Supporting Information

Highly Efficient Reduction of Carbonyls, Azides, and Benzyl Halides by NaBH4 in Water Catalyzed by PANF-immobilized Quaternary Ammonium Salts

*Jianguo Du, Gang Xu, Huikun Lin, Guangwei Wang,*Minli Tao,*Wenqin Zhang**

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1. General Information

A commercially available polyacrylonitrile fiber (**PANF**) with a length of 10 cm and a diameter of 30 ± 0.5 μm (from the Fushun Petrochemical Corporation of China) was used. Reagents were purchased from commercial sources and used as received. Other materials were prepared by the known methods.

FTIR spectra (Fourier transform infrared spectroscopy) were obtained with an AVATAR360 FTIR spectrometer (Thermo Nicolet). Elemental analyses were performed on an Elementar vario EL analyzer. A Hitachi SU-8010 scanning electron microscopy (SEM) was used to characterize the surface of the modified fibers. ^{1}H NMR spectra were recorded on a BRUKER-AVANCE III (600 MHz) and BRUKER-AVANCE III (400MHz) instrument using tetramethyl silane as the internal standard. Melting points were taken on a Yanagimoto MP-500 apparatus and are uncorrected. A Beifen-Ruili SP-1000 Gas Chromatograph was used to determine the yield of reduction. A PHS-3C (INESA) pH meter was used to determine the pH values of solvent. HPLC analysis was performed on Waters Modol 510.

2. Synthesis of the PANF-QAS

All the **PANF-QAS** were prepared by amination and quaternization subsequently from PANF.

Step 1: The amination of PANF.

Dried **PANF** (5.000 g), *N*,*N*-dimethyl-1,3-propanediamine (70 mL) or *N*,*N*-diethyl-1,3-propanediamine (70 mL), and deionized water (30 mL) were added to a three-necked flask. The mixture was stirred and heated at reflux for 4 h 40 min (6 h for *N*,*N*-diethyl-1,3-propanediamine). The treated fiber was filtered out and repeatedly washed with hot water (60-70 °C) until the filtrate was neutral. It was then dried overnight at 60 °C under vacuum to give the aminated fiber **1a** or **1b**.

The degree of amination for both fibers (**1a** and **1b**) was determined using the weight gain and acid exchange capacities.[1] The amination of **PANF** can be enhanced

by increasing the reaction temperature or by prolonging the reaction time. However, a higher percentage of weight gain notably reduces the strength of the fibers and decreases the recyclability of the catalysts.[2]

Step 2: Quaternization of aminated PANF.

Dried aminated PANF **1a** (1.000 g, 2.3 mmol/g tertiary amine calculated by weight gain), the corresponding halides (9.2 mmol), and ethanol (30 mL) were added to a three-necked flask. The mixture was stirred and heated at reflux for 5 h. The modified fiber was filtered out and washed with ethanol and deionized water subsequently. The fiber was then dried overnight at 60 °C under vacuum to give the corresponding PANF-QAS. **A-Et-Br** (1.42 mmol/g) **A-Bu-Br** (1.58 mmol/g), **A-Hp-Br** (1.56 mmol/g), **A-Dd-Br** (1.30 mmol/g), **A-Bn-Cl** (1.74 mmol/g), and **A-BuOH-Br** (1.36 mmol/g) were obtained from aminated PANF **1a** and the corresponding halides. The catalyst loading was determined by weight gain.

Dried aminated PANF **1b** (1.000 g, 1.74 mmol/g tertiary amine calculated by weight gain), halides (benzyl chloride for A_E**-Bn-Cl** and benzyl bromide for A_E**-Bn-Br**) (12 mmol) and 30 mL of ethanol were added to a three-necked flask. The mixture was stirred and heated at reflux for 6 h. The fiber was filtered out and washed with ethanol and then with deionized water. The fiber was dried overnight at 60°C under vacuum to afford catalysts A_E**-Bn-Cl** (1.18 mmol/g) and A_E**-Bn-Br** (1.10 mmol/g).

Under the same condition, only A_E**-Bn-Cl** and A_E**-Bn-Br** could be prepared from **1b** which is due to the high activity of benzyl chloride and benzyl bromide. The other alkyl bromides failed to react with **1b** even at increased temperatures or prolonged reaction times. These results indicated that the steric effect is the most crucial factor for the quaternization of the aminated PANF.

Catalyst **A-BnBu-Cl, A-BnEtSH-Cl,** and **A-BnEtOH-Cl**: Before preparation of the tertiary aminated fiber **1a**, **PANF** was reacted with butylamine, cysteamine or ethanolamine. Dried **PANF** (1.000 g), butylamine, (cysteamine hydrochloride 10 g with 1 equivalent of Na_2CO_3 for catalyst **A-BnEtSH-Cl**) or ethanolamine (10 mL) and 25 mL of deionized water were added to a three-necked flask. The mixture was

stirred and heated to reflux for 5 h. The fiber was filtered out and repeatedly washed with hot water (60-70 °C) until the wash water was neutral. The fiber was dried overnight at 60 °C under vacuum to give the corrseponding aminated fibers. The weight gain based on **PANF** of butylamine aminated fiber is 15%, cysteamine aminated fiber is 11%, and ethanolamine aminated fiber is 13%. The aminated fibers were reacted with via *N,N*-dimethyl-1,3-propanediamine to afford fiber **1c, 1d,** and **1e**, which were subjected to quaternization to give the catalysts **A-BnBu-Cl** (1.10 mmol/g), **A-BnEtSH-Cl** (1.23 mmol/g) and **A-BnEtOH-Cl** (1.36 mmol/g).

3. Acid exchange capacities of the aminatied PANF.

Dried aminatied PANF **1a** and **1b** (0.200 g) were immersed into 20 mL of 0.1000 M HCl aqueous solution for 6 h. The fibers were then filtered out and the concentration of HCl of the remaining solution was determined by titration with 0.1000 M NaOH aqueous solution. The exchange capacity was calculated based on the amount of acid consumed.

4. Preparation of non-commercial materials

***N,N*-diethyl-1,3-propanediamine**

A mixture of acrylonitrile (0.8 g, 15 mmol), diethylamine (0.73 g, 10 mmol), and water (10 mL) was stirred at room temperature for 2 h. The reaction mixture was extracted with ethyl acetate (3 × 50 mL) and the combined extracts were dried over anhydrous Na_2SO_4. The solvent was evaporated to give the crude 3-(*N,N*-diethylamino)propionitrile (1.13 g, 90% yield).

A solution of 5.05 g 3-(*N,N*-diethylamino)propionitrile in ethanol (45 mL) in a three-necked-flask was refluxed for a few minutes. Sodium (4.14 g) was slowly added to the flask and the resulted solution was refluxed for 3 h. The mixture was quenched with water (30 mL) and extracted with dichloromethane (3 × 50 mL). The combined extracts were dried over anhydrous Na_2SO_4 and the product *N,N*-diethyl-1,3-propanediamine was obtained after reduced pressure distillation. Yield: 56%. ^{1}H NMR (400 MHz, D_2O) δ 2.57 – 2.27 (m, 8H), 1.50 (dt, J = 15.0, 7.4 Hz, 2H), 1.01 –

0.81 (m, 6H).

4-Butoxybenzaldehyde (2c). A solution of 4-hydroxybenzaldehyde (63 mmol) and potassium hydroxide (69 mmol) in CH_3CN (120 mL) was stirred at room temperature for 1 h and then 1-bromobutane (69 mmol) was added. The reaction mixture was refluxed for 4 h and the precipitate was filtered off. The filtrate was evaporated in vacuum and the residue was purified by distillation under reduced pressure. Yield: 75%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 4.05 (t, J = 6.3 Hz, 2H), 1.91 – 1.70 (m, 2H), 1.62 – 1.35 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H).

4-Benzyloxybenzaldehyde (2d). A solution of K_2CO_3 (12.5 mmol), benzyl chloride (6 mmol), and 4-hydroxybenzaldehyde (5 mmol) in DMF (10 mL) was stirred at 90 ºC for 3 h. The reaction mixture was cooled to room temperature, and then H_2O (50 mL) and EtOAc (50 mL) were added. The aqueous layer was separated and extracted with EtOAc (50 mL × 2). The combined organic phases were washed successively with H_2O (50 mL × 2) and brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was recrystallized using petroleum ether to give desired product. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.57–7.31 (m, 5H), 7.11 (d, J = 8.6 Hz, 2H), 5.18 (s, 2H).

4-Heptyloxybenzaldehyde (2f). This compound was prepared according to the procedure for **2c**. Yield: 72%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 4.04 (t, J = 6.5 Hz, 2H), 1.90 – 1.74 (m, 2H), 1.55 – 1.22 (m, 8H), 0.90 (t, J = 6.5 Hz, 3H).

3-Heptyloxybenzaldehyde (2g). This compound was prepared according to the procedure for **2c**. Yield: 56%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.51 – 7.34 (m, 3H), 7.21 – 7.11 (m, 1H), 4.01 (t, J = 6.6 Hz, 2H), 1.92 – 1.73 (m, 2H), 1.56 – 1.15 (m, 8H), 0.89 (t, J = 7.4 Hz, 3H).

7-Methyl-6-phenylmethoxy-1,3-benzodioxole-5-carbaldehyde (2m).

This compound was prepared according to the reported procedure.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.51 – 7.36 (m, 5H), 6.05 (s, 2H), 4.95 (s, 2H), 2.23 (s,

3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.51, 158.32, 152.60, 144.20, 128.76, 135.83, 128.74, 128.32, 123.66, 113.82, 103.23, 102.13, 78.55, 9.14.

