text{C}(\text{CH}_3)-$ ), 2.15-1.47 (m,  $-\text{CH}_2\text{C}(\text{CH}_3)-$ ), 4.23-3.41 (m,  $\text{AQCOOCH}_2\text{CH}_2-$ ), 8.75-7.93 (m, Ar-**H**).  $M_{n,\text{GPC}} = 43,000$ ,  $M_w/M_n = 1.53$ .

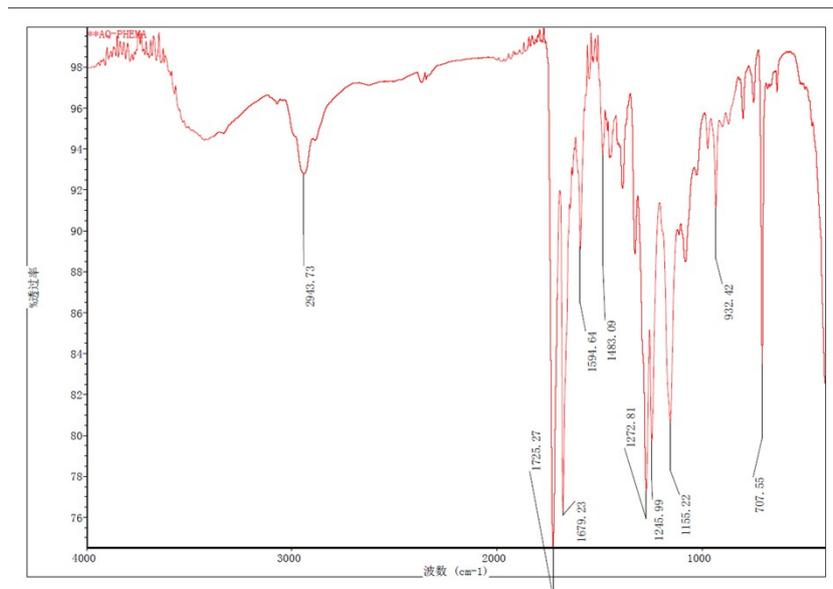


**Scheme S1.** The synthetic procedure for AQ-PHEMA.

The  $^1\text{H}$  NMR spectra for AQ-2-COOH, PHEMA and AQ-PHEMA were shown in **Figure S3**. According to our previous work,<sup>1</sup> the structure of AQ could be confirmed by the characteristic resonance signal on phenyl at 8.73-7.92 ppm. The characteristic resonance signals for methylene protons ( $\text{HOCH}_2\text{CH}_2-$ ) of PHEMA could be clearly discriminated at 4.05-3.42 ppm, and signal for methyl protons ( $-\text{CH}_2\text{CBr}(\text{CH}_3)-$ ) could be observed at 1.00-0.65 ppm. The characteristic resonance signals for the alkyl and phenyl groups were substantially identical to that of PHEMA and AQ-2-COOH. We also performed IR spectrum characterization of AQ-PHEMA and found that hydroxyl groups were not all modified (**Figure S4**).

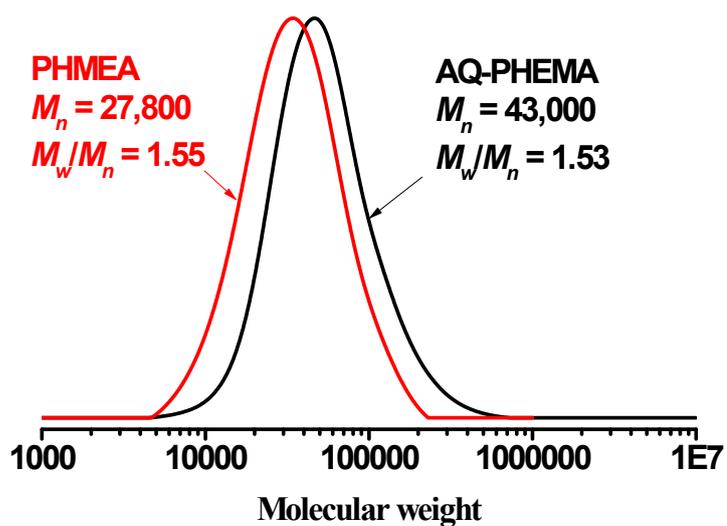


**Figure S3.**  $^1\text{H}$  NMR spectra for AQ-2-COOH, PHEMA and AQ-PHEMA in  $d_6$ -DMSO.



**Figure S4.** IR spectrum of AQ-PHEMA.

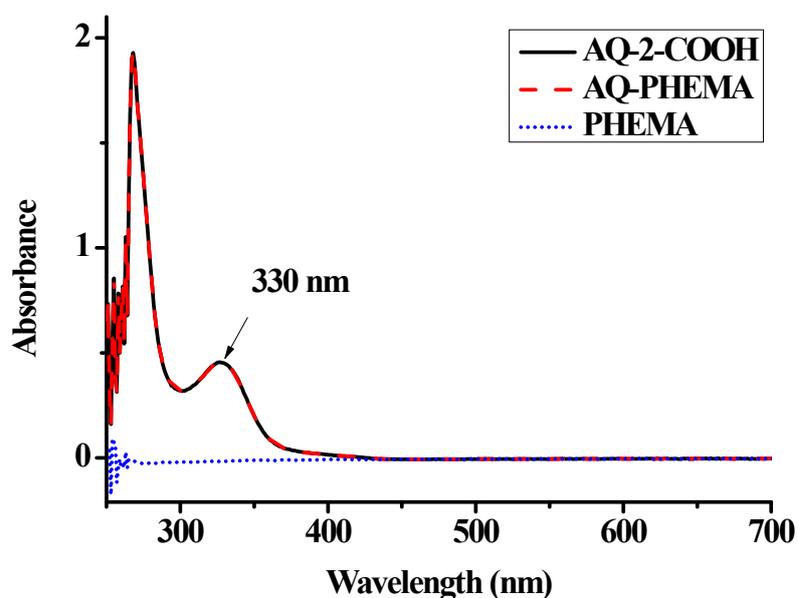
The apparent molecular weight of PHEMA was calibrated as 27,800 g/mol by SEC instrument using PMMA as calibration. Obviously, the GPC curve of AQ-PHEMA is significantly shift to the higher molecular weight region (43,000 g/mol) (**Figure S5**). The above results indicated that the AQ functional group was successfully attached to PHEMA.



**Figure S5.** The GPC traces of PHEMA and AQ-PHEMA.

*Calculate the ratio of AQ in AQ-PHEMA by UV-Vis spectrophotometer*

Next, AQ-2-COOH, PHEMA and AQ-PHEMA DMF solutions were measured by UV-Vis spectrophotometer to determine the ratio of AQ in AQ-PHEMA. As shown in **Figure S6**, at the range of 250-700 nm wavelengths, PHEMA had no absorption, AQ-PHEMA had two absorption peaks at 268 nm and 330 nm, which was identical with AQ-2-COOH. However, the absorption at 268 nm was significantly interfered by solvent. Therefore, 330 nm was selected as the maximum absorption wavelength. Five different concentrations of AQ-2-COOH DMF standard solutions were prepared to obtain a calibration curve (**Figure S7**). Finally, a DMF solution of AQ-PHEMA (0.044 mg/mL) was measured at 330 nm with the absorbance as 0.772. Since PHEMA had no absorption at 330 nm, the absorption signal in the AQ-PHEMA solution was solely from its AQ functional group. According to the linear regression equation from the calibration curve of AQ-2-COOH, the concentration of AQ in AQ-PHEMA DMF solution (0.044 mg/mL) was calculated as  $1.302 \times 10^{-4}$  mmol/mL. Thus, the ratio of AQ in AQ-PHEMA was calculated as 2.959 mmol/g.



**Figure S6.** UV-Vis absorption spectra of AQ-2-COOH, PHEMA and AQ-PHEMA in DMF.

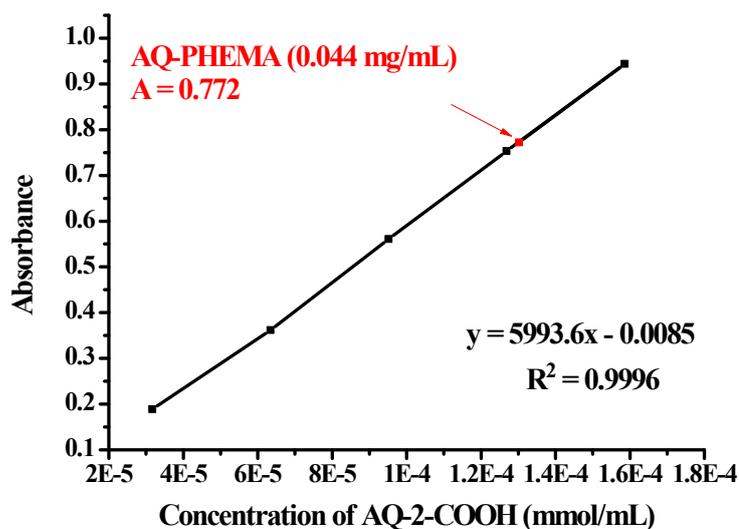
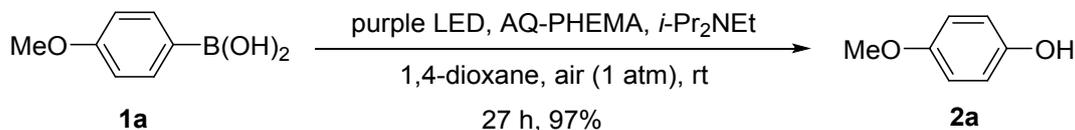


Figure S7. Calibration curve of AQ-2-COOH measured by UV-Vis spectrophotometry at 330 nm.

#### Typical Procedure for the reaction under Condition A. (2a-2aa and 4a-4e)

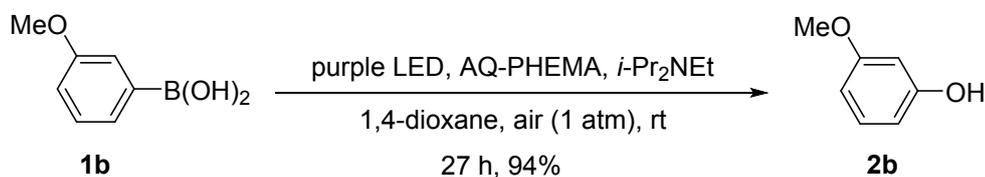
##### 4-Methoxyphenol (2a)<sup>2</sup>



**1a** (152 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) were added to a dry 25 mL Schlenk bottle. The mixture was irradiated by purple LED at rt under air atmosphere. The photoreaction was completed after 27 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 2/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1 $\rightarrow$ 5/1) to afford **2a** as a solid (120 mg, 97%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.82–6.73 (m, 4H), 4.94 (brs, 1H), 3.76 (s, 3H).

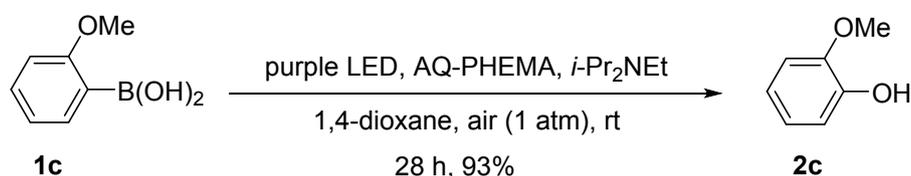
The following compounds were prepared according to Typical Procedure

##### 3-Methoxyphenol (2b)<sup>2</sup>



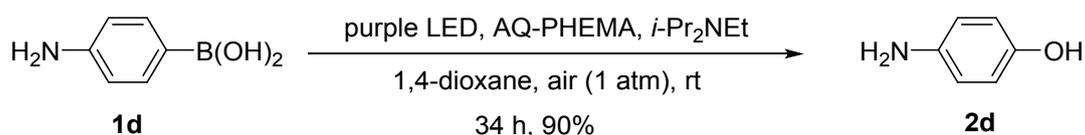
The reaction of **1b** (152 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2b** as a liquid (117 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 (t, *J* = 8.0 Hz, 1H), 6.50–6.39 (m, 3H), 5.14 (brs, 1H), 3.72 (s, 3H).

### 2-Methoxyphenol (**2c**)<sup>2</sup>



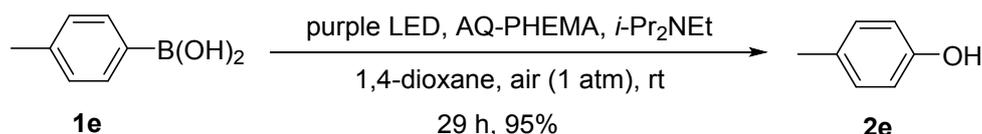
The reaction of **1c** (152 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2c** as a liquid (115 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.95–6.79 (m, 4H), 5.67 (brs, 1H), 3.86 (s, 3H).

### 4-Aminophenol (**2d**)<sup>3</sup>



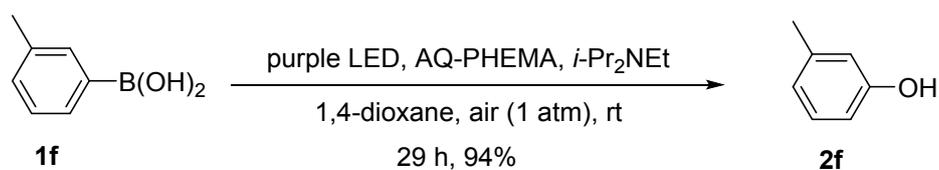
The reaction of **1d** (173 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2d** as a solid (98 mg, 90%); <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.35 (brs, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 8.0 Hz, 2H), 4.39 (brs, 2H).

### 4-Methylphenol (**2e**)<sup>2</sup>



The reaction of **1e** (136 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2e** as a solid (103 mg, 95%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.01 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 2H), 5.87 (brs, 1H), 2.26 (s, 3H).

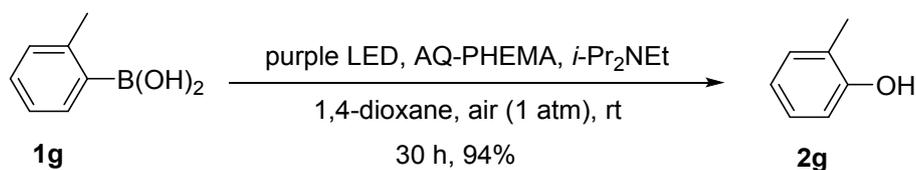
### 3-Methylphenol (**2f**)<sup>2</sup>



The reaction of **1f** (136 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2f** as a liquid (100 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.11 (t, *J* =

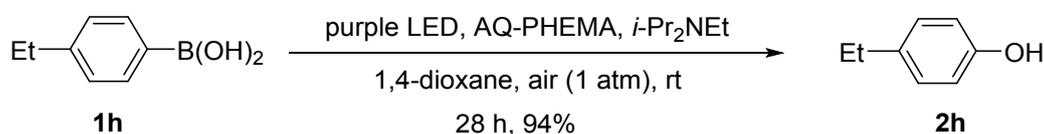
7.6 Hz, 1H), 6.74 (d,  $J = 7.6$  Hz, 1H), 6.67-6.61 (m, 2 H), 5.49 (s, 1H), 2.28 (s, 3H).

### 2-Methylphenol (**2g**)<sup>2</sup>



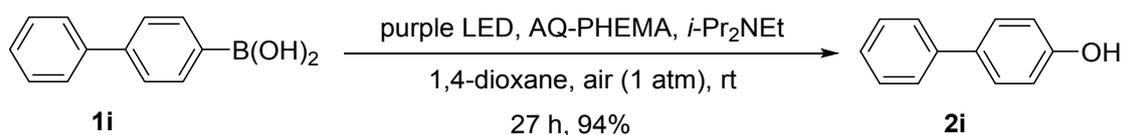
The reaction of **1g** (136 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2g** as a solid (100 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16-7.03 (m, 2 H), 6.85 (t,  $J = 7.4$  Hz, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 4.79 (brs, 1H), 2.25 (s, 3H).

### 4-Ethylphenol (**2h**)<sup>2</sup>



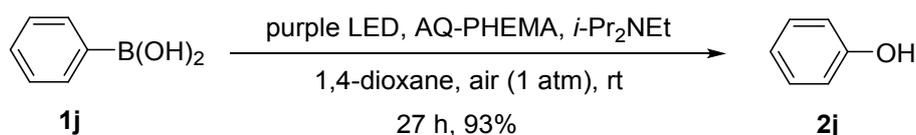
The reaction of **1h** (150 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2h** as a solid (115 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.05 (d,  $J = 8.4$  Hz, 2H), 6.75 (d,  $J = 8.4$  Hz, 2H), 5.59 (brs, 1H), 2.57 (q,  $J = 7.6$  Hz, 2H), 1.19 (t,  $J = 7.6$  Hz, 3H).

### 4-Phenylphenol (**2i**)<sup>2</sup>



The reaction of **1i** (198 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2i** as a solid (181 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d,  $J = 7.6$  Hz, 2H), 7.48 (d,  $J = 8.0$  Hz, 2H), 7.41 (t,  $J = 7.4$  Hz, 2H), 7.30 (t,  $J = 7.4$  Hz, 1H), 6.90 (d,  $J = 8.4$  Hz, 2H), 4.75 (brs, 1H).

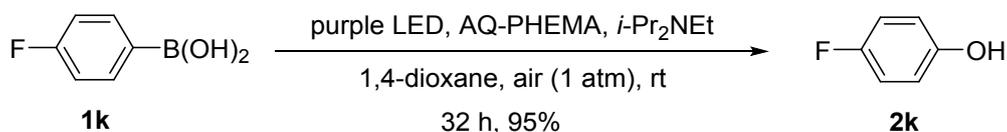
### Phenol (**2j**)<sup>2</sup>



The reaction of **1j** (122 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2j** as a solid (88 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (t,  $J = 7.4$

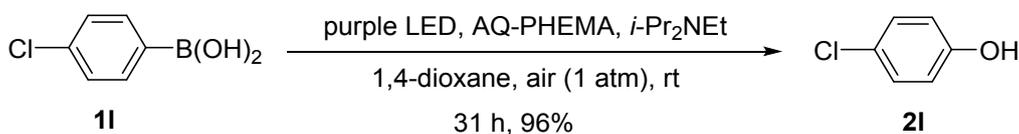
Hz, 2H), 6.93 (t,  $J = 7.4$  Hz, 1H), 6.83 (d,  $J = 7.6$  Hz, 2H), 5.13 (brs, 1H).