***Trans*-Chalcone (2s).** To a solution of benzaldehyde (10 mmol) and acetophenone (10 mmol) in ethanol (30 mL) was added 10% NaOH aqueous solution (10 mL) dropwise at 0 ^{o}C then keep at room temperature for 2 h. The pH of the solution was adjusted to 3-4 with 5% HCl aqueous solution. The reaction mixture was filtered and the solid was recrystallized with ethanol. Yield: 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (m, 2H), 7.74 (d, J = 15.7 Hz, 1H), 7.55 (t, J = 10.9 Hz, 2H), 7.54 – 7.39 (m, 4H), 7.34 (s, 3H).

1-Azidonaphthalene (4a). To a solution of sodium azide (7.15 g, 0.11 mol) in water (30 mL) and acetone (50 mL) was added was added a solution of 1-aminonaphthalene (14.32 g, 0.1 mol) in acetone (50 mL) rapidly. The mixture was stirred at room temperature for 2 h and then acetone was removed in vacuum. After that dichloromethane (20 mL) was added. The organic phase was separated, washed with water (2 × 20 mL), dried over anhydrous Na_2SO_4, and evaporated to a constant weight in vacuum. The crude 1-azidonaphthalene was obtained and purified by column chromatograph. Yield: 86%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (t, J = 7.5 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.24 (d, J = 8.2 Hz, 1H).

Azidobenzene (4b). This compound was prepared according to the procedure for **4a**. Yield: 56%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H).

1-Azido-4-methoxybenzene (4c). This compound was prepared according to the procedure for **4a**. Yield: 81%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 – 6.91 (m, 2H), 6.91 – 6.84 (m, 2H), 3.79 (s, 3H).

4-Methylbenzenesulfonyl azide (4d). This compound was prepared according to the procedure for **4a**. Yield: 87%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H).

2-Nitroazidobenzene (4e). 2-Nitroaniline (20 g, 0.144mol) was dissolved in a 1:1 mixture of HCl and water (90 mL) at room temperature. The obtained solution was

cooled to 0 °C and a solution of $NaNO_2$ (10 g, 0.144 mol) was added. After stirring for 10 min at 0-5°C, a solution of sodium azide (1.2 equiv.) in ice cold water (52 mL) was added dropwise to the above mixture. The solution was stirred at room temperature for 2 h. The mixture was diluted with EtOAc. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography. Yield: 94%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H).

5. NMR data of products 3a-5g.

General procedure: Aldehydes (ketones, azides and halides) (4 mmol), $NaBH_4$, and 10 mol% catalyst **A-Hp-Br** was added to 15 mL of pH = 12 NaOH aqueous solution. The solution was stirred at appropriate temperature for some time and then quenched with 10% HBr aqueous solution. The mixture was filtered to recycle the catalyst, which was washed with ethyl acetate at reflux for 5 h and dried in vacuum overnight at 60 ^{o}C prior to the next run's use. The filtrate was extracted with ethyl acetate (3×10 mL) and dried over Na_2SO_4. After removal of solvent, the crude product was purified by silica gel column chromatograph.

1-Naphthylenemethanol (3a)

The product was prepared according to general procedure to afford a white solid of 97% yield. m.p. 56 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 7.2 Hz, 1H), 7.92 – 7.75 (m, 2H), 7.62 – 7.38 (m, 4H), 5.11 (d, J = 9.6 Hz, 2H), 1.87 (s, 1H).

benzyl alcohol (3b)

The product was prepared according to general procedure to afford a colorless oil of 99% yield. ^{1}H NMR (600 MHz, $CDCl_3$,): δ 7.24–7.36 (m, 5H), 4.60 (s, 2H), 2.38 (s, 1H).

4-Butoxybenzyl alcohol (3c)

The product was prepared according to general procedure to afford a white solid of 95% yield. m.p. 32 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.59 (s, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.85 – 1.67 (m, 2H), 1.57 – 1.41 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

4-Benzyloxybenzyl alcohol (3d)

The product was prepared according to general procedure to afford a white solid of 99% yield. m.p. 85 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 5H), 7.20 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 4.98 (s, 2H), 4.52 (s, 2H), 1.67 (s, 1H).

4-Hydroxymethylbiphenyl (3e)

The product was prepared according to general procedure to afford a white solid of 96% yield. m.p. 99 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 7.5 Hz, 4H), 7.35 (dd, J = 11.5, 7.3 Hz, 4H), 7.27 (t, J = 7.3 Hz, 1H), 4.64 (s, 2H), 2.47 (s, 1H).

4-(Heptyloxy)benzaldehydes (3f)

The product was prepared according to general procedure to afford a white solid of 94% yield. m.p. 46 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 4.60 (s, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.88 – 1.71 (m, 2H), 1.68 (brs, 1H), 1.51 – 1.15 (m, 8H), 1.01 – 0.78 (m, 3H).

3- Heptyloxybenzyl alcohol (3g)

The product was prepared according to general procedure to afford a colorless oil of 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (dd, J = 9.2, 7.0 Hz, 1H), 6.91 (d, J = 7.4 Hz, 2H), 6.86 – 6.77 (m, 1H), 4.65 (s, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.93 (brs, 1H), 1.81 – 1.74 (m, 2H), 1.48 – 1.41 (m, 2H), 1.38 – 1.23 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H).

***n*-Capryl alcohol (3h)**

The product was prepared according to general procedure to afford a colorless oil of 99% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (t, J = 6.5 Hz, 2H), 1.63 (s, 1H), 1.56 (dd, J = 13.9, 6.8 Hz, 2H), 1.31 (dd, J = 34.2, 9.9 Hz, 10H), 0.88 (t, J = 6.7 Hz, 3H).

Cinnamyl alcohol (3i)

The product was prepared according to general procedure to afford a white solid of 98% yield. m.p. 32 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.16 (m, 5H), 6.64 (d, J = 15.6 Hz, 1H), 6.40 (dt, J = 15.4, 7.7 Hz, 1H), 4.16 (d, J = 7.7 Hz, 2H).

Geraniol (3j)

The product was prepared according to general procedure to afford a yellow oil of 99% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.42 (t, J = 6.3 Hz, 1H), 5.12 (d, J = 32.4 Hz, 1H), 4.15 (d, J = 6.8 Hz, 2H), 2.19 – 1.98 (m, 4H), 1.68 (s, 6H), 1.61 (s, 3H).

2-Thiophenemethanol (3k)

The product was prepared according to general procedure to afford a colorless oil of 98% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, J = 5.7 Hz, 1H), 7.03 – 6.94 (m, 2H), 4.79 (s, 2H), 2.29 (s, 1H).

(2-Chloro-3-quinolinyl)methanol (3l)

The product was prepared according to general procedure to afford a white solid of 99% yield. m.p. 164 ^{o}C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.49 (s, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.80 (dd, J = 8.2, 7.1 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 5.76 (t, J = 5.0 Hz, 1H), 4.72 (d, J = 5.0 Hz, 2H).

7-Methyl-6-phenylmethoxy-1,3-benzodioxole-5-hydroxymethyl (3m)

The product was prepared according to general procedure to afford a white solid of 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.30 (m, 5H), 6.68 (s, 1H), 5.94 (s, 2H), 4.83 (s, 2H), 4.53 (s, 2H), 2.21 (s, 3H), 1.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.11, 146.38, 143.25, 137.08, 128.66, 128.31, 128.09, 126.64, 113.69, 105.96, 101.23, 76.09, 61.13, 9.56.

1-(4-Chlorophenyl)ethanol (3o)

The product was prepared according to general procedure to afford a colorless oil of 99% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.17 (m, 4H), 4.87 (q, J = 6.2 Hz, 1H), 2.01 (br.s, 1H),1.46 (d, J = 6.4 Hz, 3H).

1-Phenylethanol (3p)

The product was prepared according to general procedure to afford a colorless oil of 97% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 4H), 7.30 – 7.20 (m, 1H), 4.87 (q, J = 6.4 Hz, 1H), 2.10 (brs, 1H), 1.48 (d, J = 6.5 Hz, 3H)..

1-(Naphtalen-2-yl)ethanol (3q)

The product was prepared according to general procedure to afford a white solid of 91% yield. m.p. 67 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 7.86 (t, J = 11.6 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 23.8, 7.1 Hz, 1H), 7.58 – 7.42 (m, 3H), 5.65 (d, J = 6.2 Hz, 1H), 1.99 (s, 1H), 1.65 (d, J = 6.3 Hz, 3H).

Diphenylmethanol (3r)

The product was prepared according to general procedure to afford a white solid of 97%

yield. m.p. 68 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 8H), 7.24 (dd, J = 15.5, 8.7 Hz, 2H), 5.79 (s, 1H) , 2.33 (s, 1H).

(*E*)-1,3-Diphenylprop-2-en-1-ol (3s)

The product was prepared according to general procedure to afford a colorless oil of 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.06 (m, 10H), 6.60 (d, J = 15.8 Hz, 1H), 6.30 (dd, J = 15.8, 6.5 Hz, 1H), 5.29 (d, J = 6.4 Hz, 1H), 2.11 – 1.85 (brs, 1H).

4-Heptanol (3t)

The product was prepared according to general procedure to afford a colorless oil of 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (d, J = 4.0 Hz, 1H), 1.69 (s, 1H), 1.55 – 1.31 (m, 8H), 1.00 – 0.86 (m, 6H).