#### 4-Fluorophenol (**2k**)<sup>2</sup>



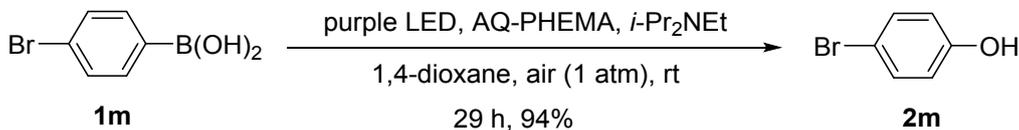
The reaction of **1k** (140 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2k** as a solid (106 mg, 95%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.92 (t,  $J = 8.2$  Hz, 2H), 6.79-6.72 (m, 2 H), 4.97 (brs, 1 H).

#### 4-Chlorophenol (**2l**)<sup>2</sup>



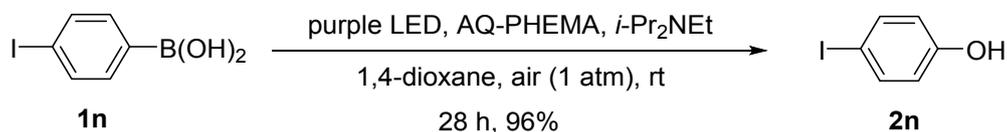
The reaction of **1l** (156 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2l** as a solid (123 mg, 96%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (d,  $J = 8.4$  Hz, 2H), 6.77 (d,  $J = 8.4$  Hz, 2H), 4.75 (brs, 1H).

#### 4-Bromophenol (**2m**)<sup>2</sup>



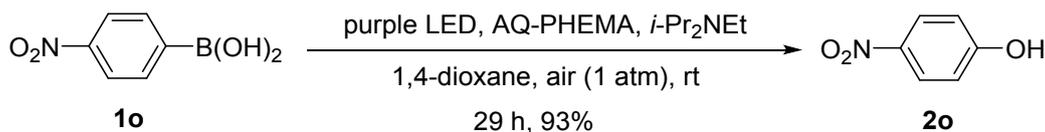
The reaction of **1m** (201 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2m** as a solid (163 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (d,  $J = 8.0$  Hz, 2H), 6.71 (d,  $J = 8.0$  Hz, 2H), 5.50 (brs, 1H).

#### 4-Iodophenol (**2n**)<sup>2</sup>



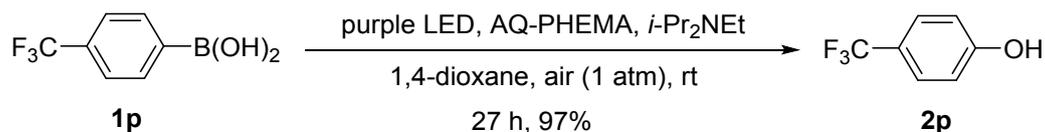
The reaction of **1n** (248 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2n** as a solid (211 mg, 96%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (d,  $J = 7.6$  Hz, 2H), 6.62 (d,  $J = 7.6$  Hz, 2H), 5.07 (brs, 1H).

#### 4-Nitrophenol (**2o**)<sup>2</sup>



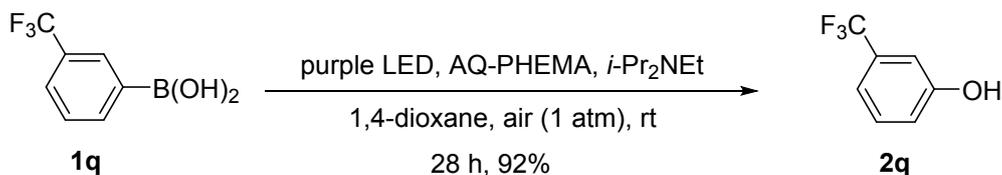
The reaction of **1o** (167 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2o** as a solid (129 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.74 (brs, 1H).

#### 4-(Trifluoromethyl)phenol (**2p**)<sup>2</sup>



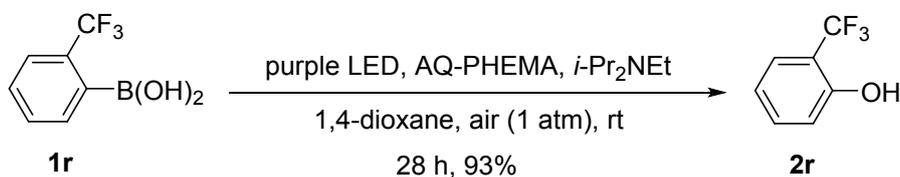
The reaction of **1p** (190 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2p** as a solid (157 mg, 97%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.12 (brs, 1H).

#### 3-(Trifluoromethyl)phenol (**2q**)<sup>2</sup>



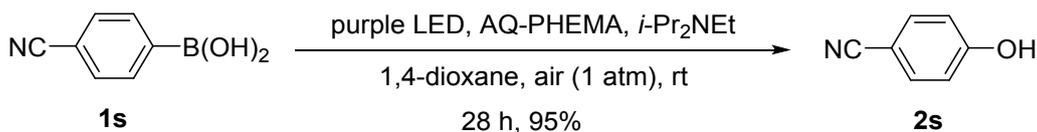
The reaction of **1q** (190 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2q** as a liquid (149 mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.54 (brs, 1H).

#### 2-(Trifluoromethyl)phenol (**2r**)<sup>2</sup>



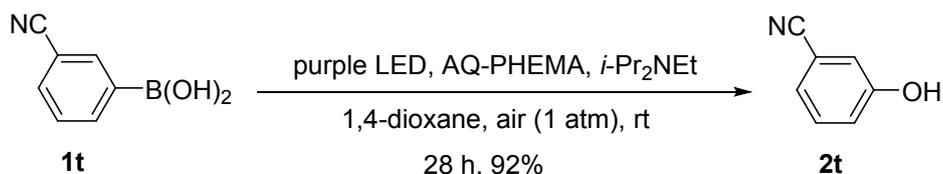
The reaction of **1r** (190 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2r** as a liquid (151 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.66 (brs, 1H).

#### 4-Cyanophenol (**2s**)<sup>2</sup>



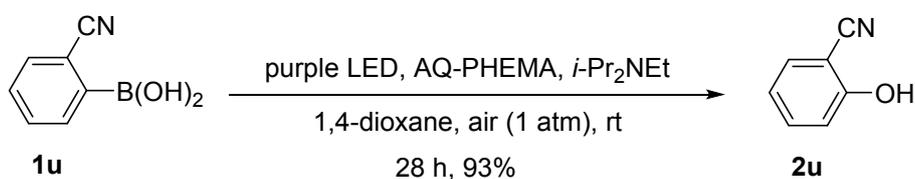
The reaction of **1s** (147 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2s** as a solid (113 mg, 95%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.89 (brs, 1H).

### 3-Cyanophenol (**2t**)<sup>4</sup>



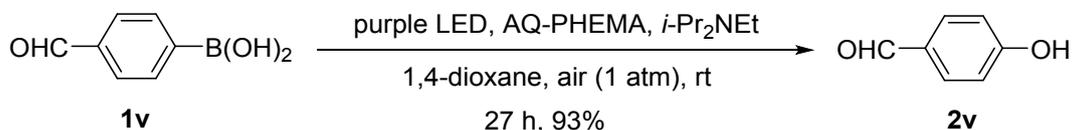
The reaction of **1t** (147 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2t** as a solid (110 mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.05 (m, 2H), 6.03 (brs, 1H).

### 2-Cyanophenol (**2u**)<sup>4</sup>



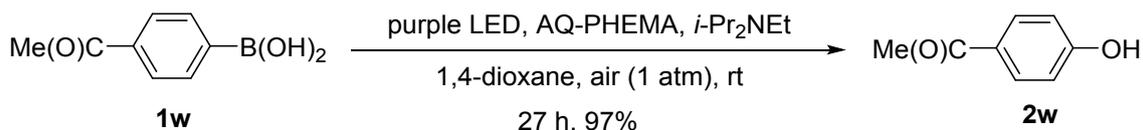
The reaction of **1u** (147 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2u** as a solid (111 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.43 (m, 2H), 7.06 – 6.94 (m, 2H), 6.80 (brs, 1H).

### 4-Formylphenol (**2v**)<sup>2</sup>



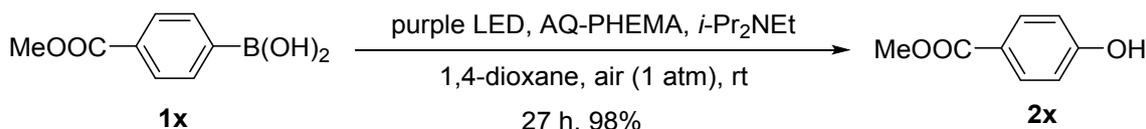
The reaction of **1v** (150 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2v** as a solid (114 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.86 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.62 (brs, 1H).

### 4-Acetylphenol (**2w**)<sup>2</sup>



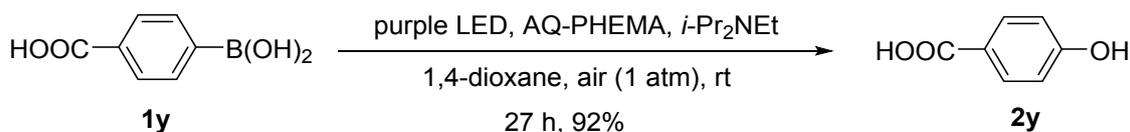
The reaction of **1w** (164 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2w** as a solid (132 mg, 97%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.70 (brs, 1H), 2.58 (s, 3H).

#### 4-Methoxycarbonylphenol (**2x**)<sup>2</sup>



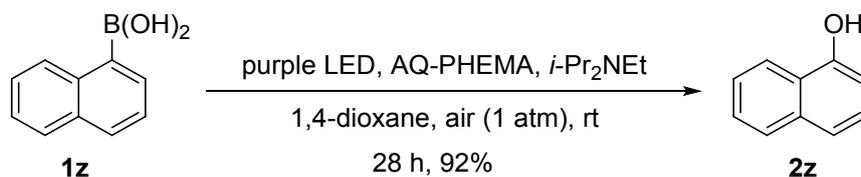
The reaction of **1x** (180 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2x** as a solid (149 mg, 98%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.44 (brs, 1H), 3.89 (s, 3H).

#### 4-Carboxyphenol (**2y**)<sup>5</sup>



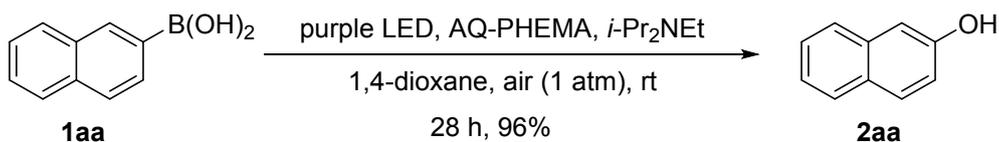
The reaction of **1y** (166 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2y** as a solid (127 mg, 92%); <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  12.41 (brs, 1H), 10.21 (brs, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H).

#### Naphthalen-1-ol (**2z**)<sup>2</sup>



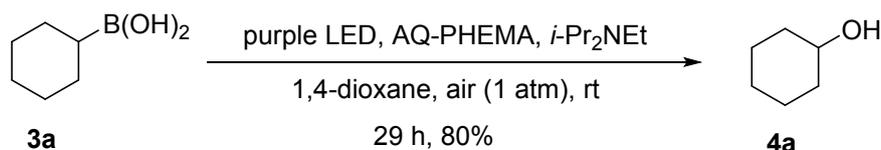
The reaction of **1z** (172 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330  $\mu$ L, 2 mmol), and 1,4-dioxane (5 mL) afforded **2z** as a solid (133 mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.22 – 8.13 (m, 1H), 7.84 – 7.75 (m, 1H), 7.53 – 7.41 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 5.20 (brs, 1H).

#### Naphthalen-2-ol (**2aa**)<sup>2</sup>



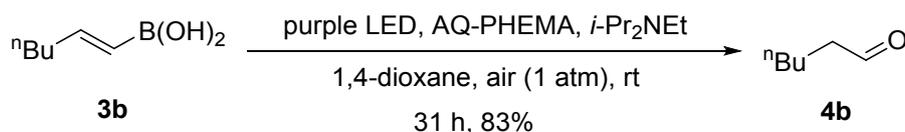
The reaction of **1aa** (172 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2aa** as a solid (138 mg, 96%); <sup>1</sup>H NMR (400 MHz, ) δ 7.75 (t, *J* = 8.0 Hz), 7.67 (d, *J* = 8.4 Hz), 7.42 (t, *J* = 7.2 Hz), 7.32 (t, *J* = 7.4 Hz), 7.17 – 7.07 (m), 5.13 (brs, 1H).

### Cyclohexanol (**4a**)<sup>2</sup>



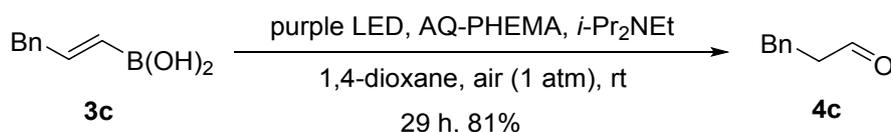
The reaction of **3a** (128 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **4a** as a liquid (80 mg, 80%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.66 – 3.54 (m, 1H), 1.94 – 1.82 (m, 2H), 1.77 – 1.69 (m, 2H), 1.59 – 1.48 (m, 2H), 1.36 – 1.09 (m, 5H).

### Hexanal (**4b**)<sup>6</sup>



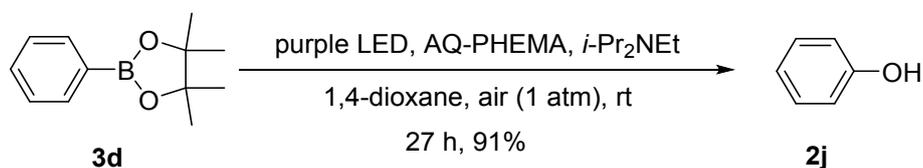
The reaction of **3b** (128 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **4b** as a liquid (83 mg, 83%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.77 (s, 1H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.38 – 1.25 (m, 4H), 0.90 (t, *J* = 6.4 Hz, 3H).

### 3-Phenylpropanal (**4c**)<sup>2</sup>



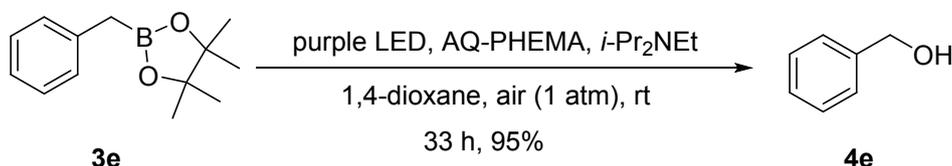
The reaction of **3c** (162 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **4c** as a liquid (109 mg, 81%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.81 (s, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H).

### Phenol (**2j**)<sup>2</sup>



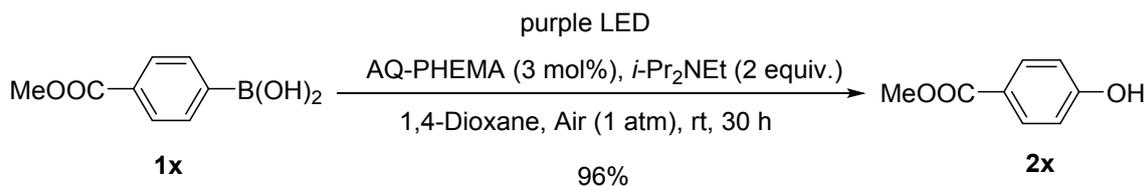
The reaction of **3d** (204 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **2j** as a solid (86 mg, 91%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 (t, *J* = 7.4 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 5.18 (brs, 1H).

### Benzyl alcohol (**4e**)<sup>2</sup>



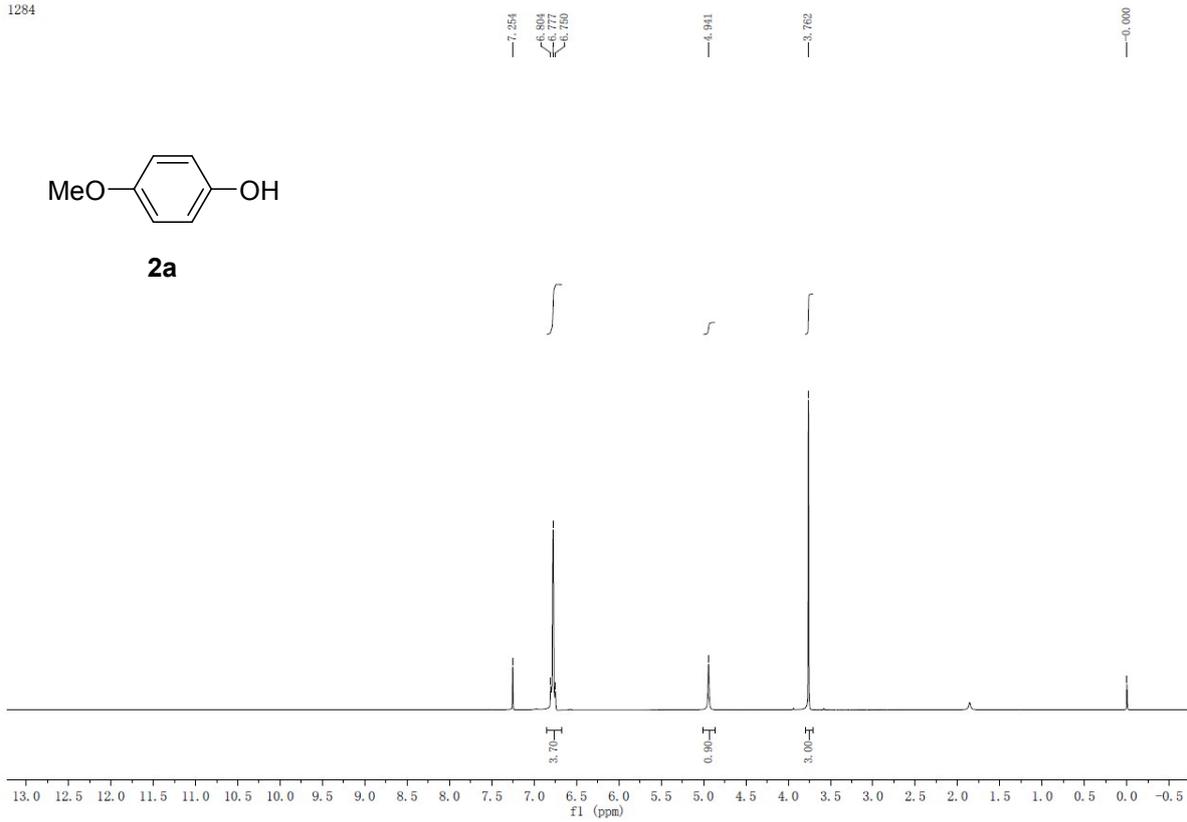
The reaction of **3e** (218 mg, 1 mmol), **AQ-PHEMA** (10 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (330 μL, 2 mmol), and 1,4-dioxane (5 mL) afforded **4e** as a liquid (103 mg, 95%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.14 (m, 5H), 4.43 (d, *J* = 5.2 Hz, 2H), 3.83 (t, *J* = 5.0 Hz, 1H).