4-Pregnene-3*S*,20*R*-diol (3u)

The product was prepared according to general procedure to afford a white solid of 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 1H), 4.15 (dd, J = 14.9, 7.4 Hz, 1H), 3.80 – 3.66 (m, 1H), 2.20 (td, J = 11.6, 5.7 Hz, 1H), 2.10 – 1.92 (m, 3H), 1.68 (m, 4H), 1.57 – 1.40 (m, 6H), 1.37 – 1.26 (m, 4H), 1.14 (d, J = 6.0 Hz, 3H), 1.07 (s, 3H), 1.04 – 0.84 (m, 2H), 0.78 (s, 3H).

1-Naphthylamine (5a)

The product was prepared according to general procedure to afford a white solid of 68% yield. m.p. 50 °C. ^{1}H NMR (600 MHz ,$CDCl_3$) δ 7.85-7.82 (m, 2H), 7.51-7.46 (m, 2H), 7.37-7.31 (m, 2H), 6.80 (dd, J = 7.1, 1.4 Hz, 1H), 4.13 (s, 2H).

Aniline (5b)

The product was prepared according to general procedure to afford a colorless oil of 98% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, 2H), 6.78 (t, 1H), 6.69 (d, 2H), 3.60 (s, 2H).

Tosylamine (5d)

The product was prepared according to general procedure to afford a white solid of 98% yield. m.p. 138 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 4.98 (s, 2H), 2.43 (s, 3H).

2-Nitroaniline (5e)

The product was prepared according to general procedure to afford a orange solid of

94% yield. m.p. 75 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.70 (t, J = 7.7 Hz, 1H), 6.10 (s, 2H).

3-Nitrotoluene (5f)

The product was prepared according to general procedure to afford a yellow oil of 99% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 12.4 Hz, 2H), 7.51 (d, 1H), 7.42 (t, J = 7.8 Hz, 2H), 2.47 (s, 3H).

4-Nitrotoluene (5g)

The product was prepared according to general procedure to afford a yellow solid of 99% yield. m.p. 57 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 2.47 (s, 3H).

Reference:

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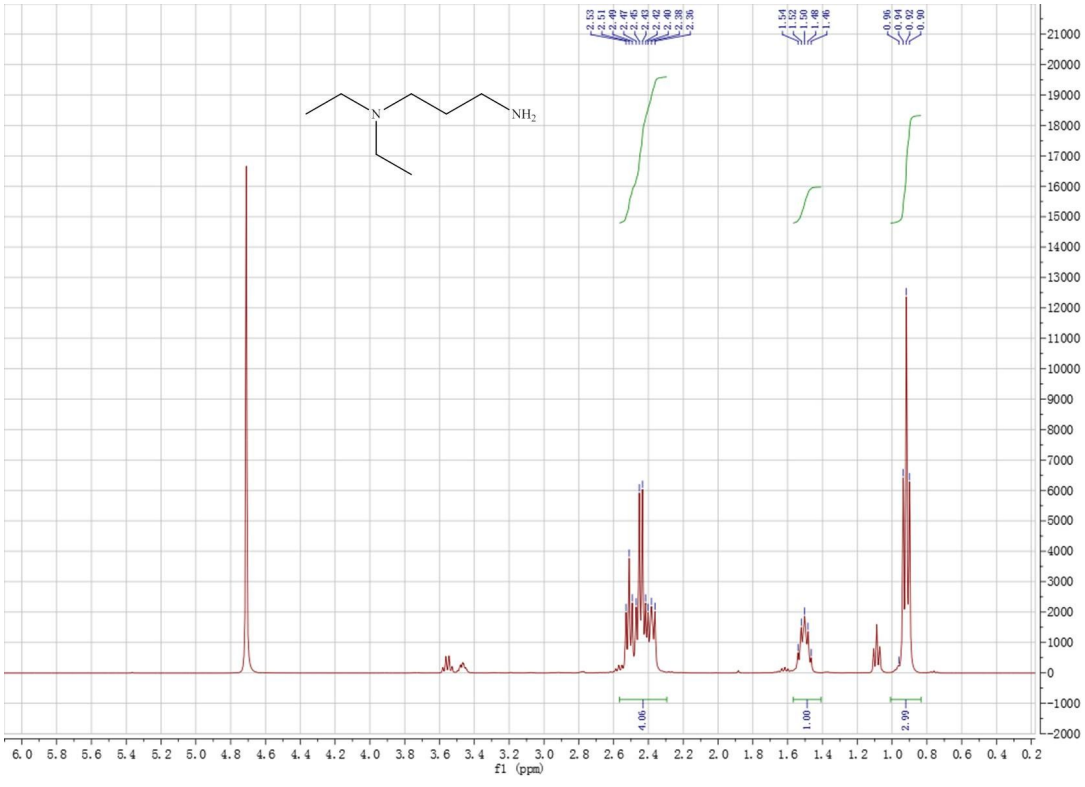
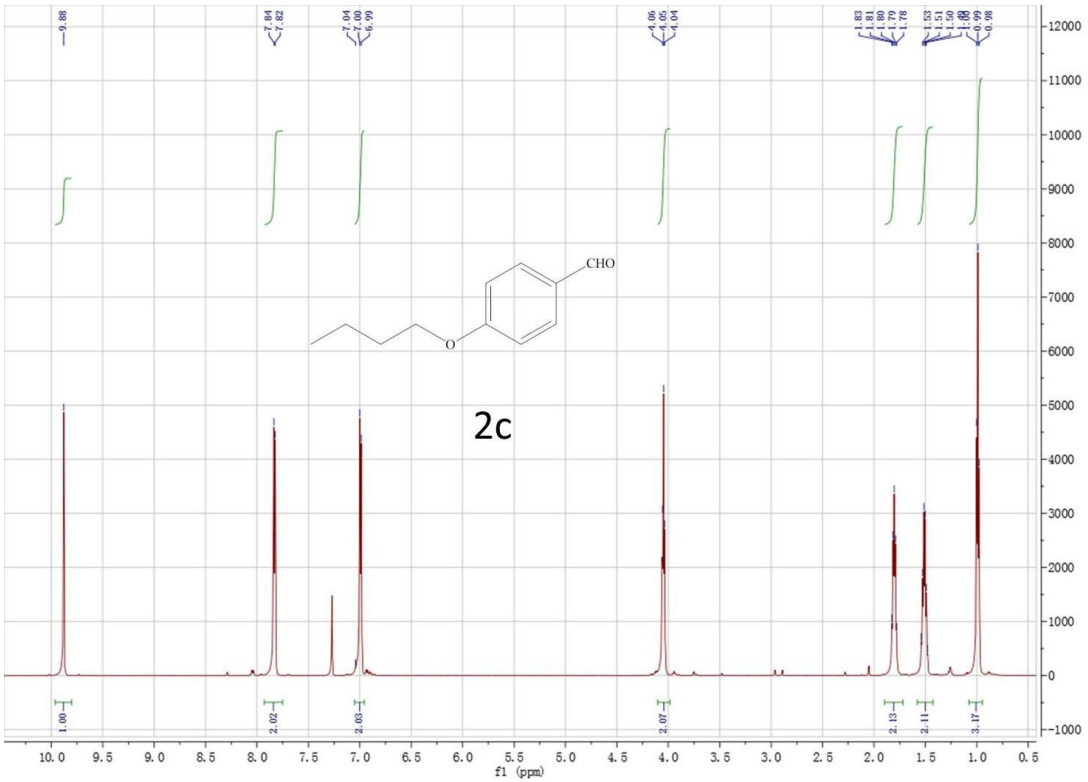
(2) Li, G.; Zhang, L.; Li, Z.; Zhang, W. *J. Hazard. Mater.* **2010**, *177*, 983.
(3) Corey, E. J.; Gin, D. Y.; Kania, R. S. *J. Am. Chem. Soc.* **1996**, *118*, 9202.

6. NMR Spectra

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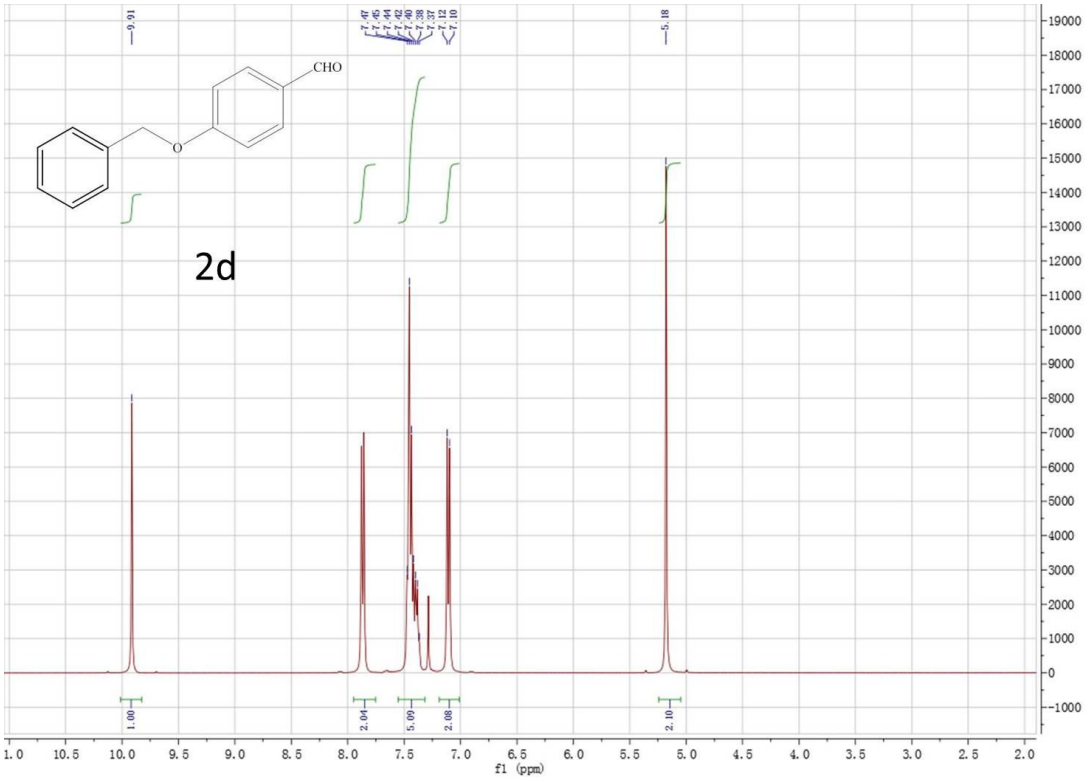
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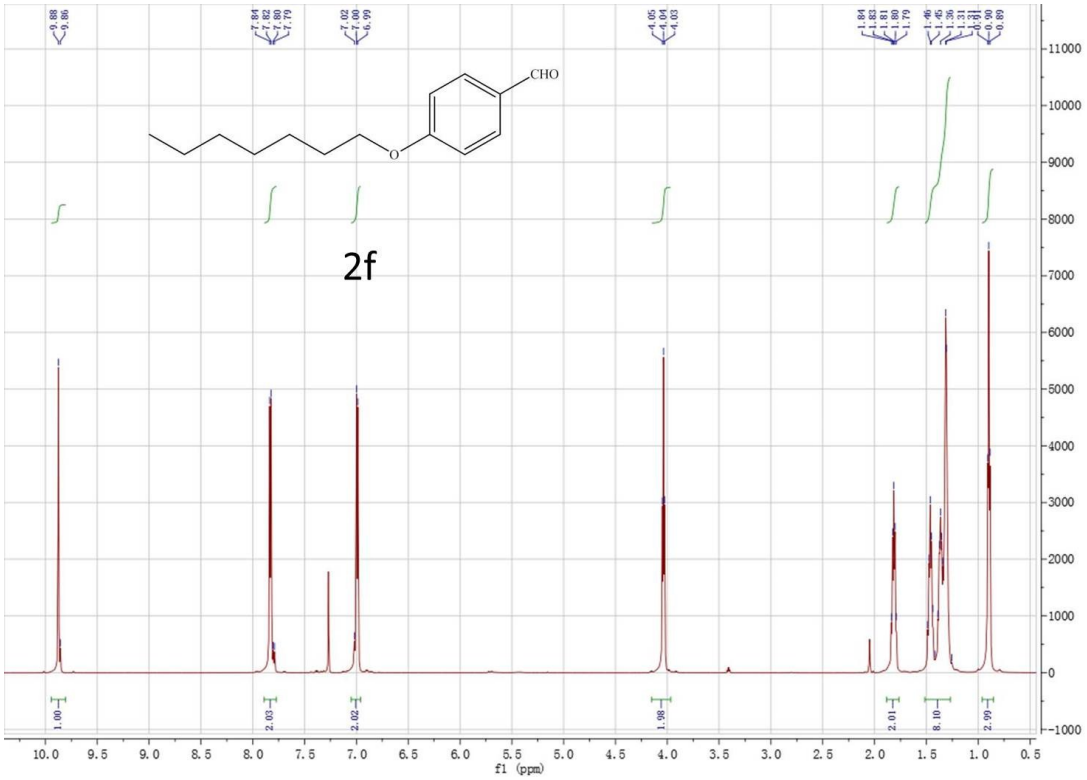
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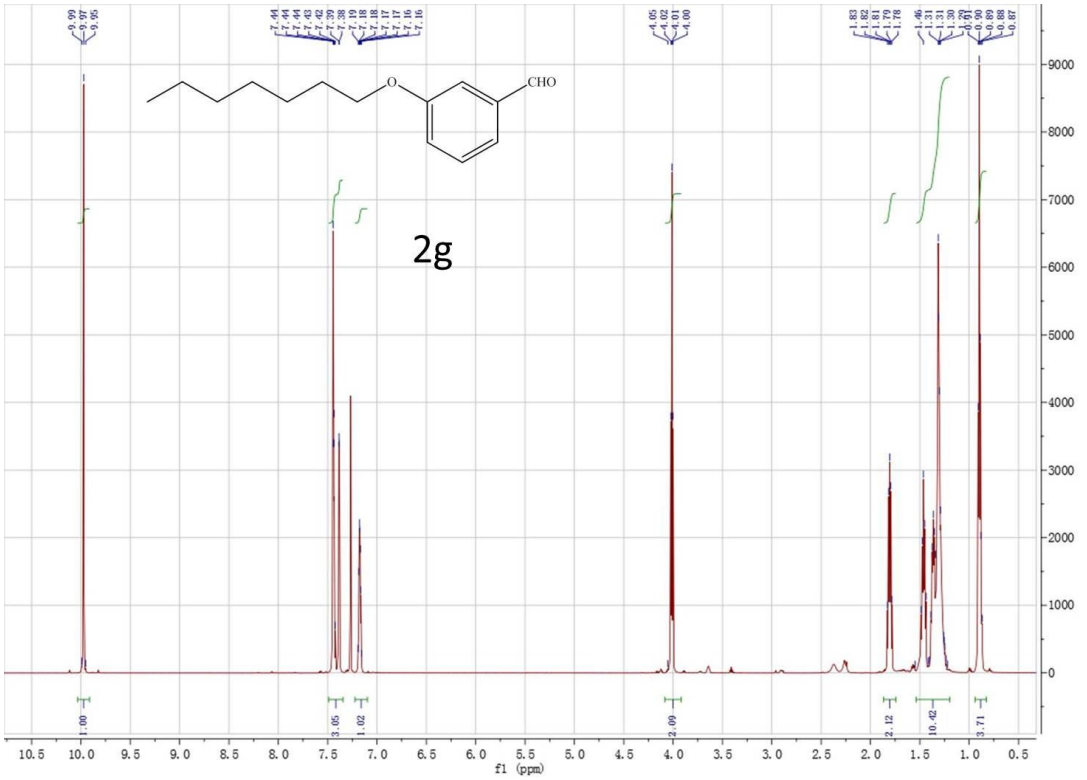
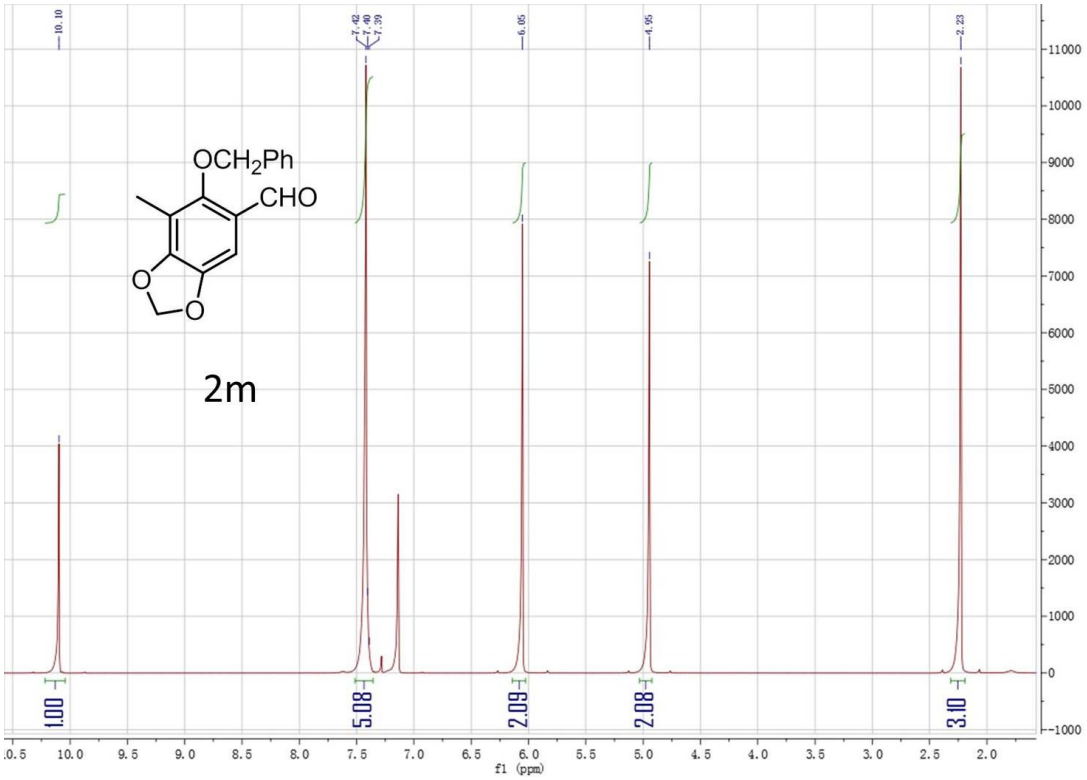
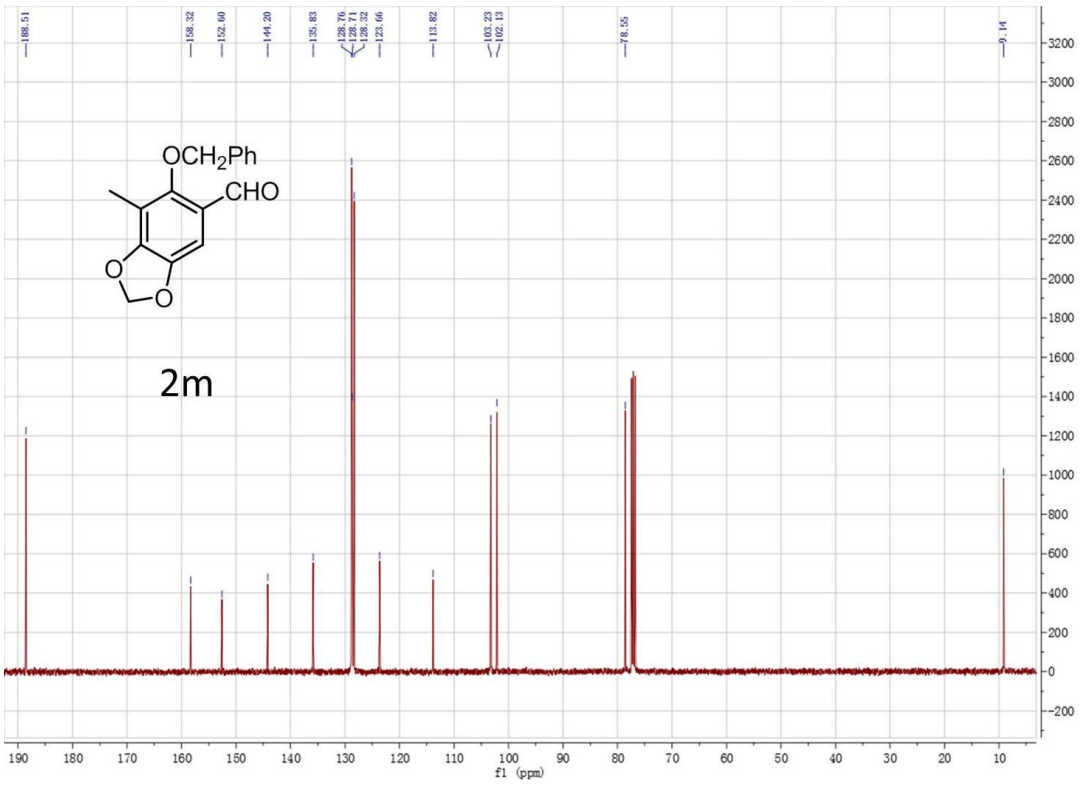
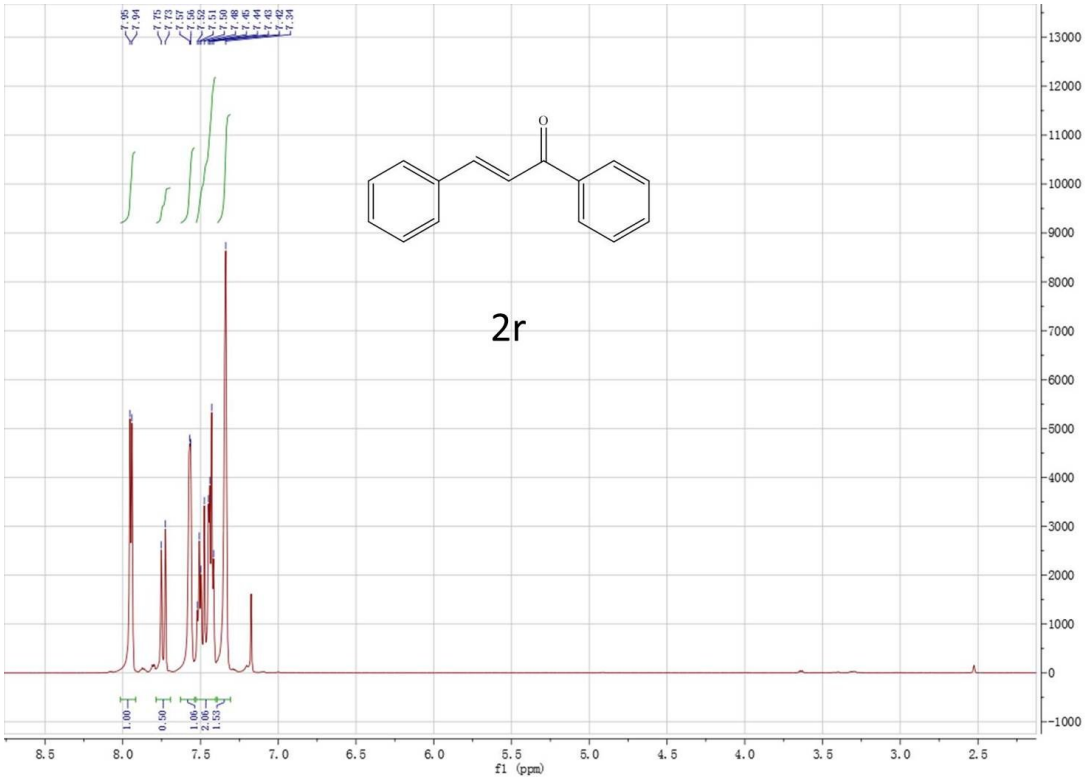
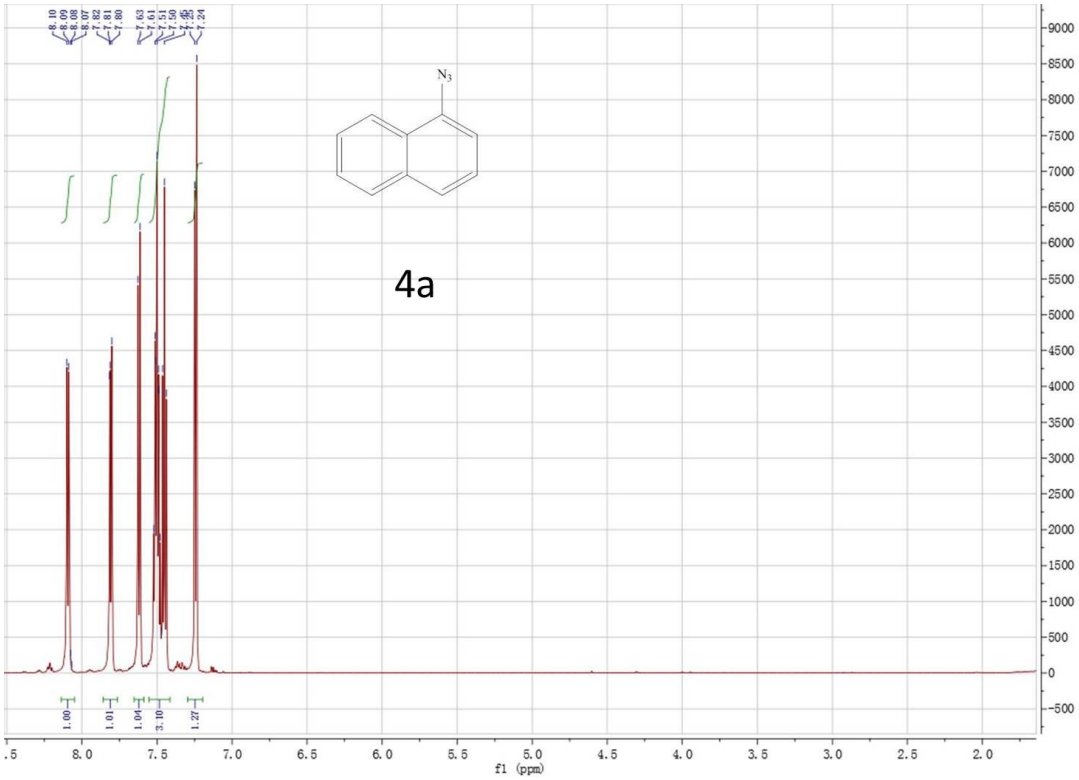
f1 (ppm)