Gram scale reaction of **2x** under Condition A.

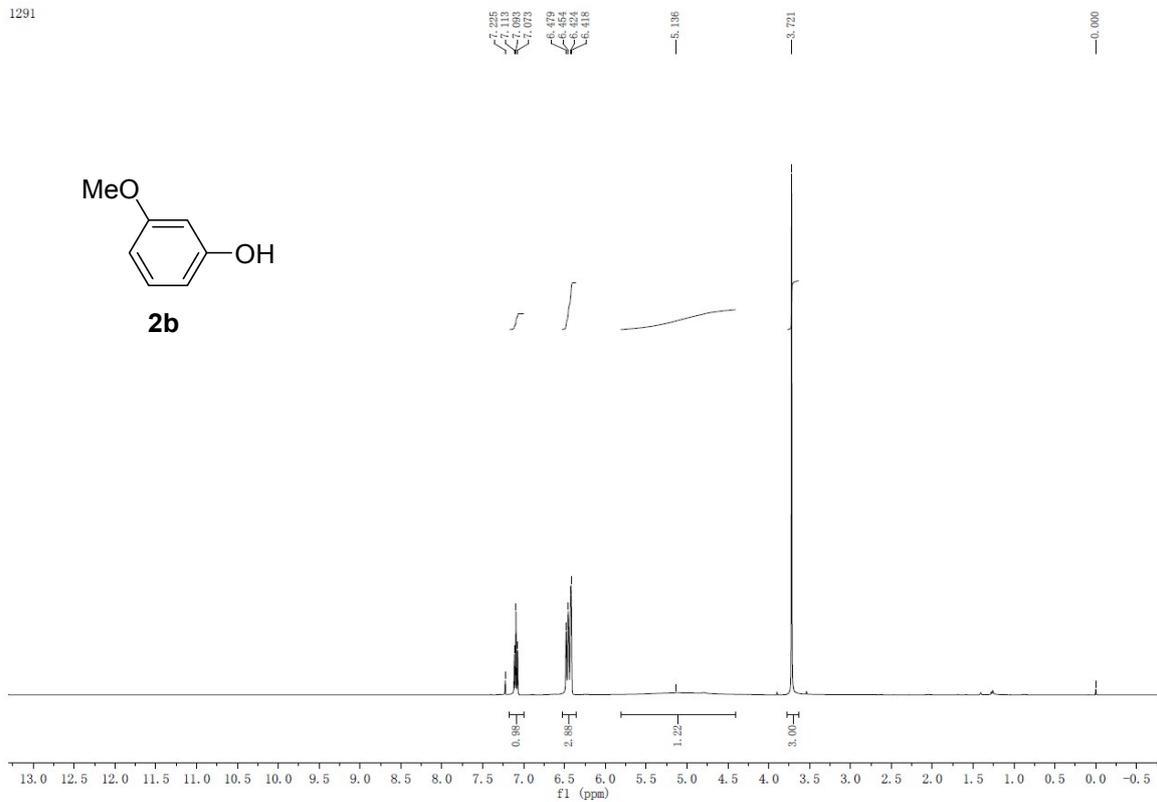


**1x** (1.824g, 10.1 mmol), **AQ-PHEMA** (101 mg, 3 mol%), *i*-Pr<sub>2</sub>NEt (3.3 mL, 20.2 mmol), and 1,4-dioxane (50 mL) were added to a dry 100 mL Schlenk bottle. The mixture was irradiated by purple LED at rt under air atmosphere. The photoreaction was completed after 30 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 2/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1→5/1) to afford **2x** as a solid (1.475g, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.48 (brs, 1H), 3.90 (s, 3H).

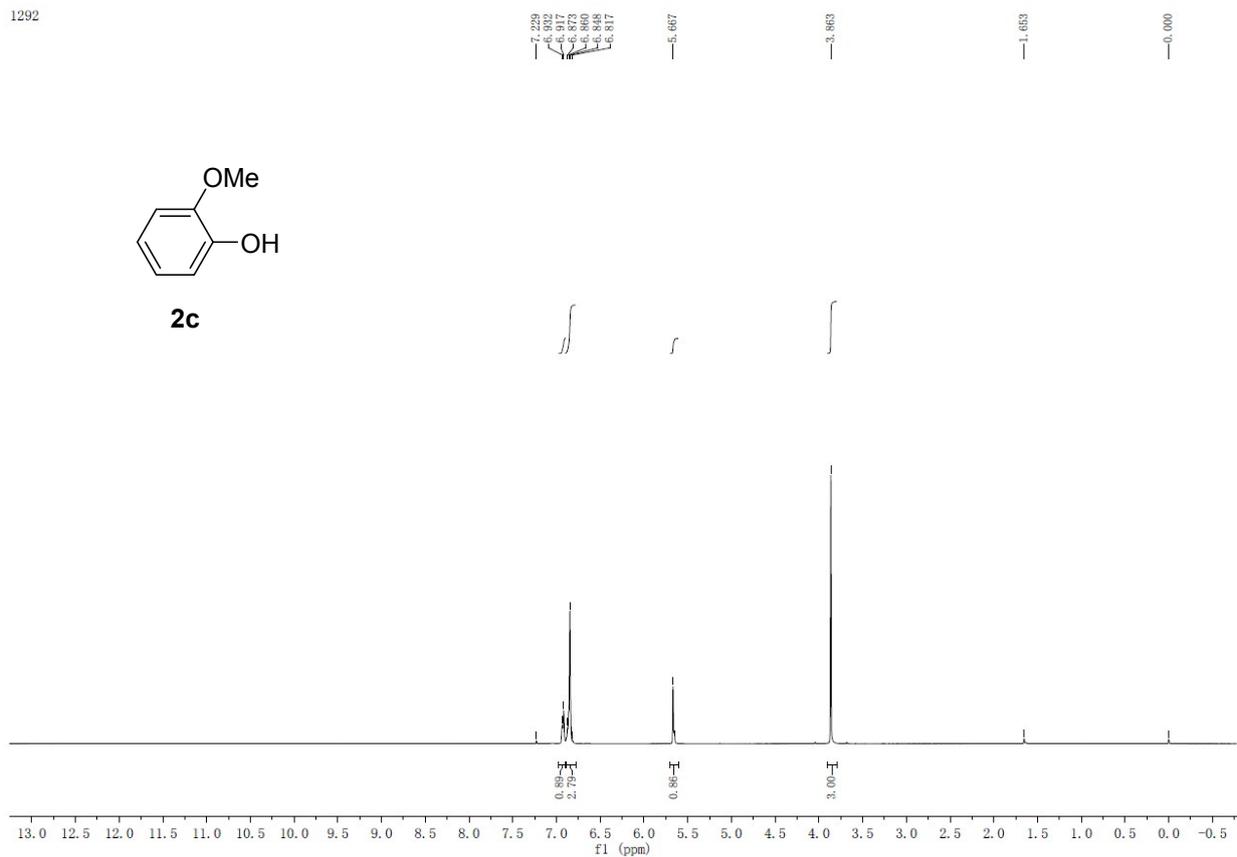
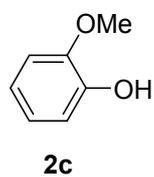
1284



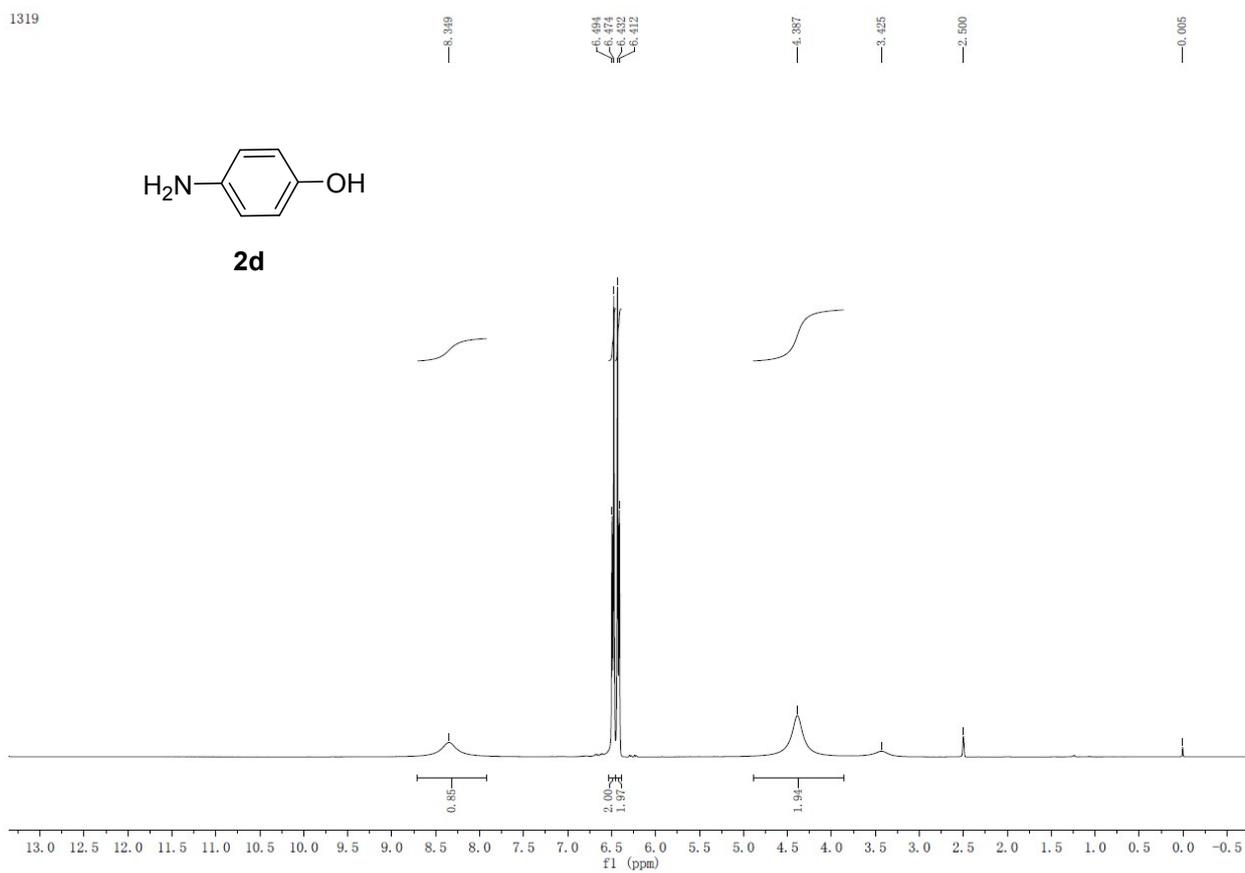
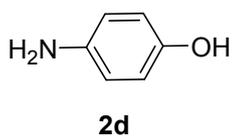
1291