CHO
O
2g
f1 (ppm)

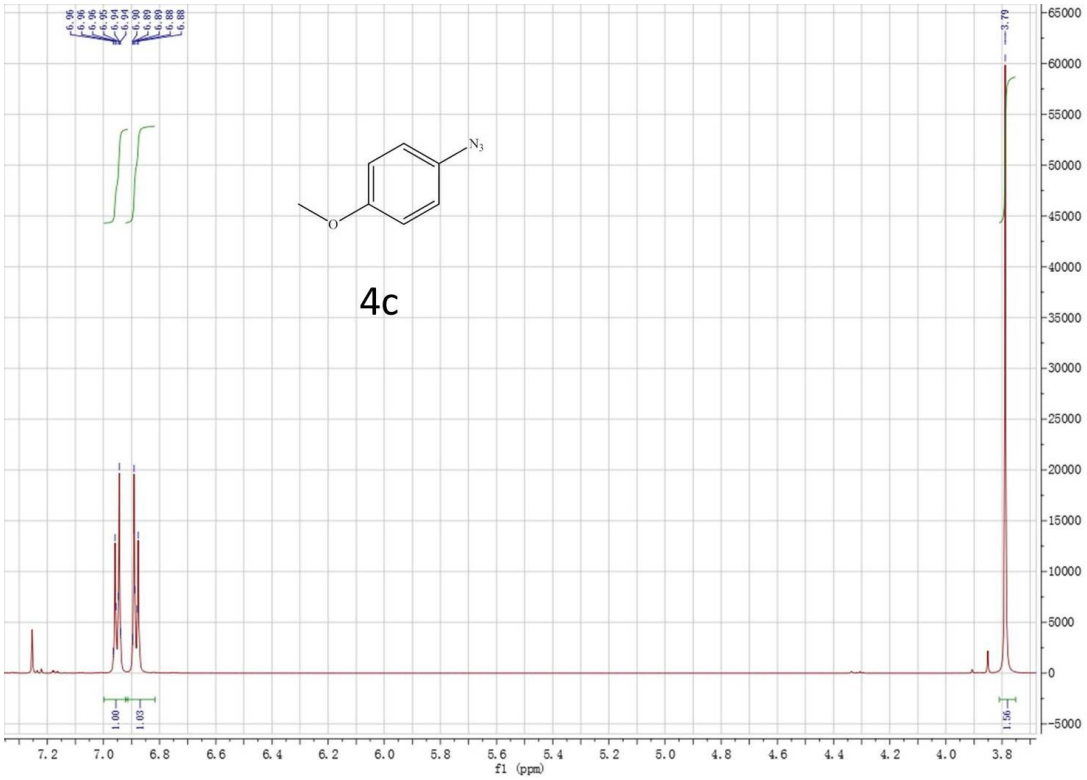

OCH2Ph
CHO
O
O
2m
10.10
7.42
7.40
7.39
6.05
4.95
2.23
1.00
5.08
2.09
2.08
3.10
f1 (ppm)