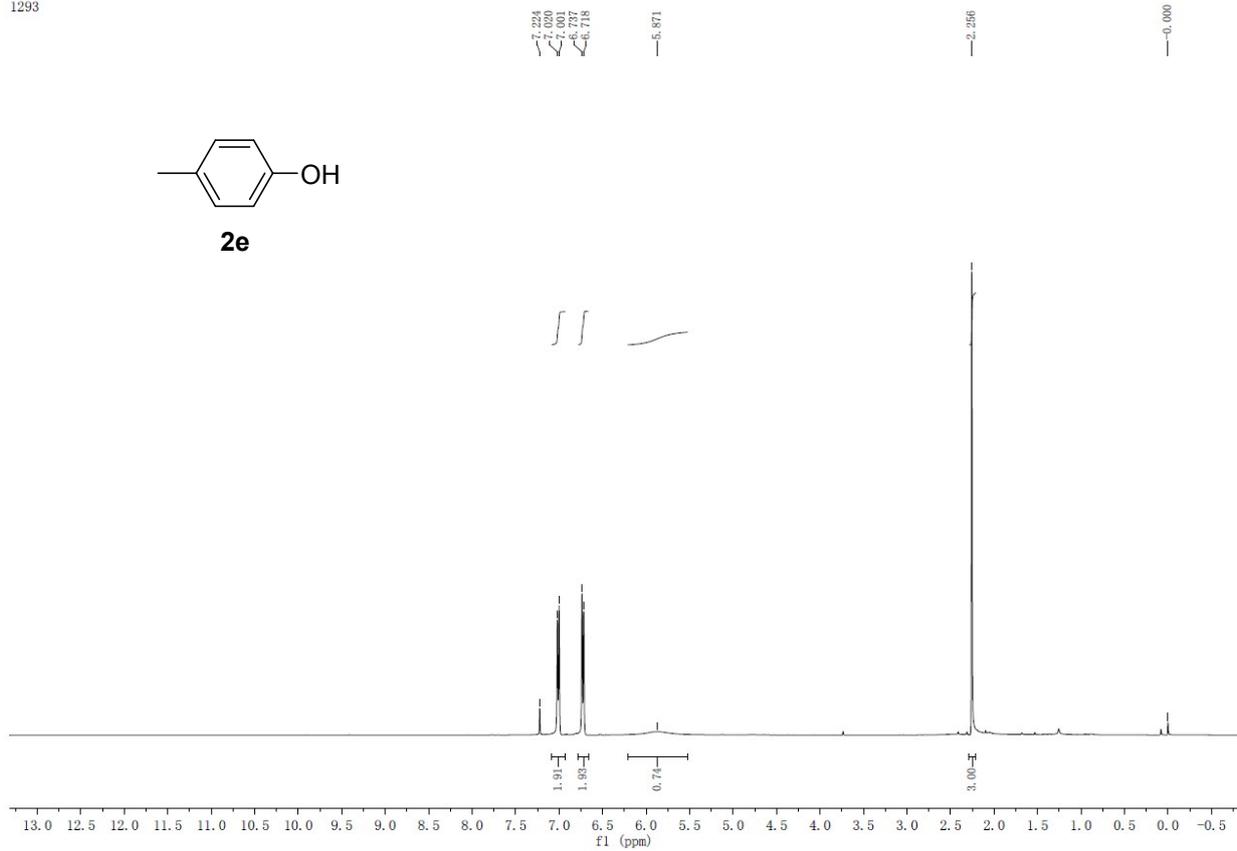
1292



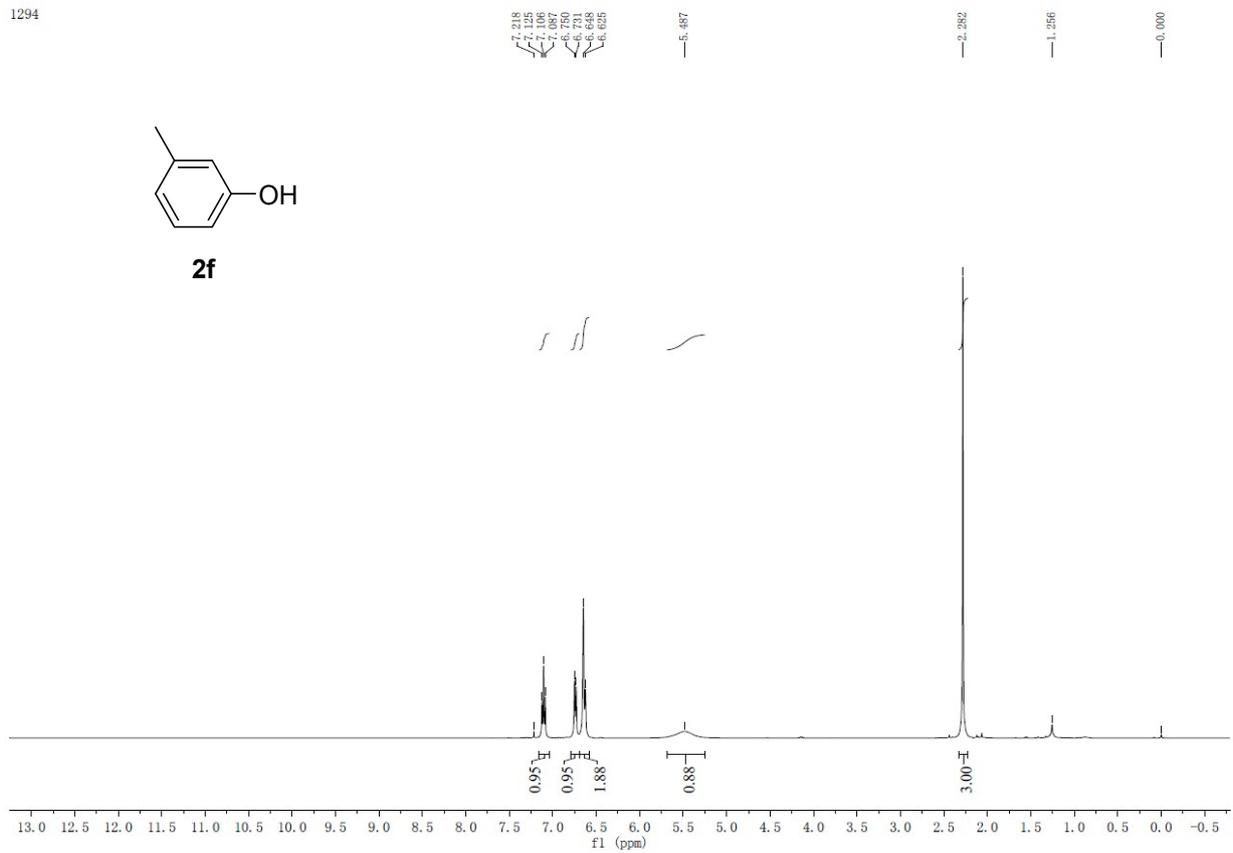
1319



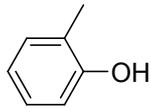
1293



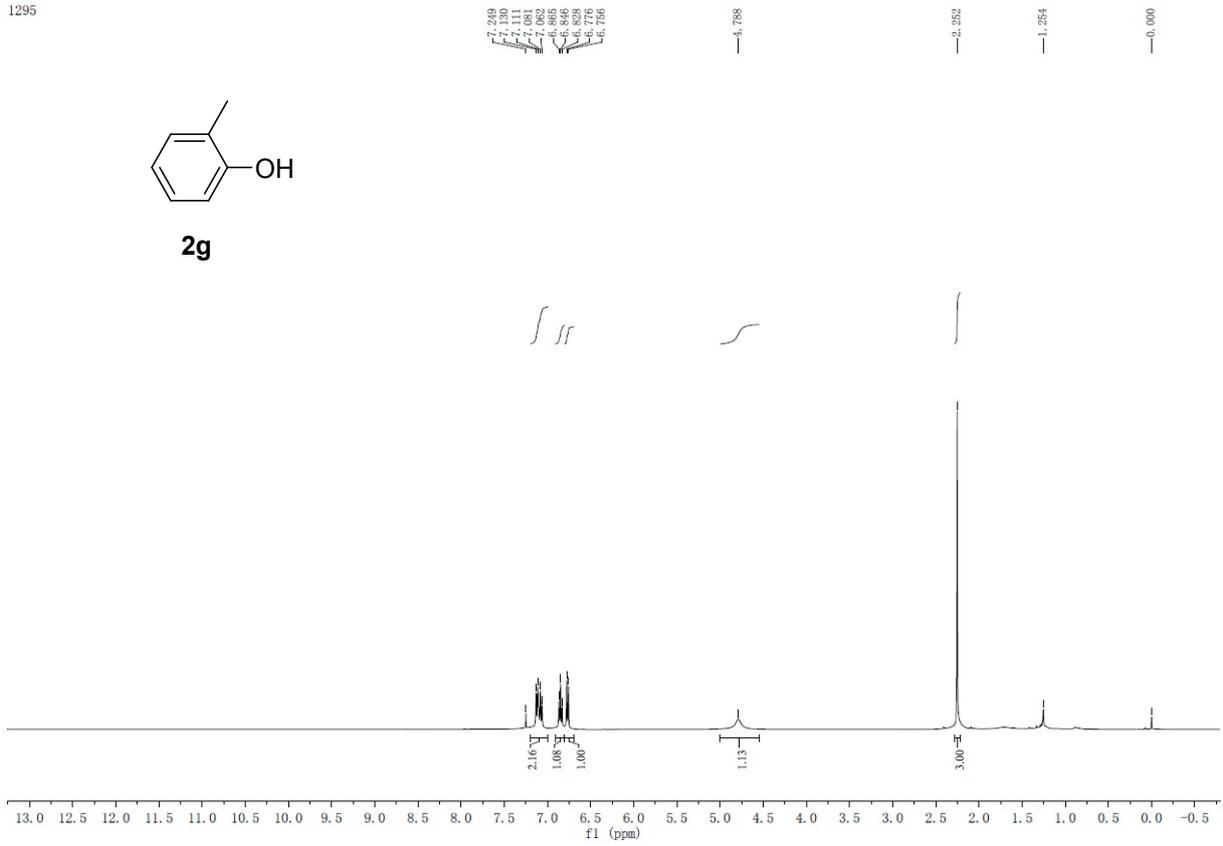
1294



1295



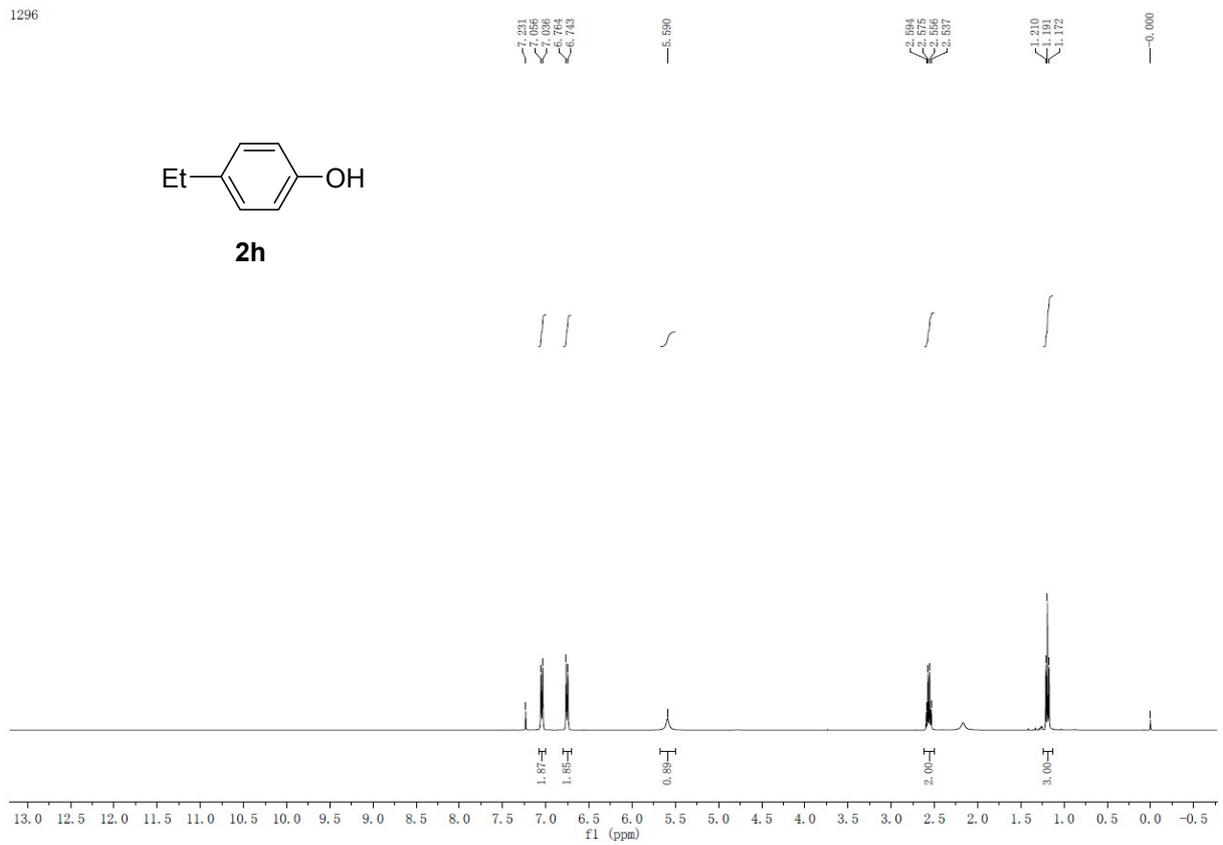
2g



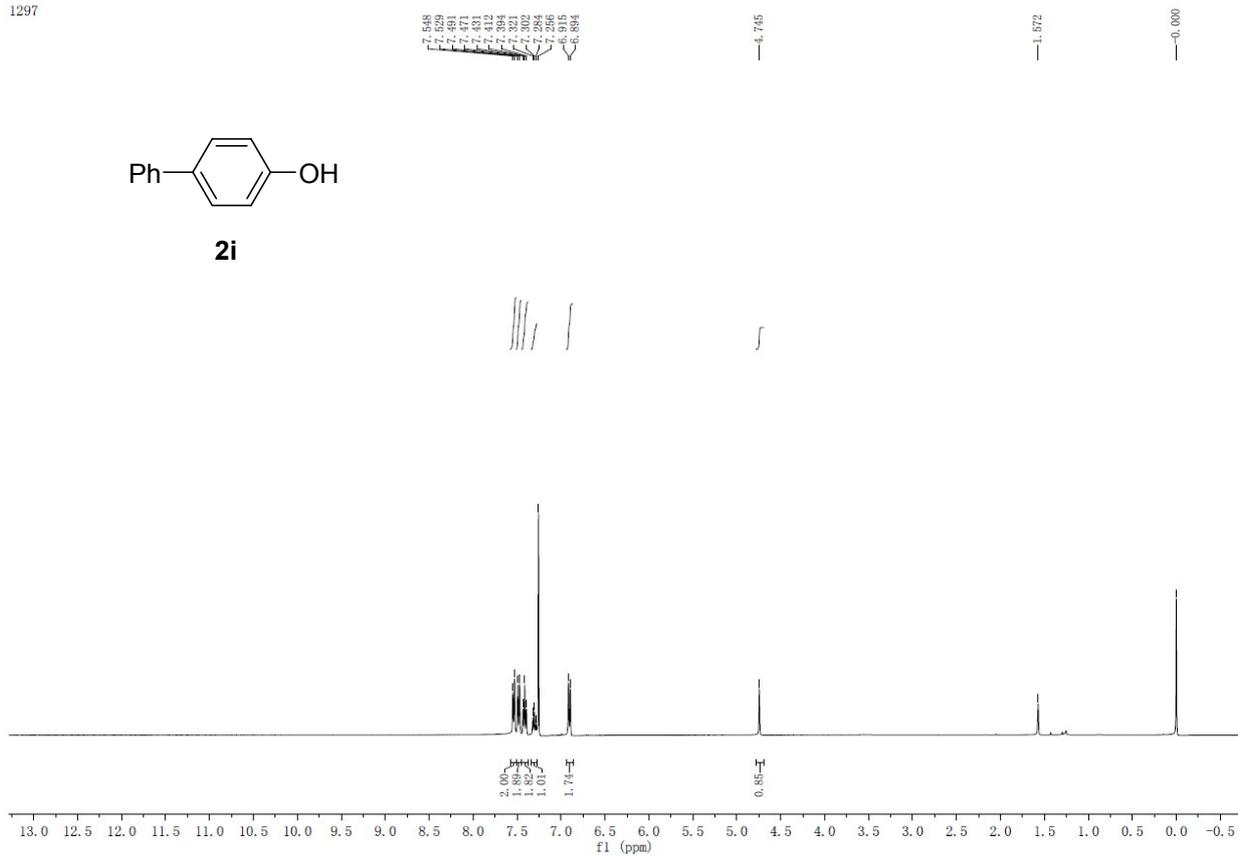
1296



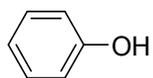
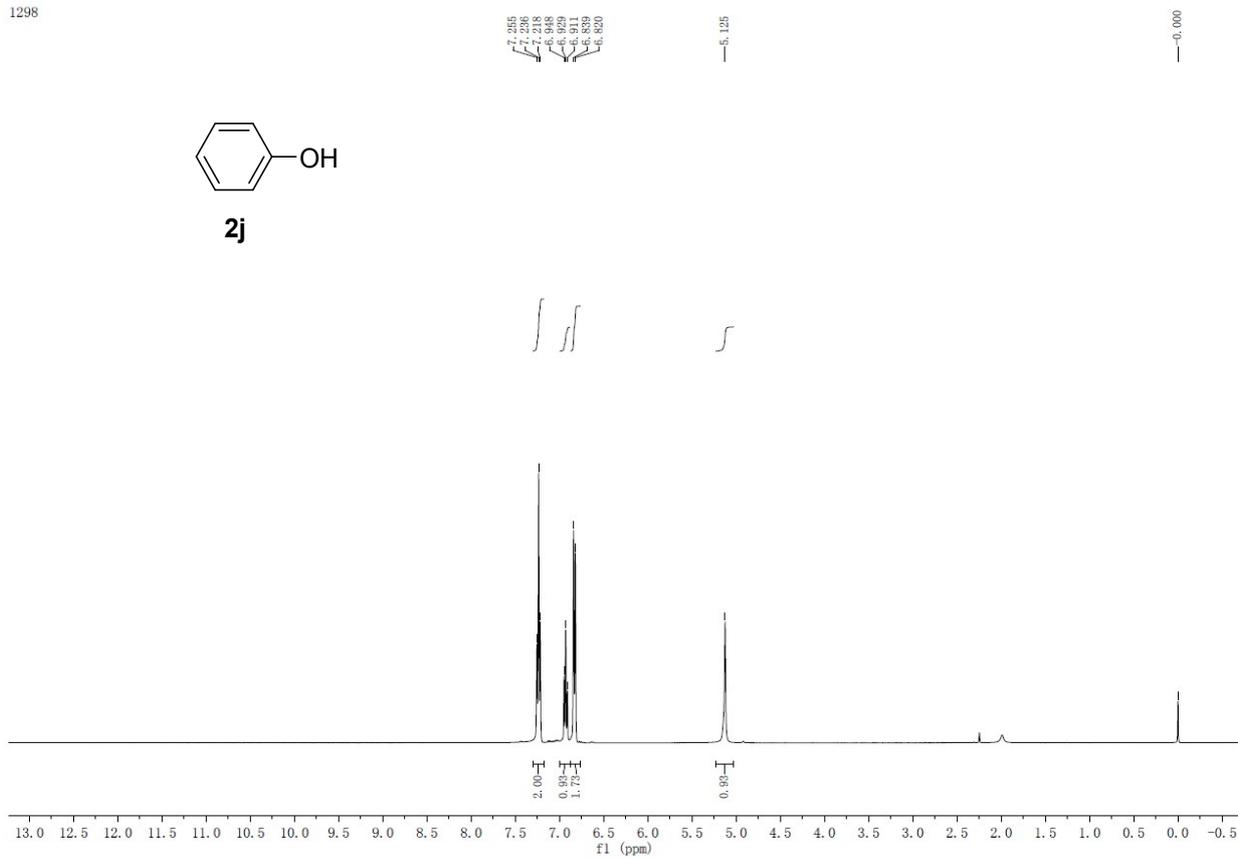
2h