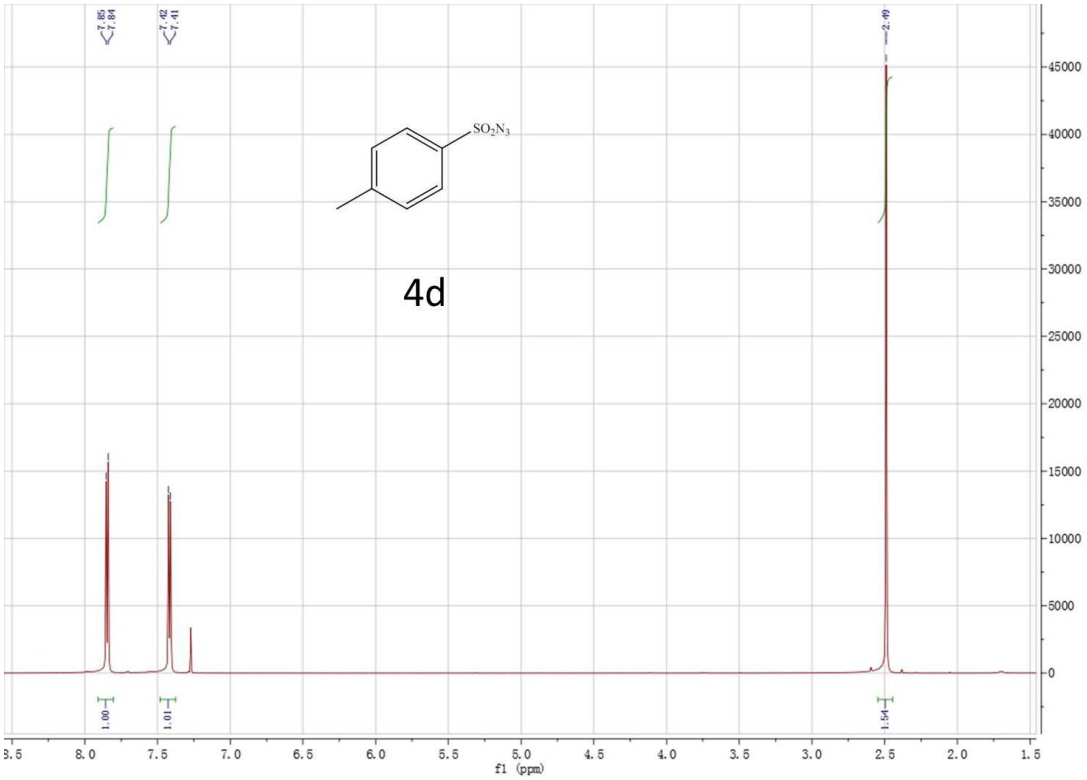

OCH2Ph
CHO
O
O
2m
188.51
158.32
152.60
144.20
135.83
128.76
128.71
128.32
123.66
113.82
103.23
102.13
78.55
9.14
f1 (ppm)

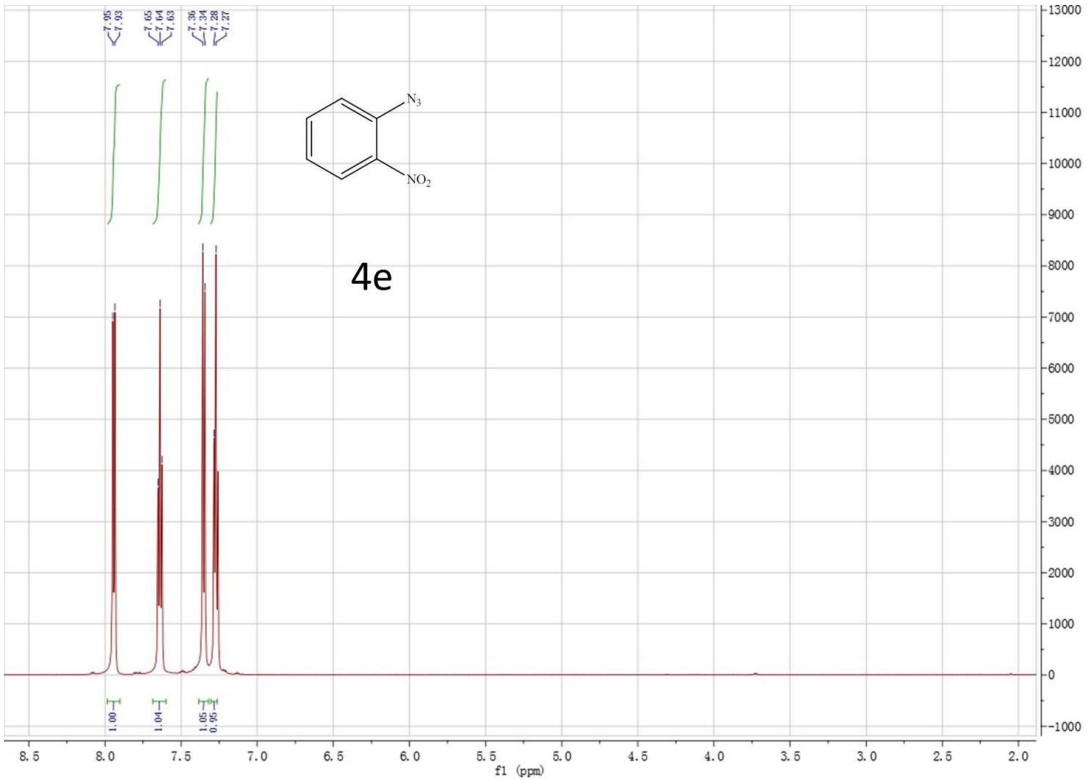

2r
f1 (ppm)

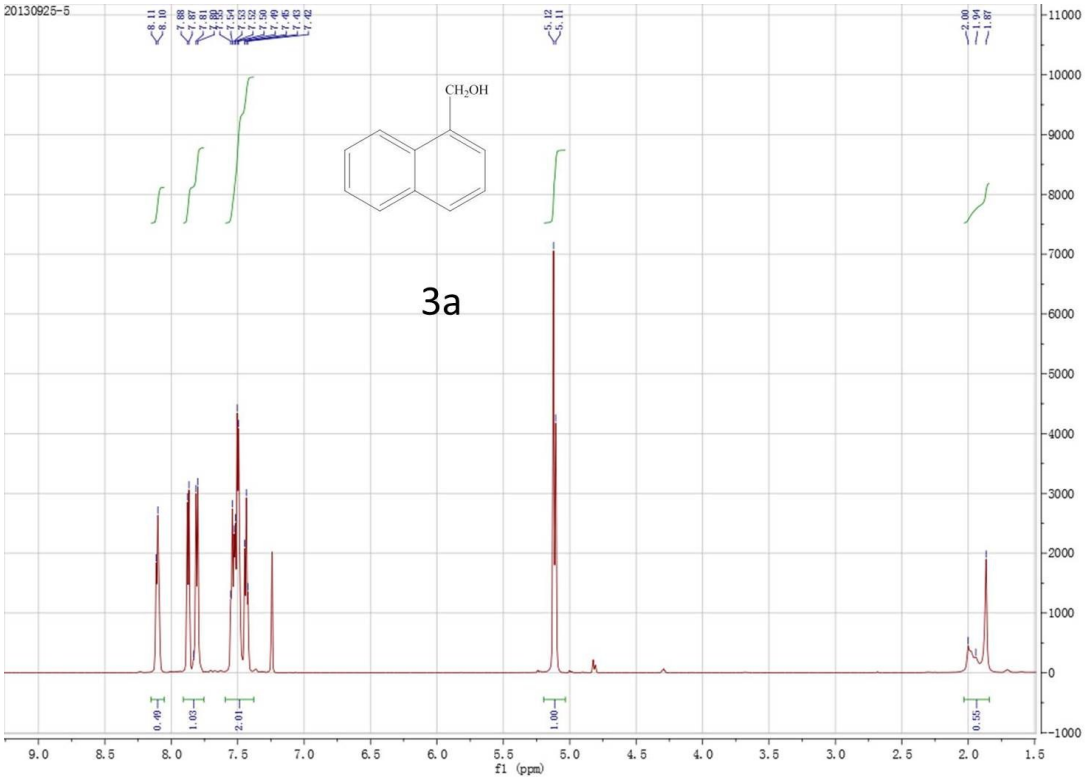

4a
f1 (ppm)