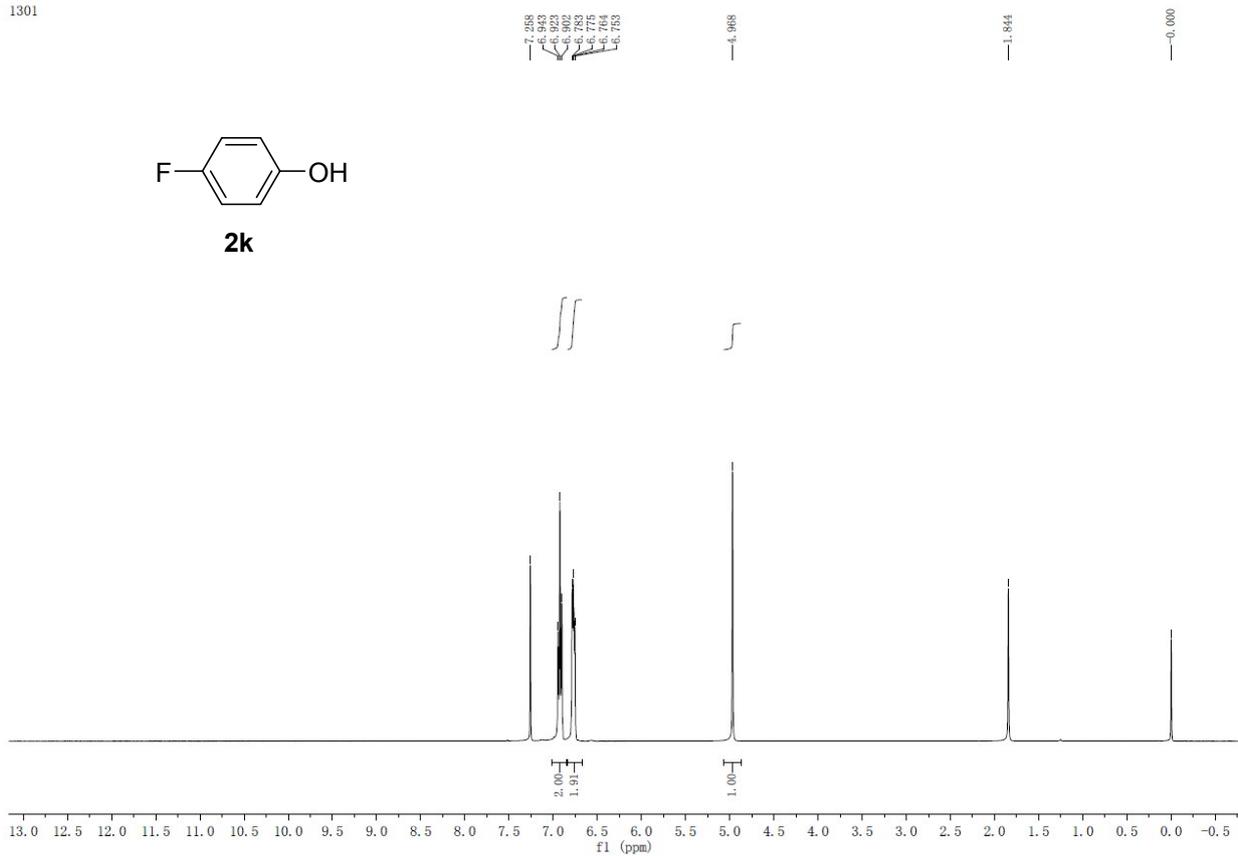
1297

**2i**

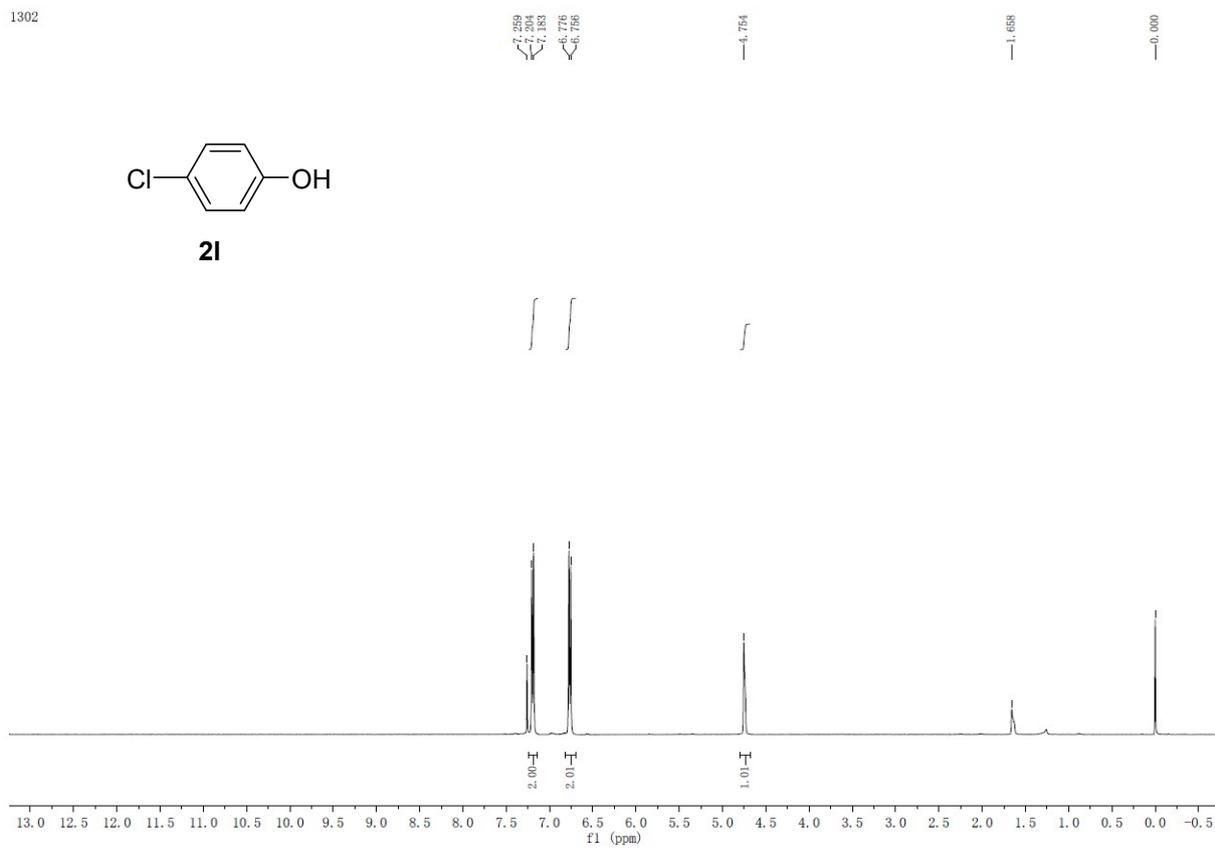
1298

**2j**

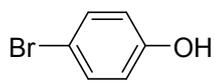
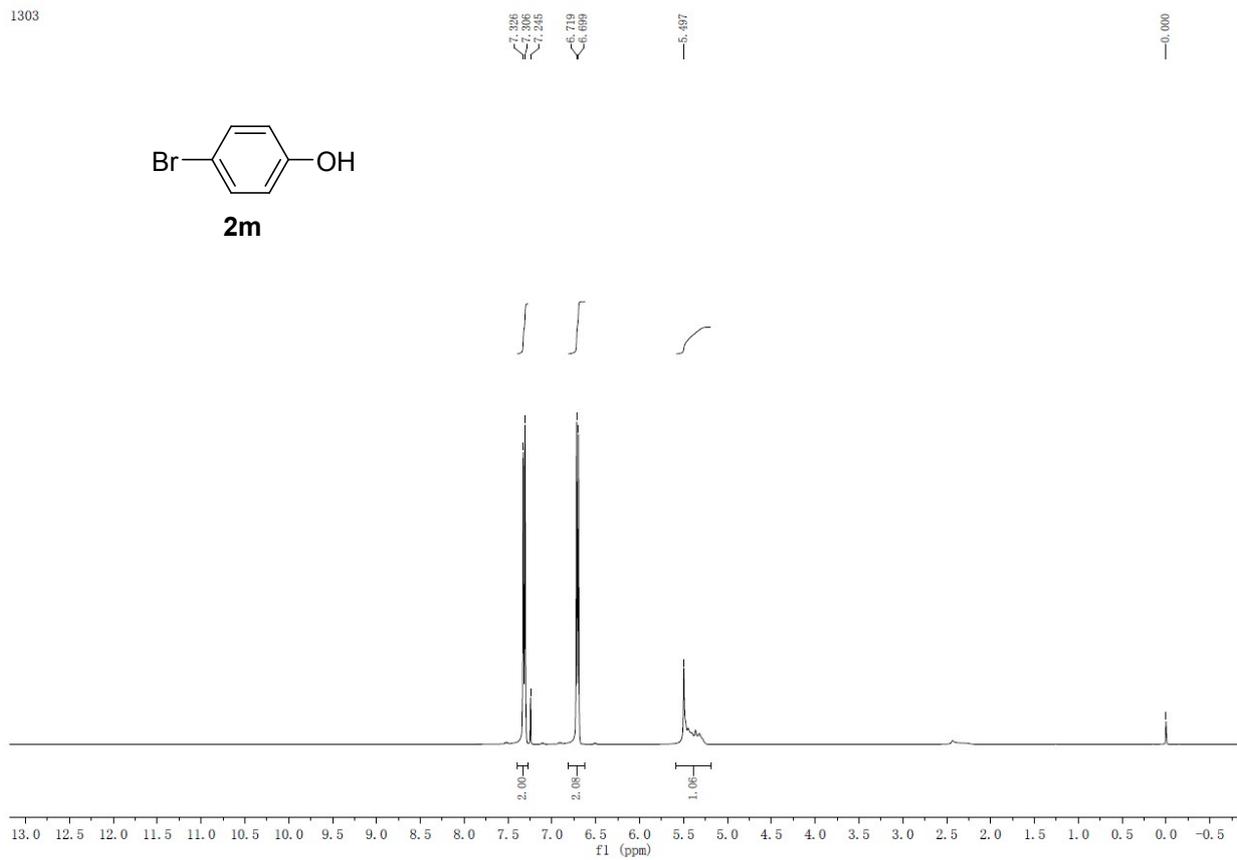
1301



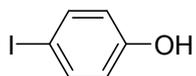
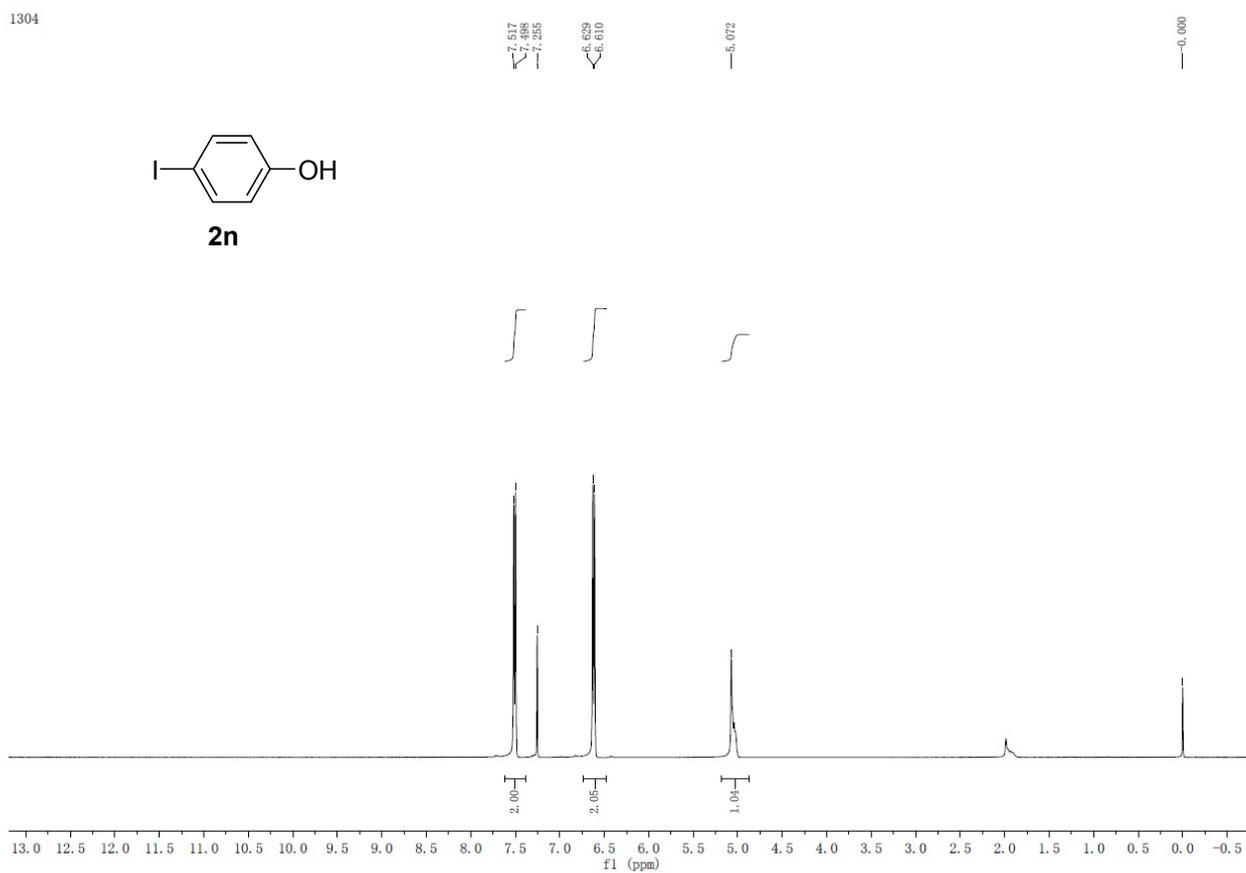
1302



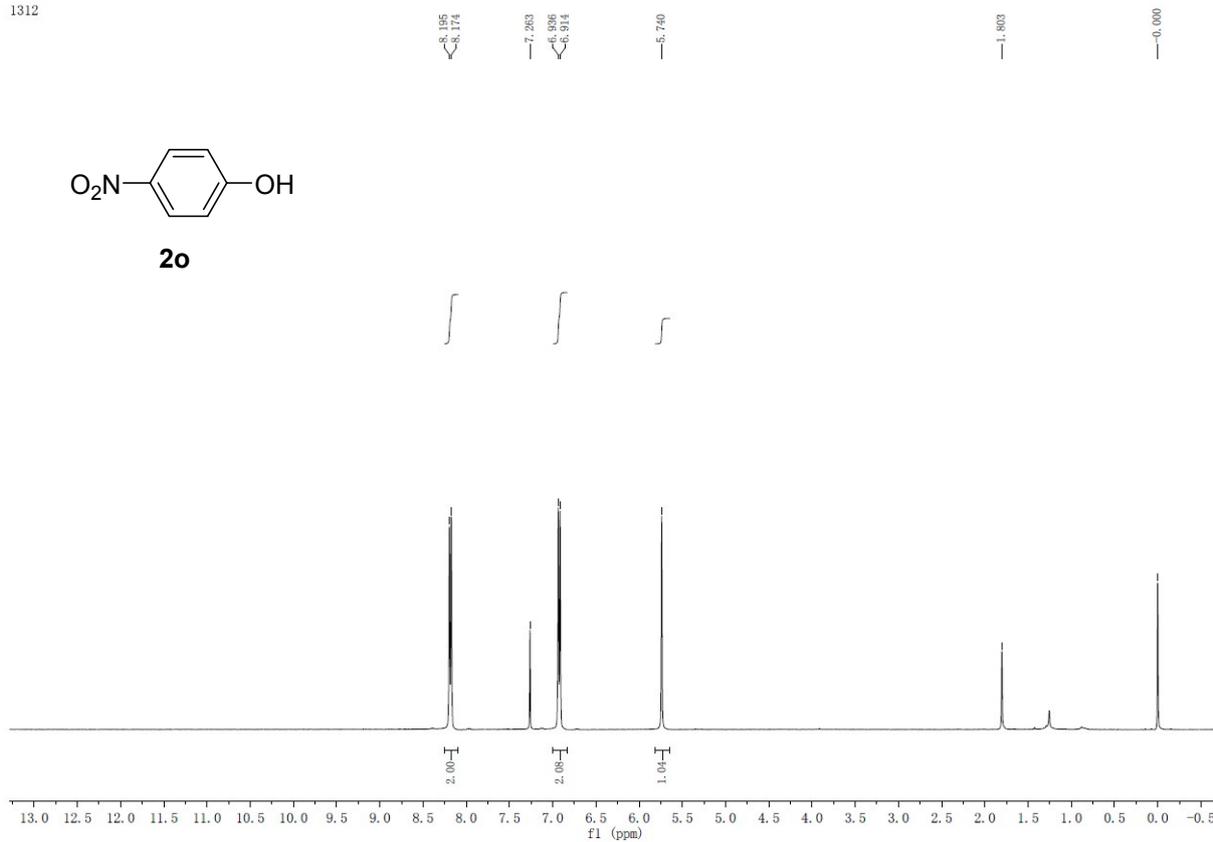
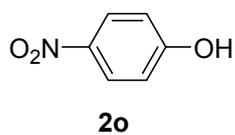
1303

**2m**

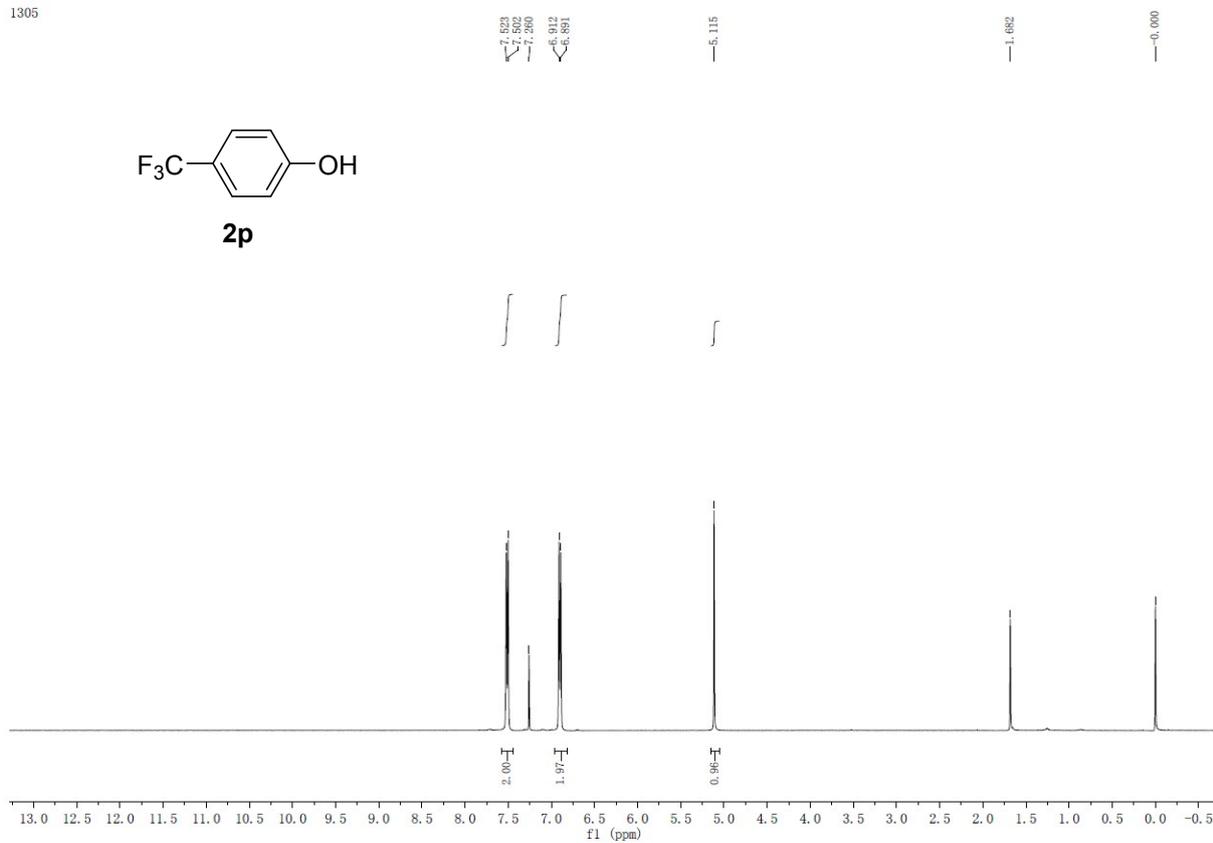
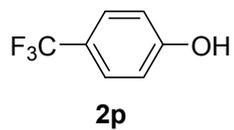
1304

**2n**

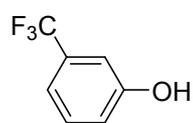
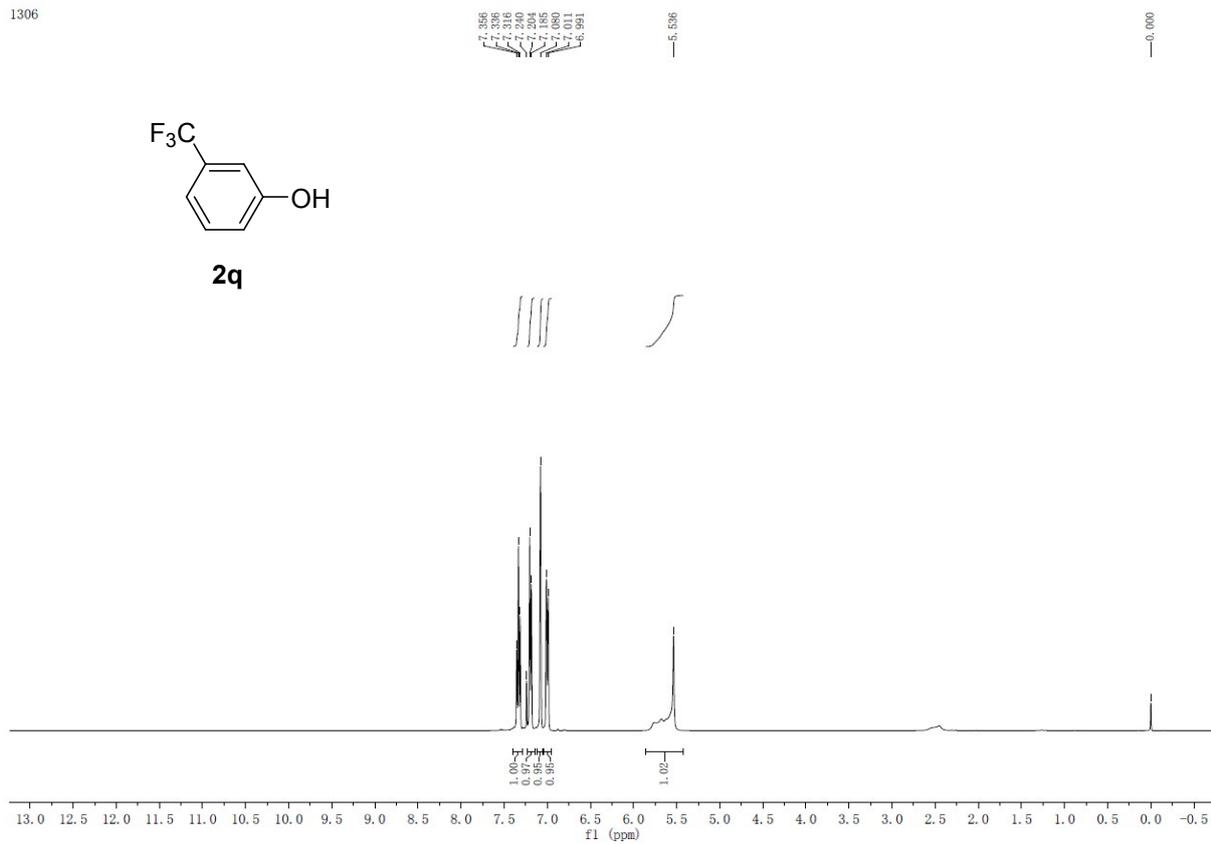
1312



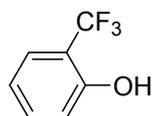
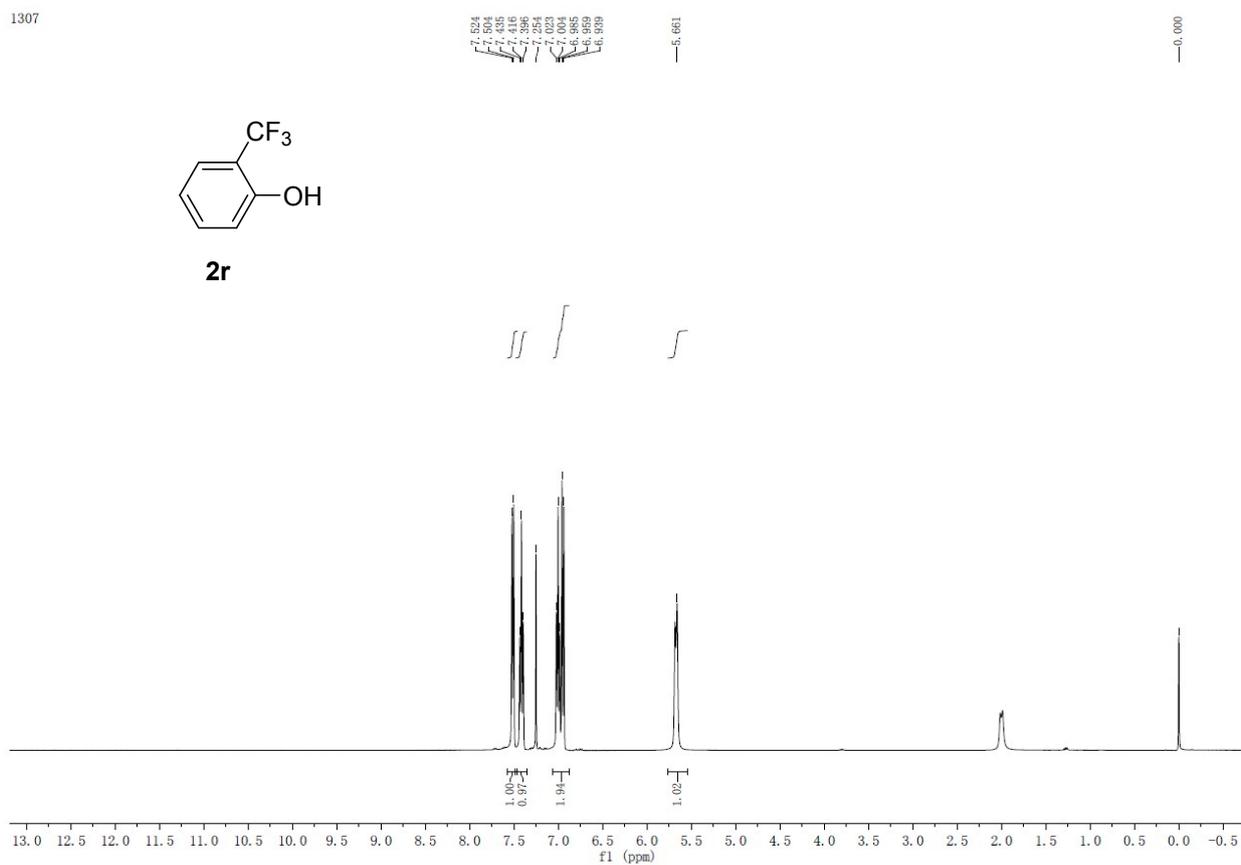
1305



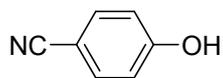
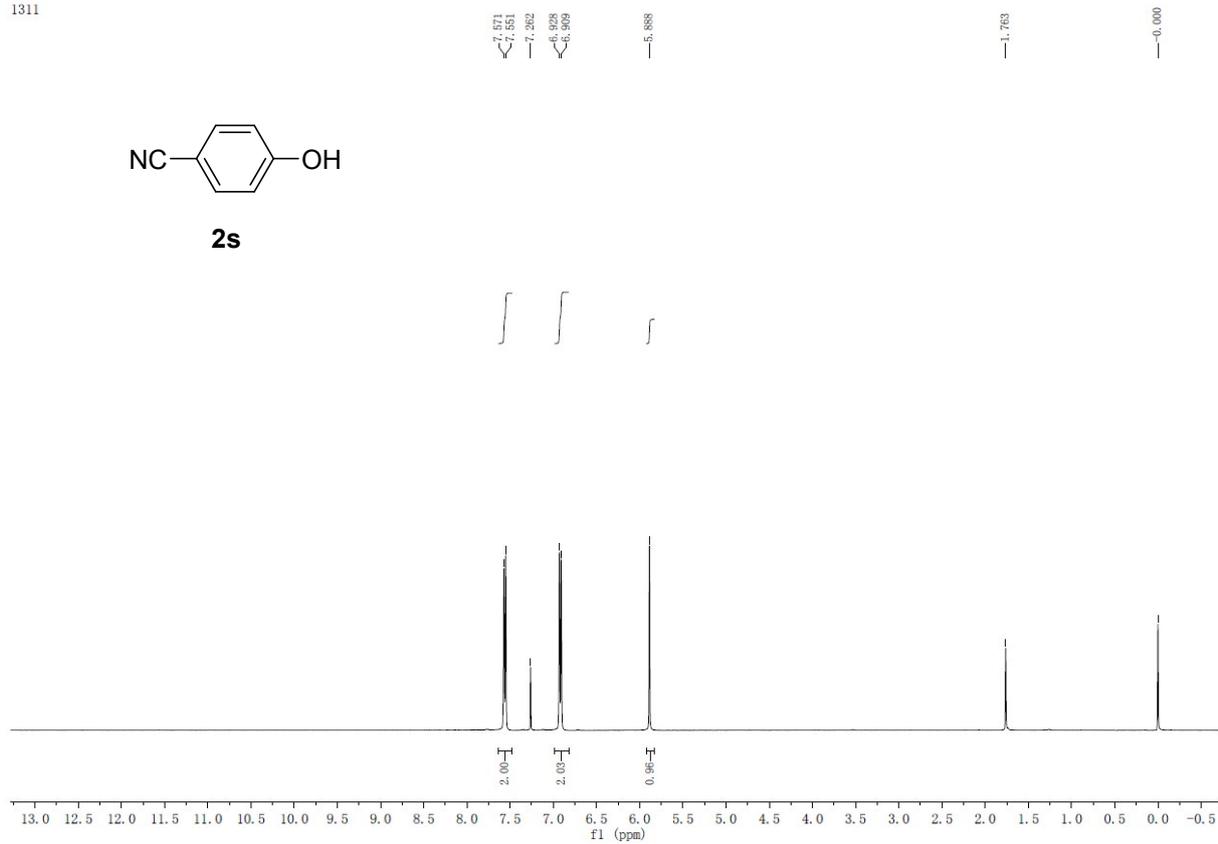
1306

**2q**

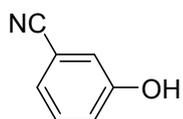
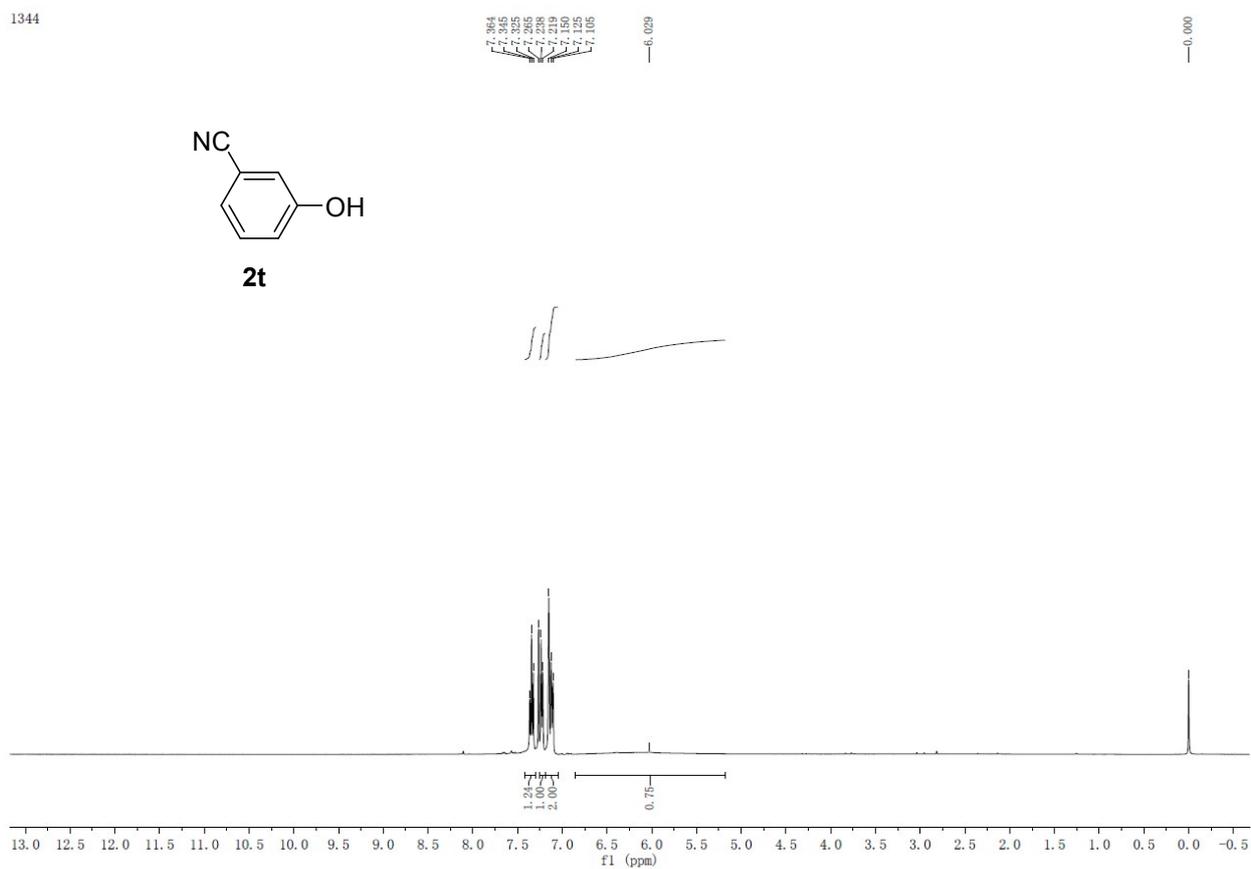
1307

**2r**

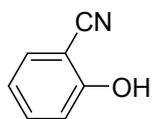
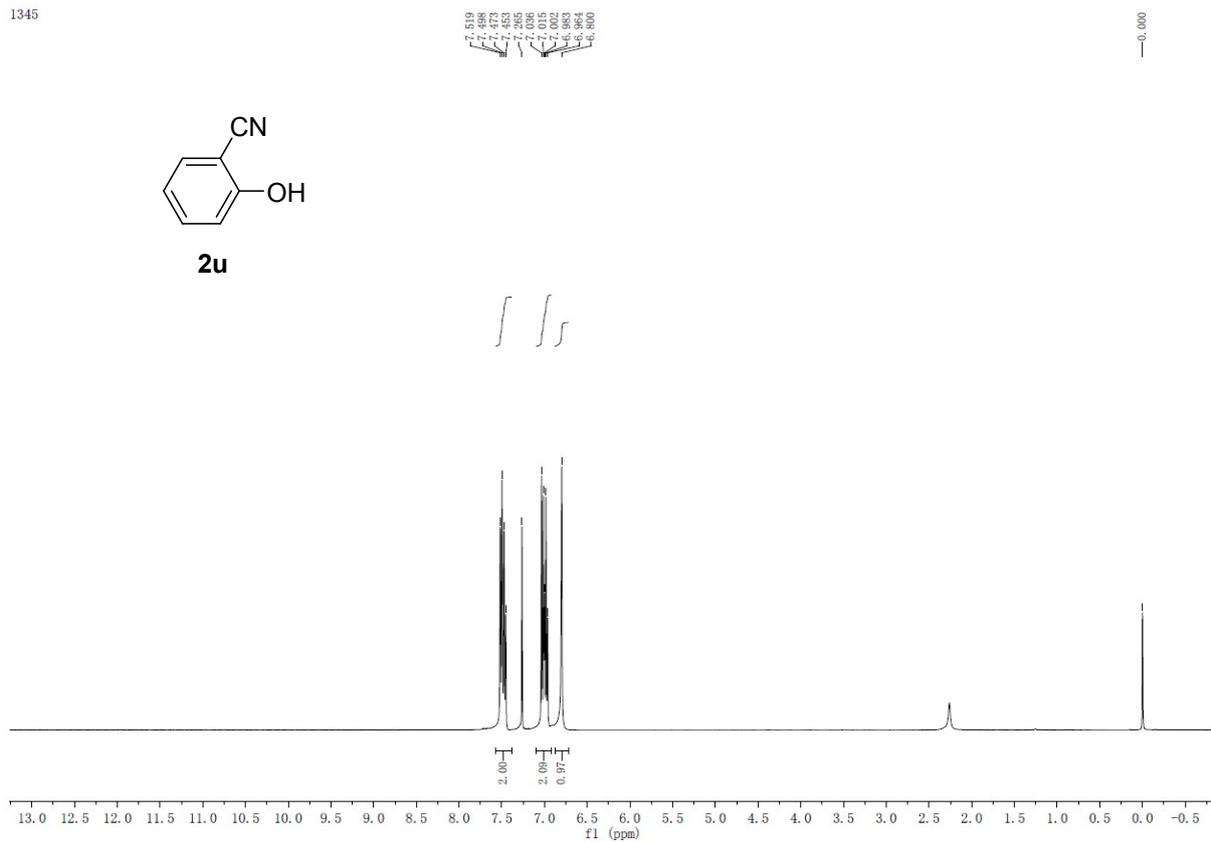
1311

**2s**

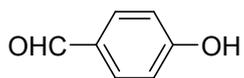
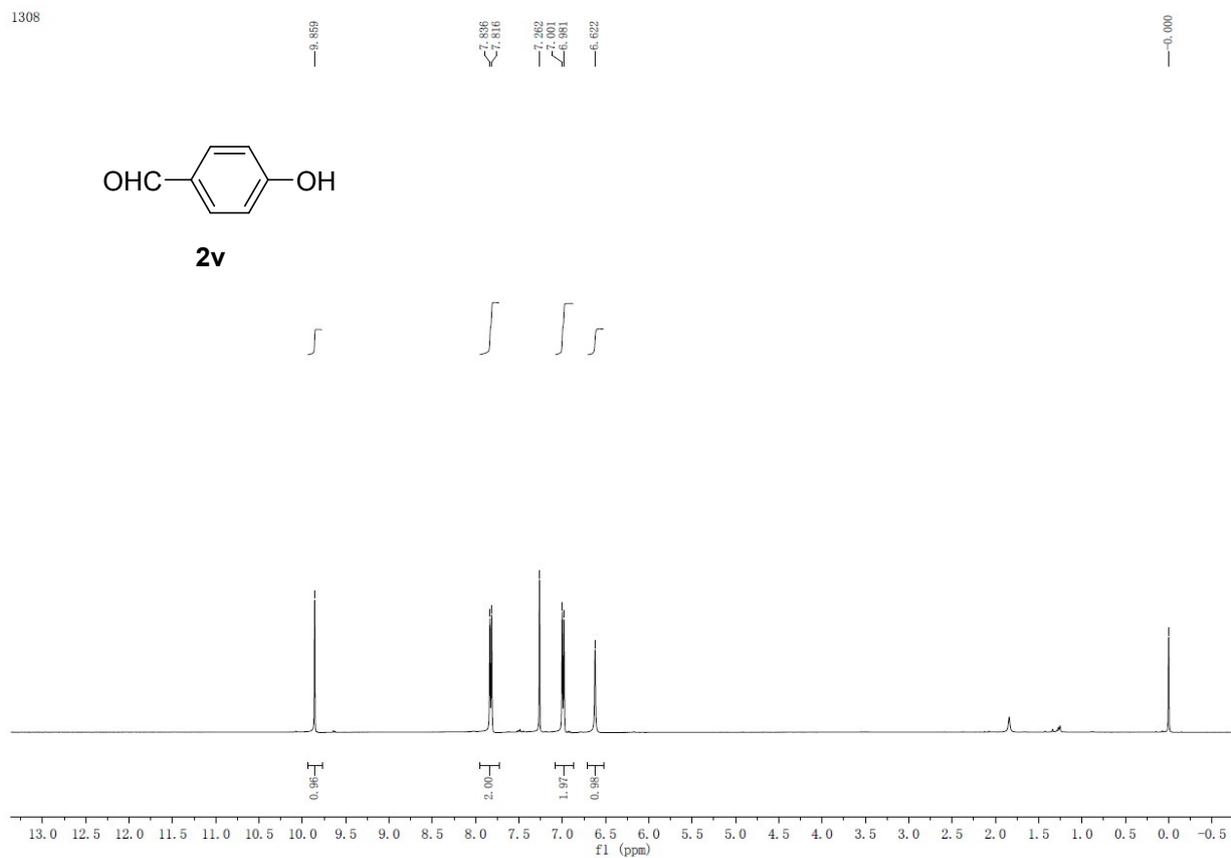
1344