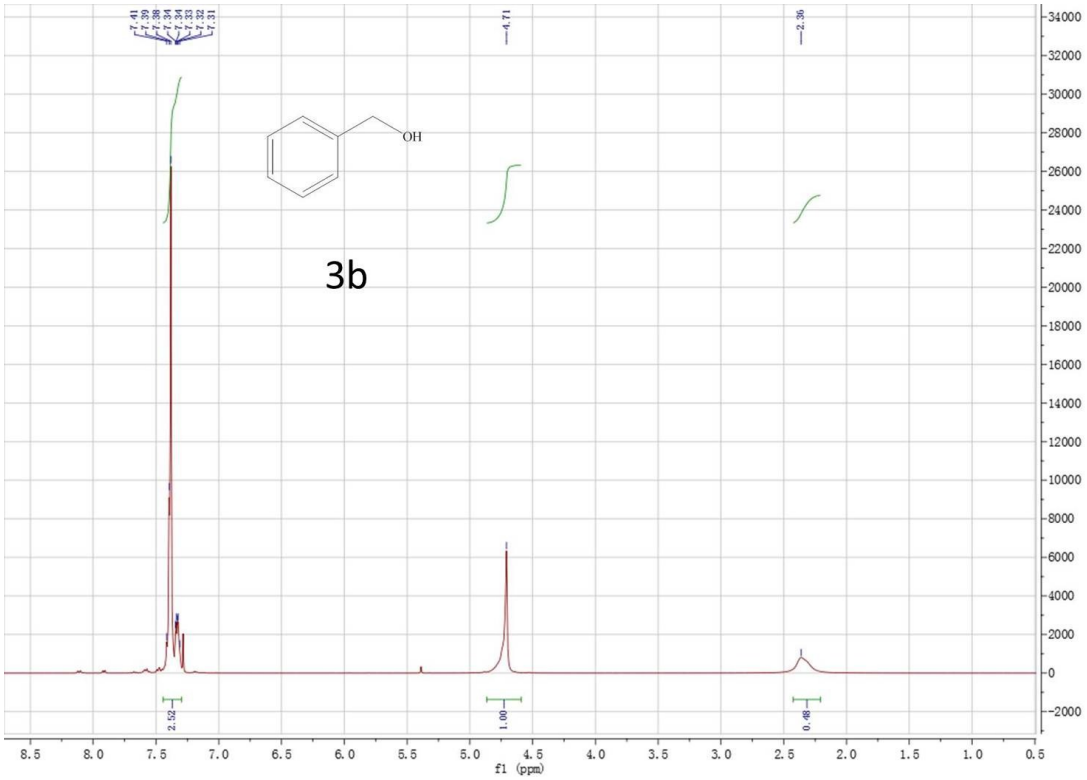

4b
N3
f1 (ppm)

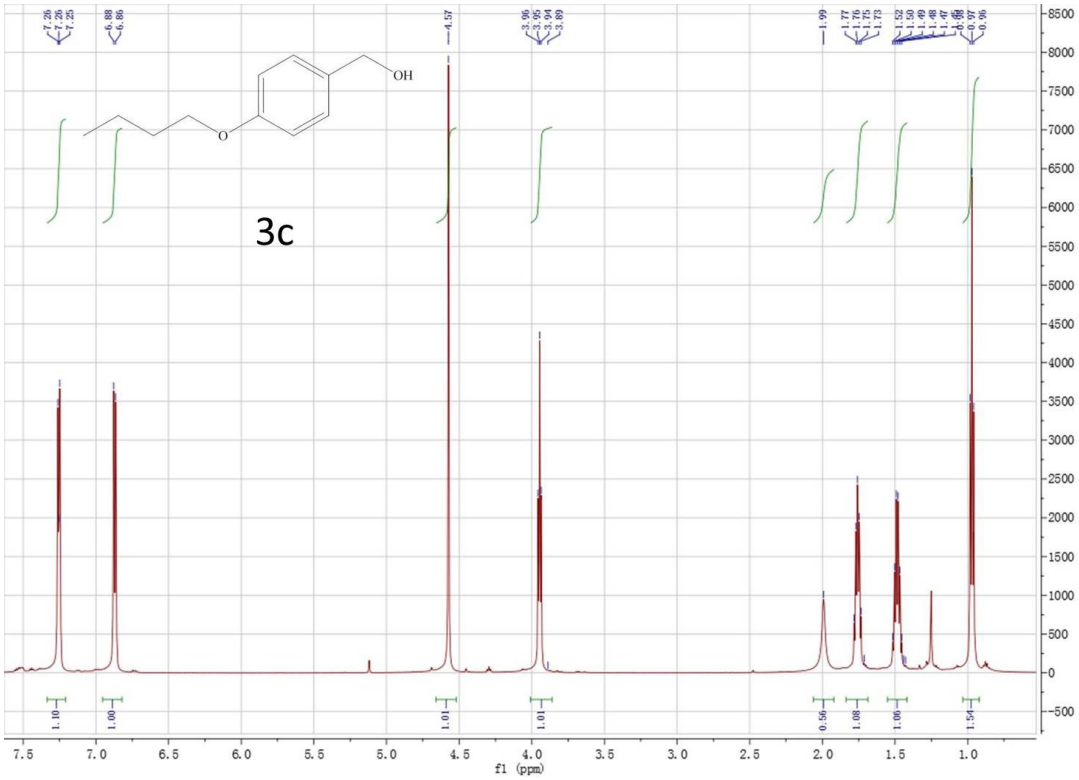

4c
N3
O
f1 (ppm)

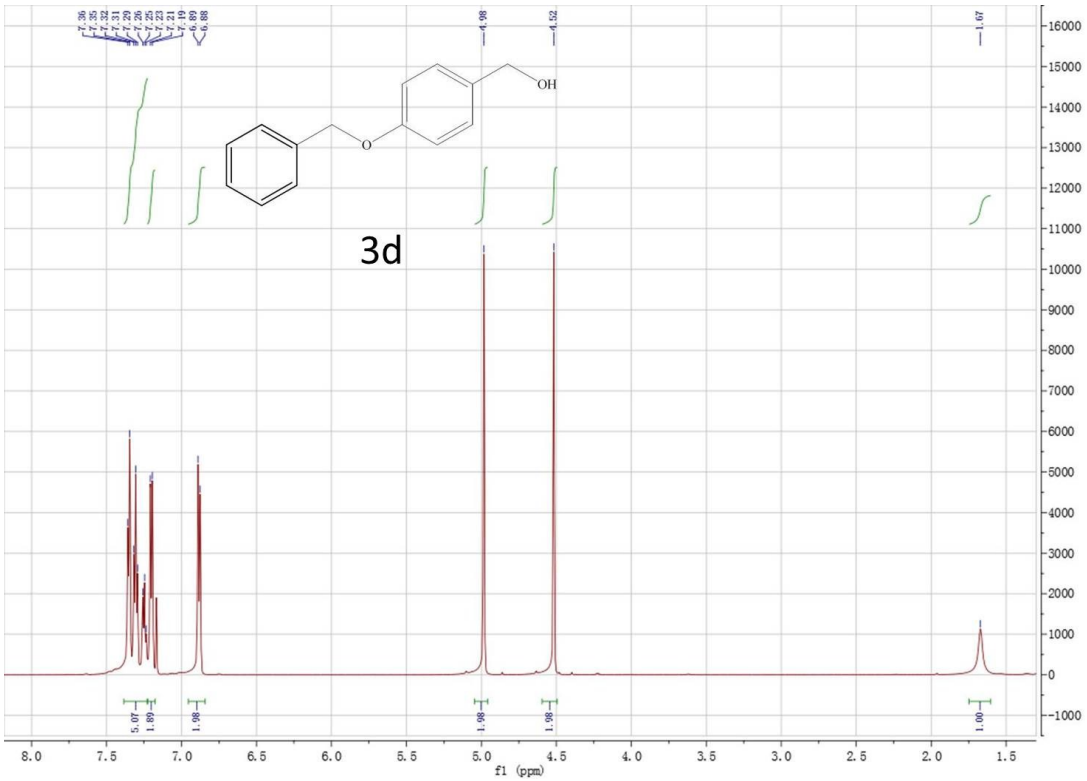

7.85
7.84
7.42
7.41
2.49
SO_2N_3
4d
1.00
1.01
1.54
f1 (ppm)

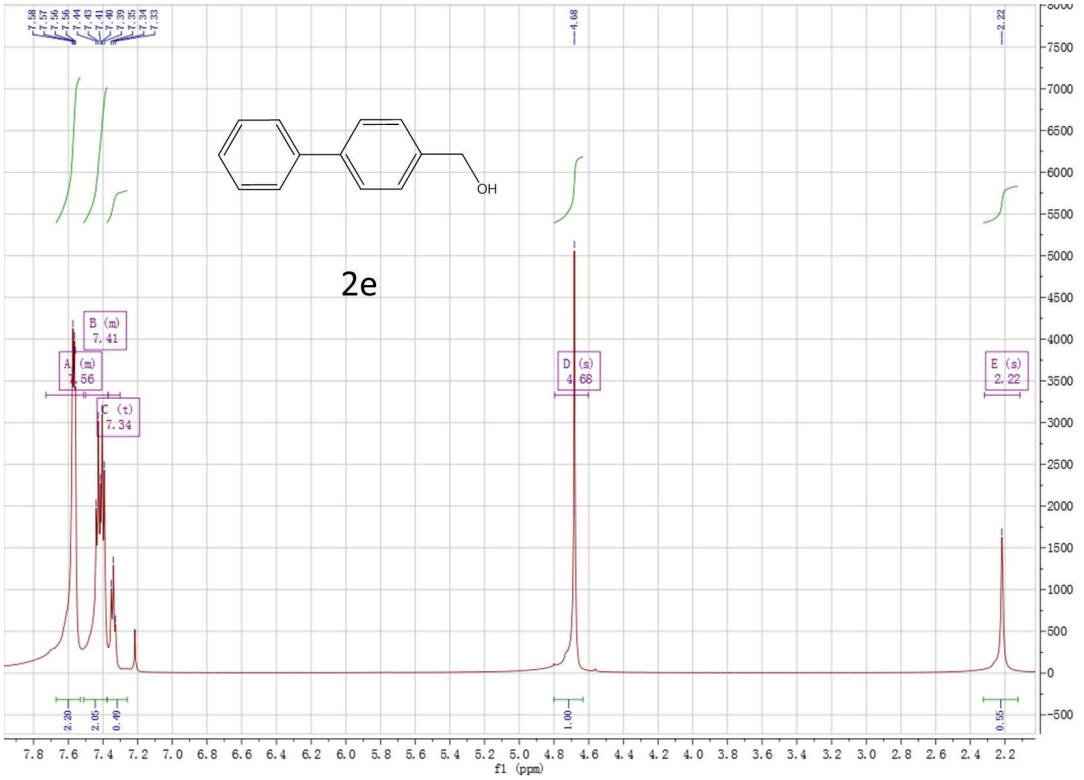

7.95
7.93
7.65
7.64
7.63
7.36
7.34
7.28
7.27
N_3
NO_2
4e
1.00
1.04
1.05
0.95
f1 (ppm)