**2t**

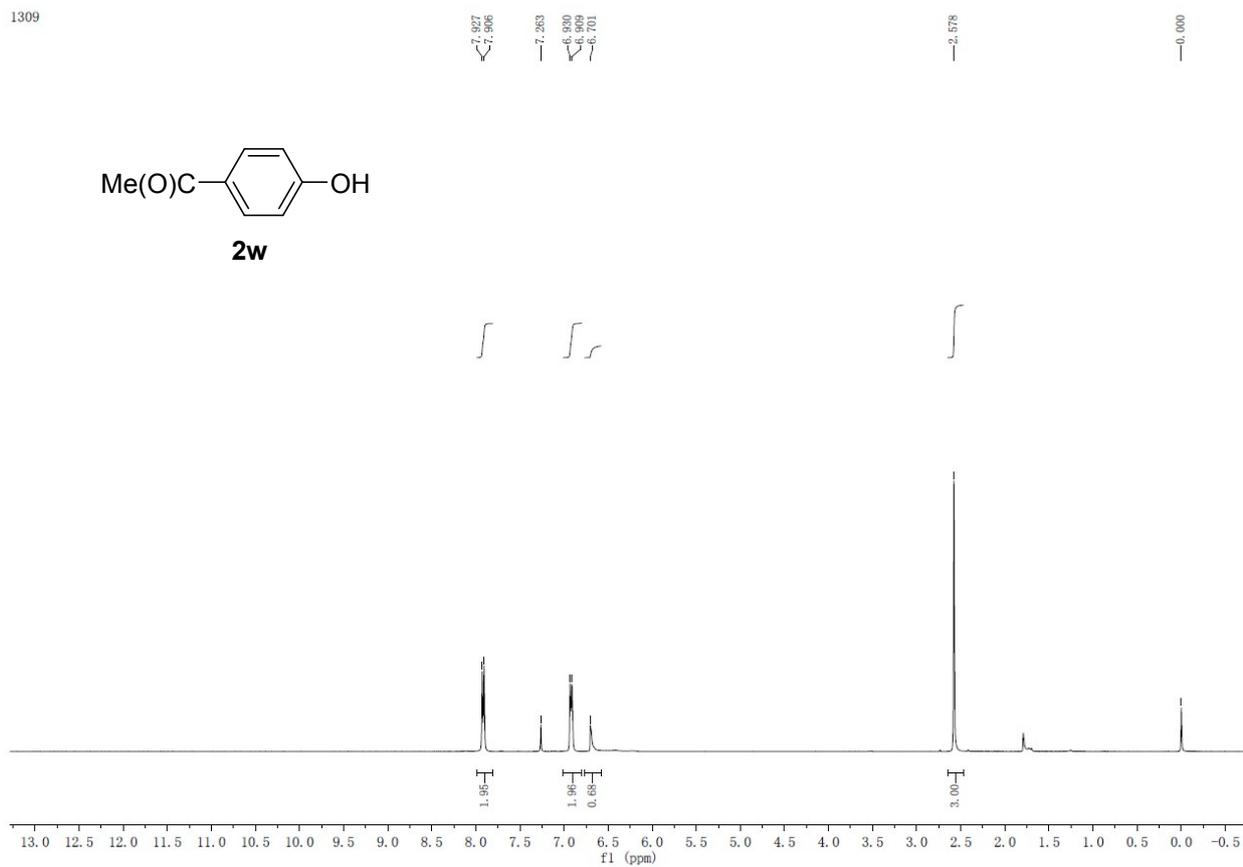
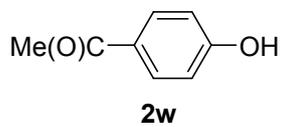
1345

**2u**

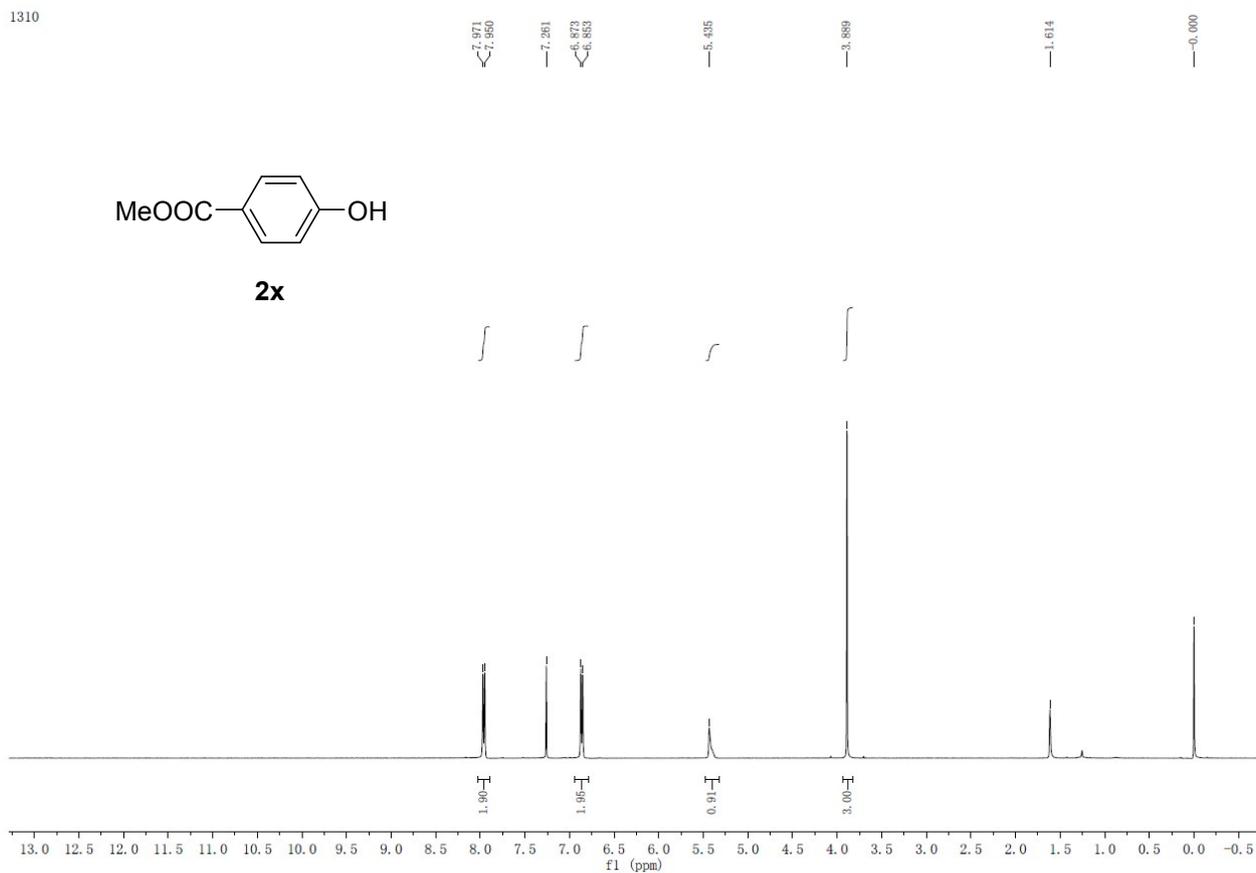
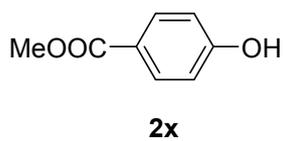
1308

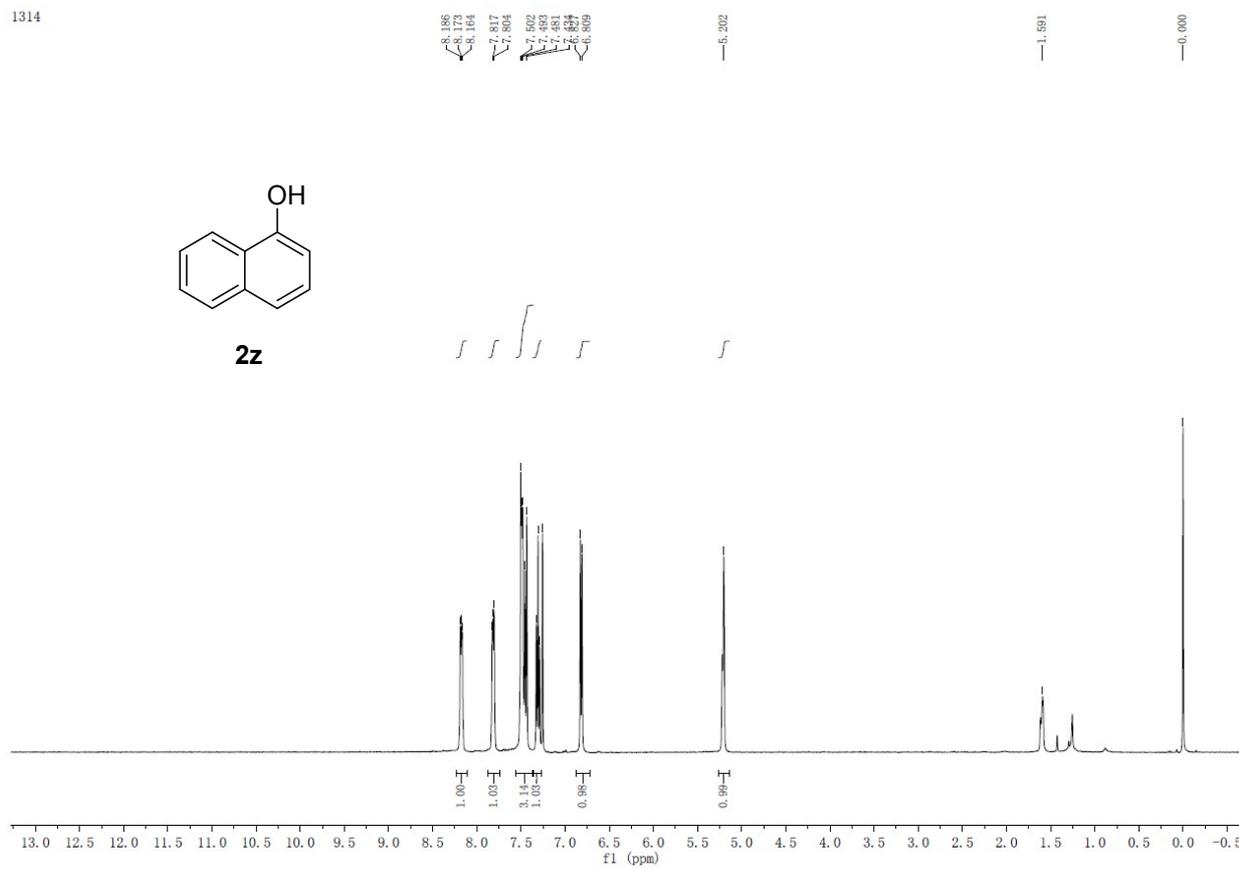
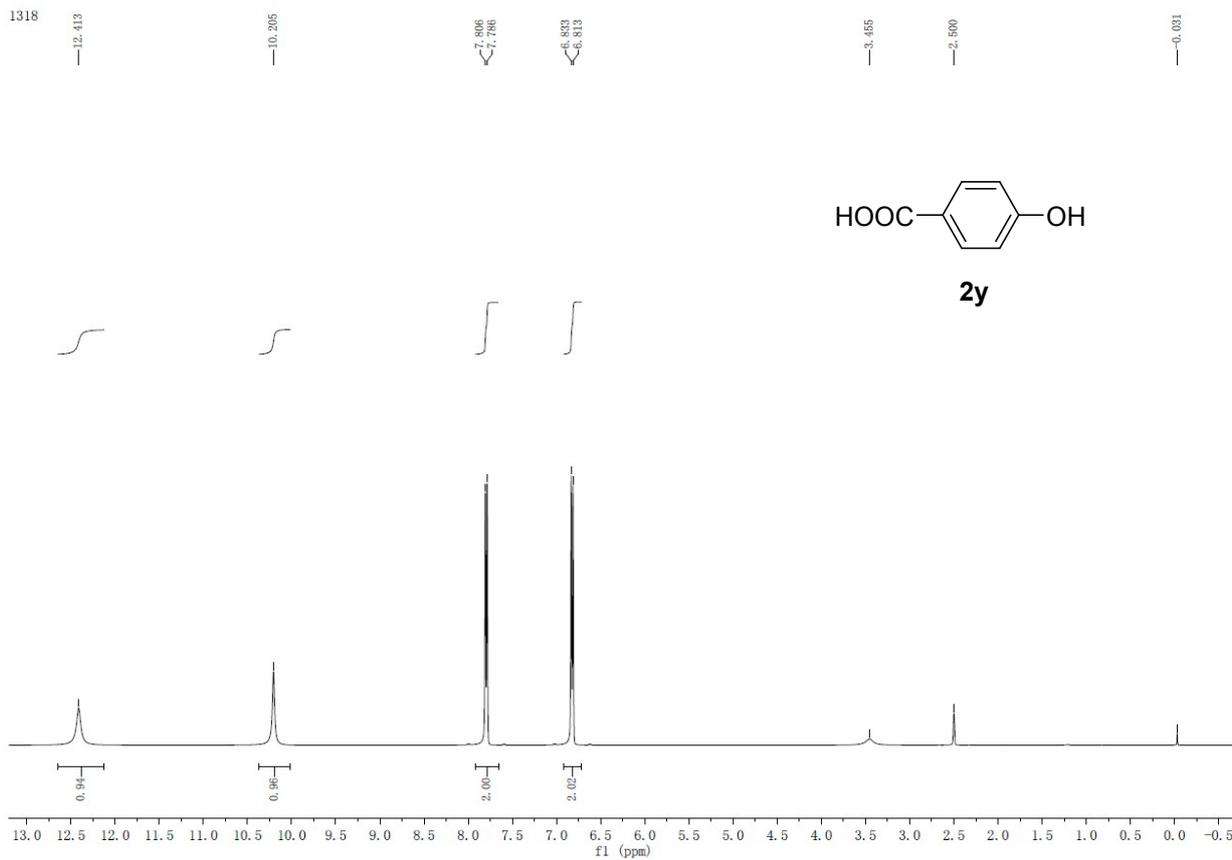
**2v**

1309

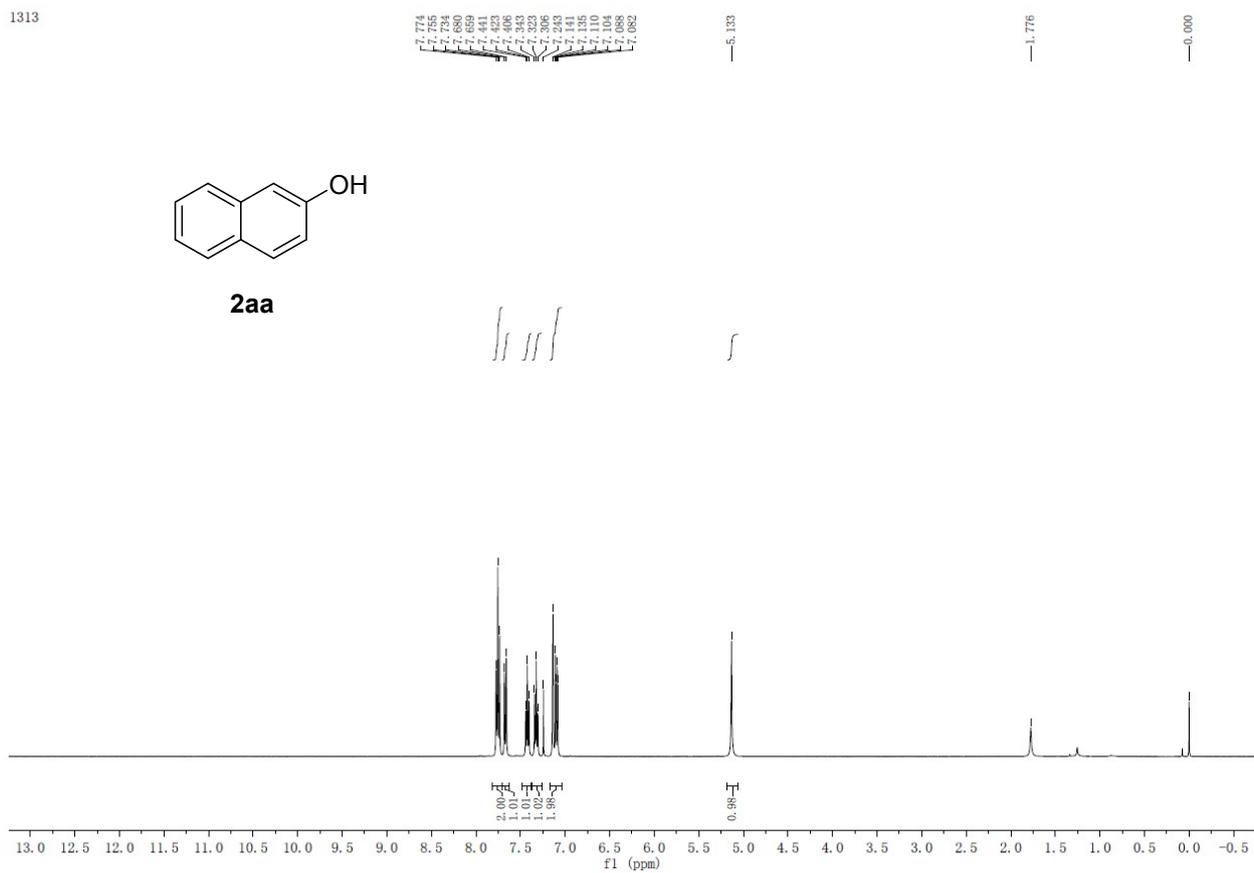


1310

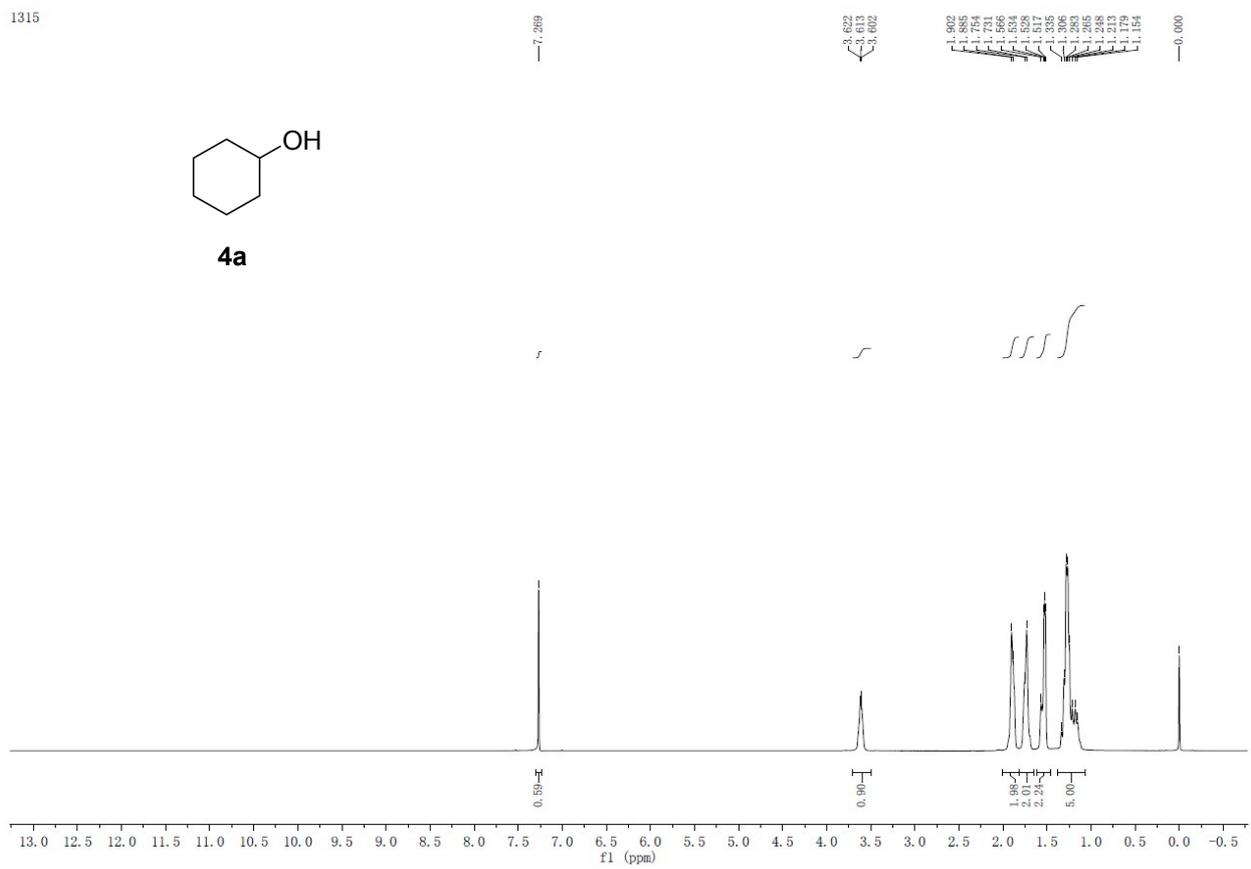




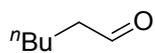
1313



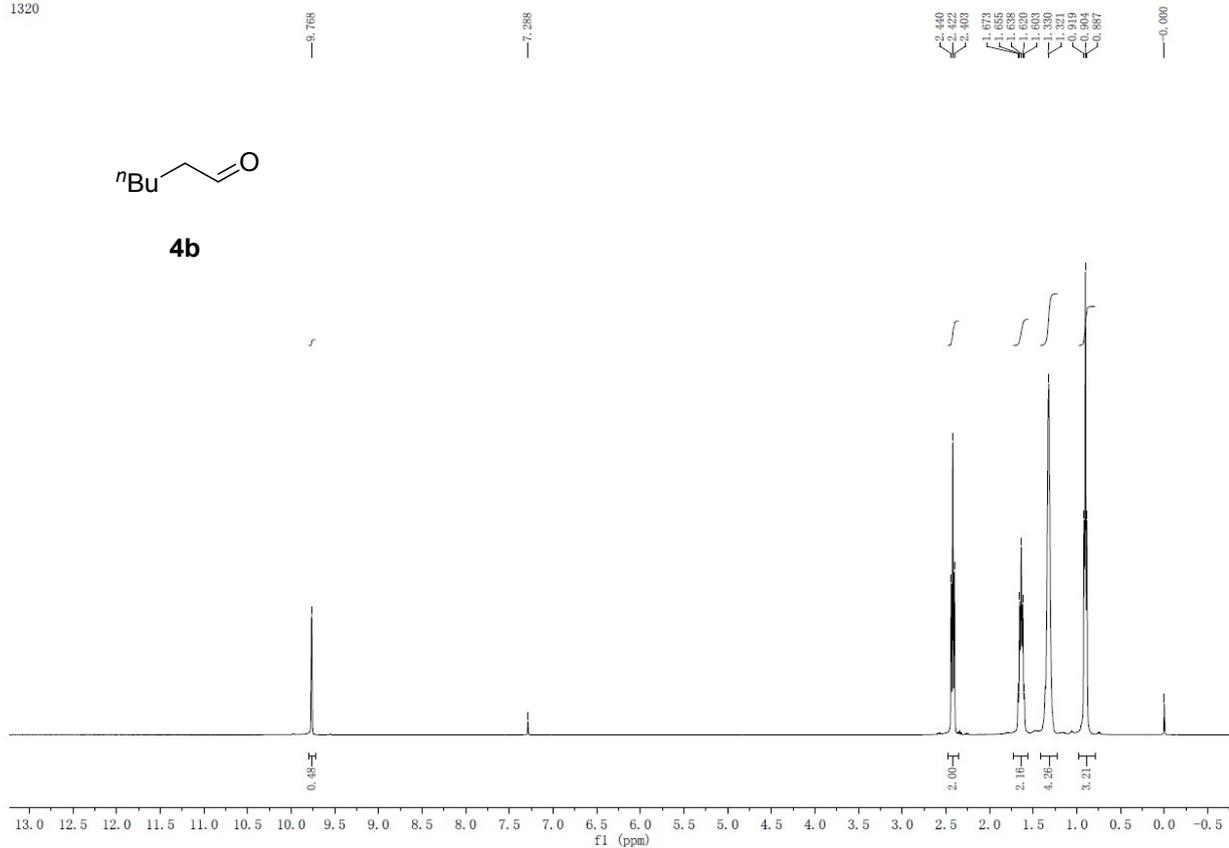
1315



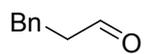
1320



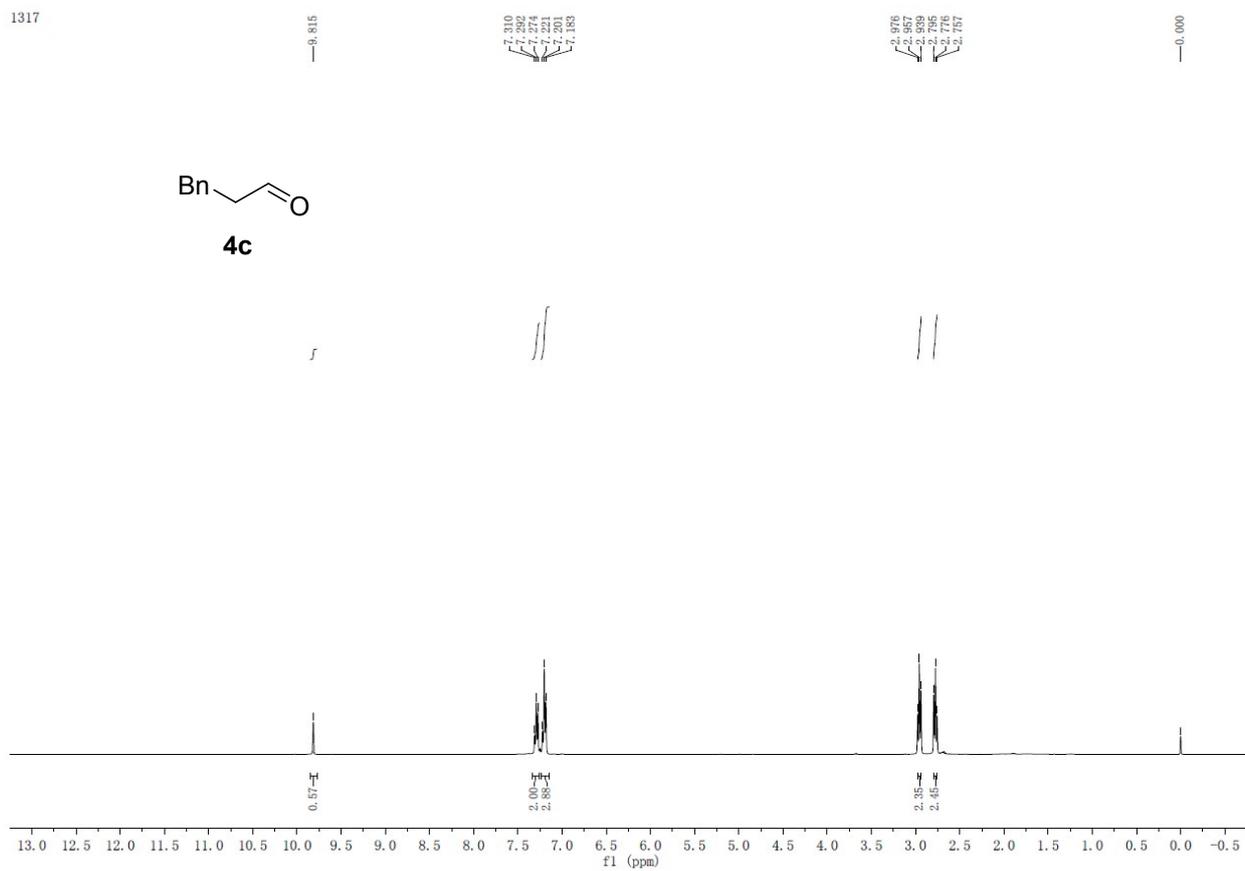
4b



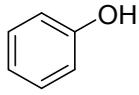
1317



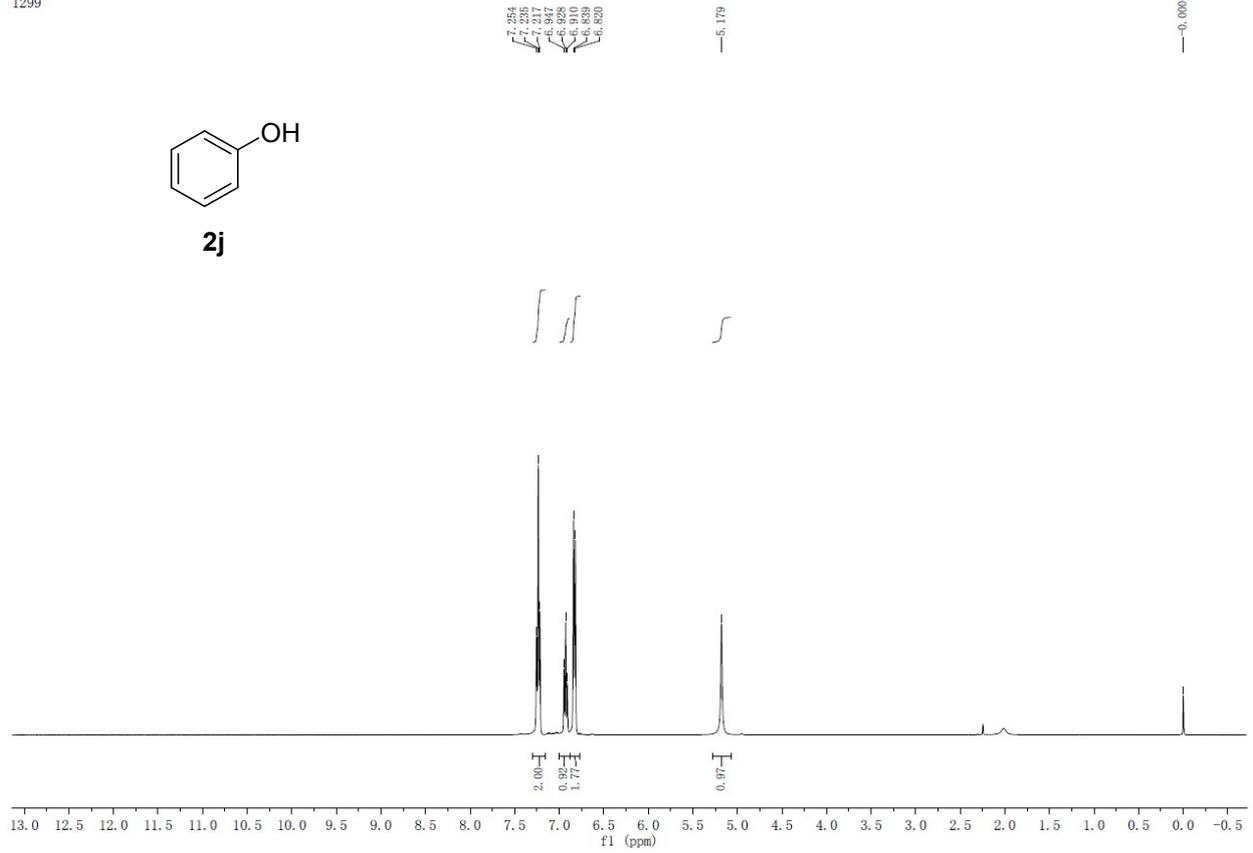
4c



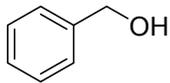
1299



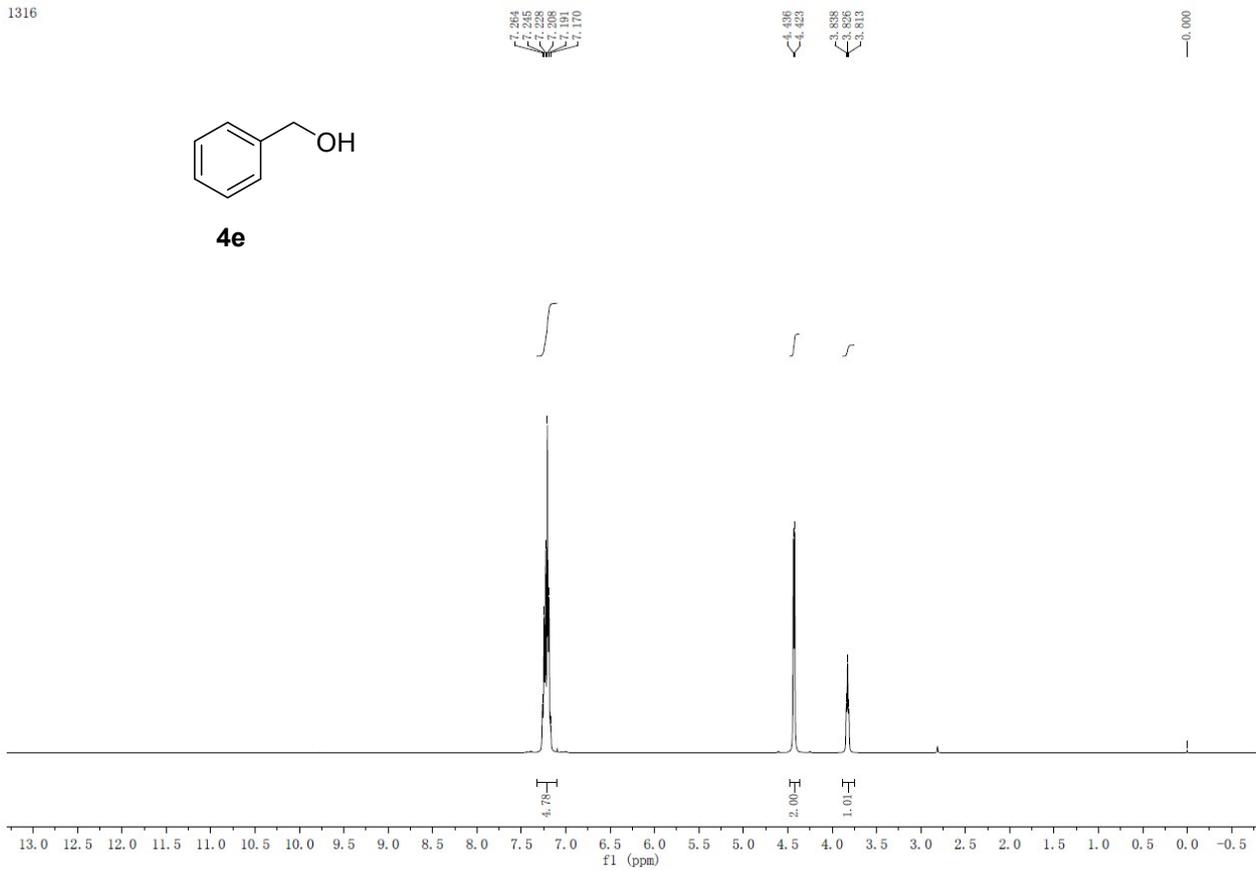
2j



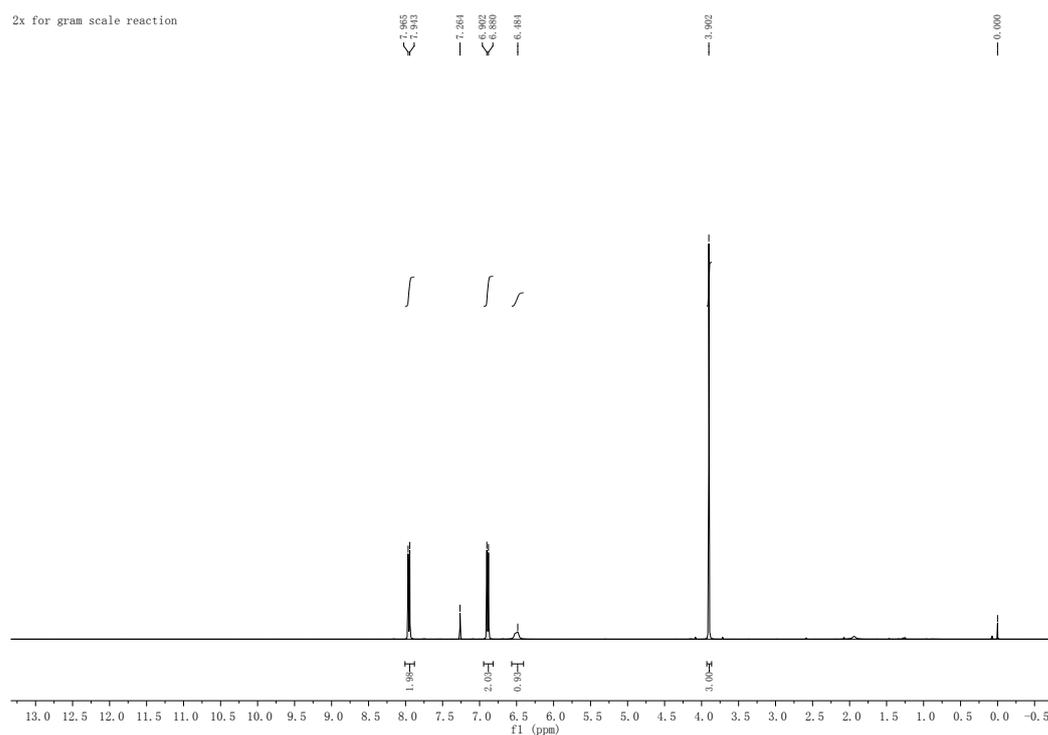
1316



4e



2x for gram scale reaction



## References

1. A. Ding, Y. Chen, G. Wang, Y. Zhang, J. Hu and H. Guo, *Polymer*, 2019, **174**, 101-108.
2. A. Ding, Y. Zhang, Y. Chen, R. Rios, J. Hu and H. Guo, *Tetrahedron Lett.*, 2019, **60**, 660-663.
3. H. Yang, S. J. Bradley, A. Chan, G. I. Waterhouse, T. Nann, P. E. Kruger and S. G. Telfer, *J. Am. Chem. Soc.*, 2016, **138**, 11872-11881.
4. I. Kumar, R. Sharma, R. Kumar, R. Kumar and U. Sharma, *Adv. Synth. Catal.*, 2018, **360**, 2013-2019.
5. Y. Mao, Y. Liu, Y. Hu, L. Wang, S. Zhang and W. Wang, *ACS Catal.*, 2018, **8**, 3016-3020.
6. S. Kim, Y. Kim, H. Jin, M. H. Park, Y. Kim, K. M. Lee and M. Kim, *Adv. Synth. Catal.*, 2019, **361**, 1259-1264.