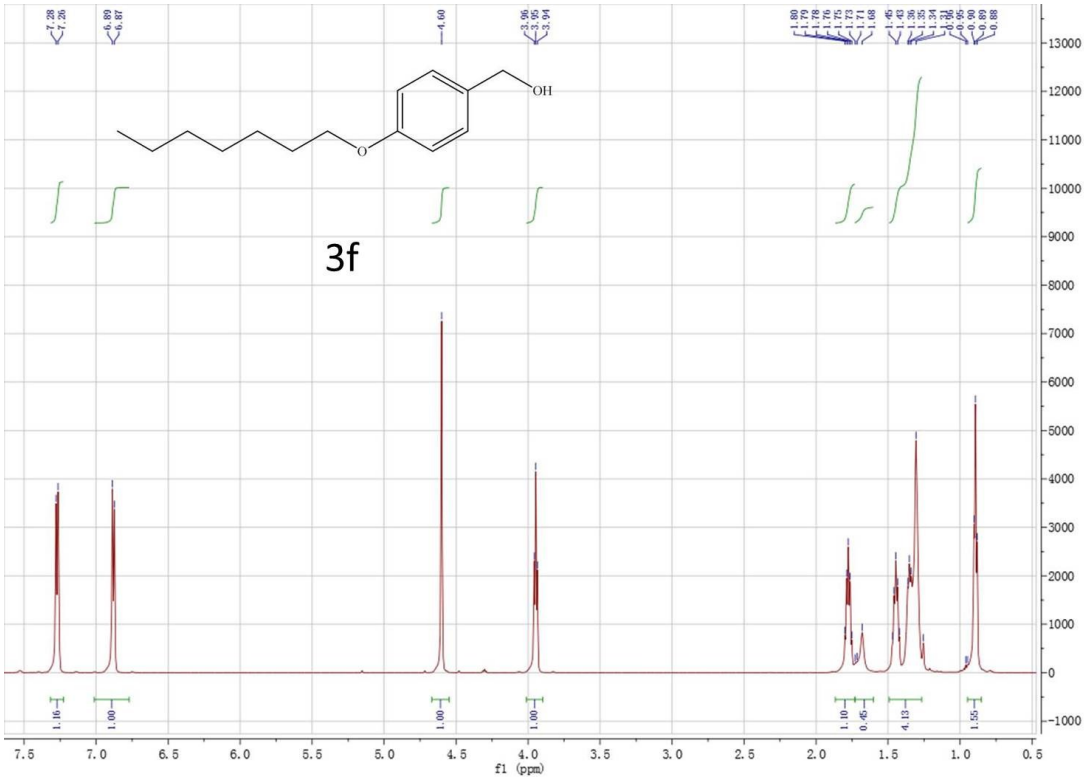

20130925-5
CH2OH
3a
f1 (ppm)

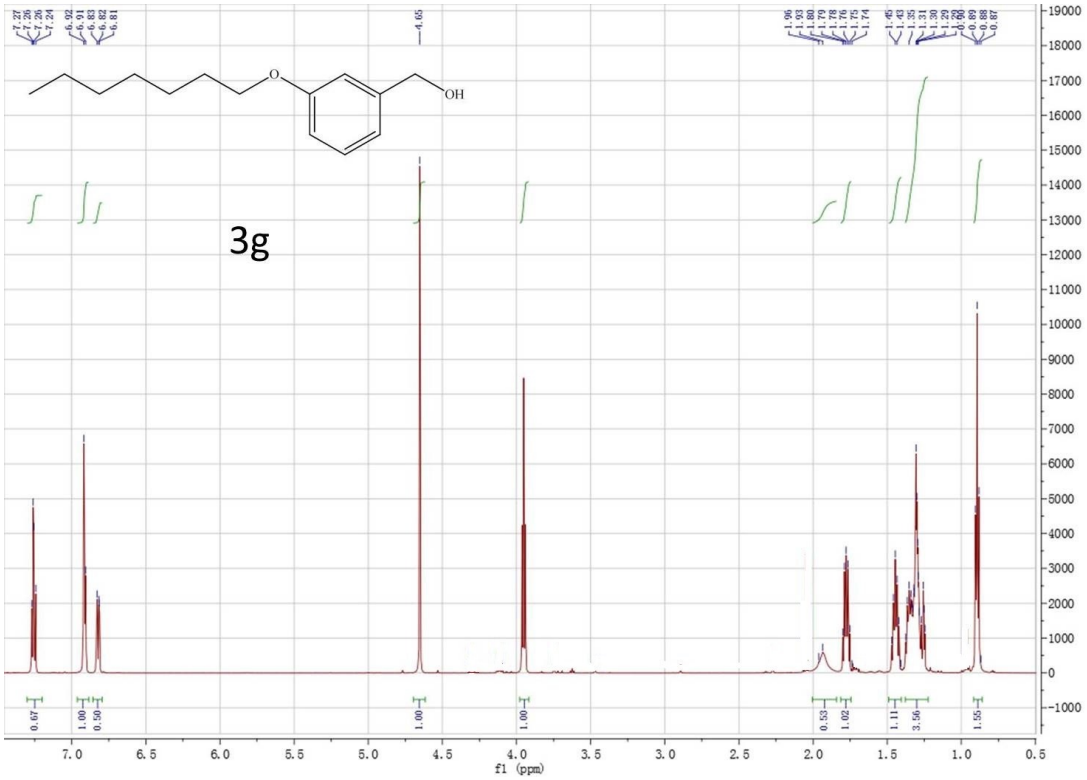

OH
3b
f1 (ppm)

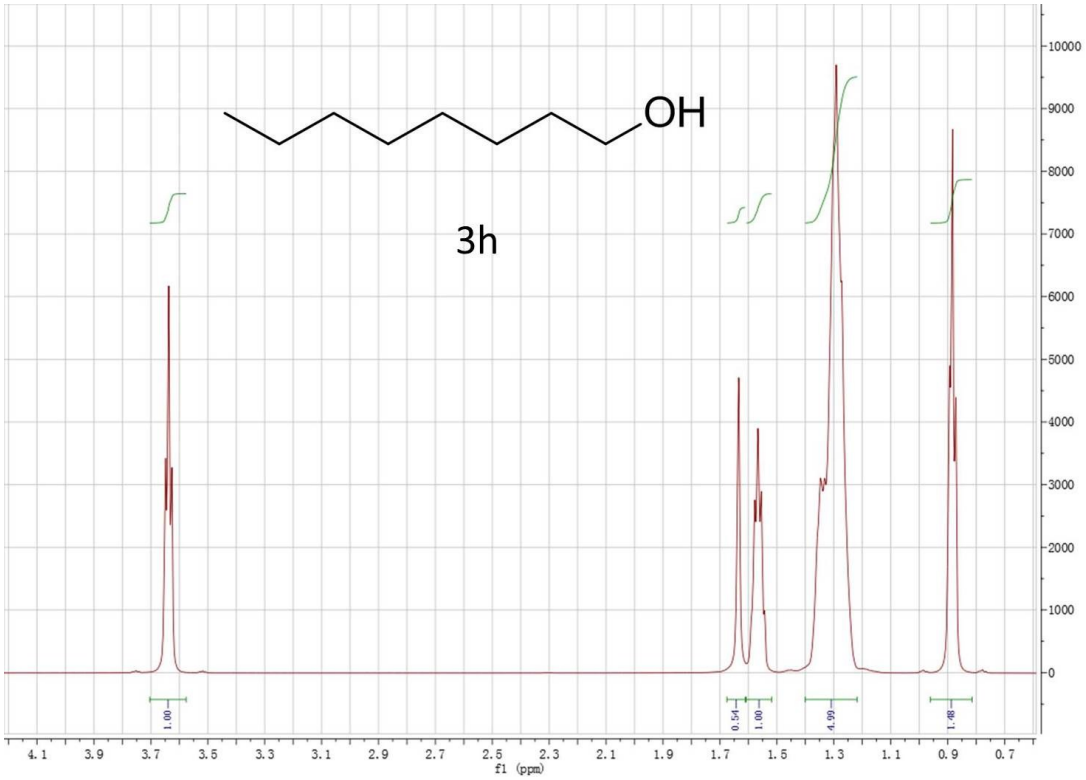

OH
O
3c
f1 (ppm)

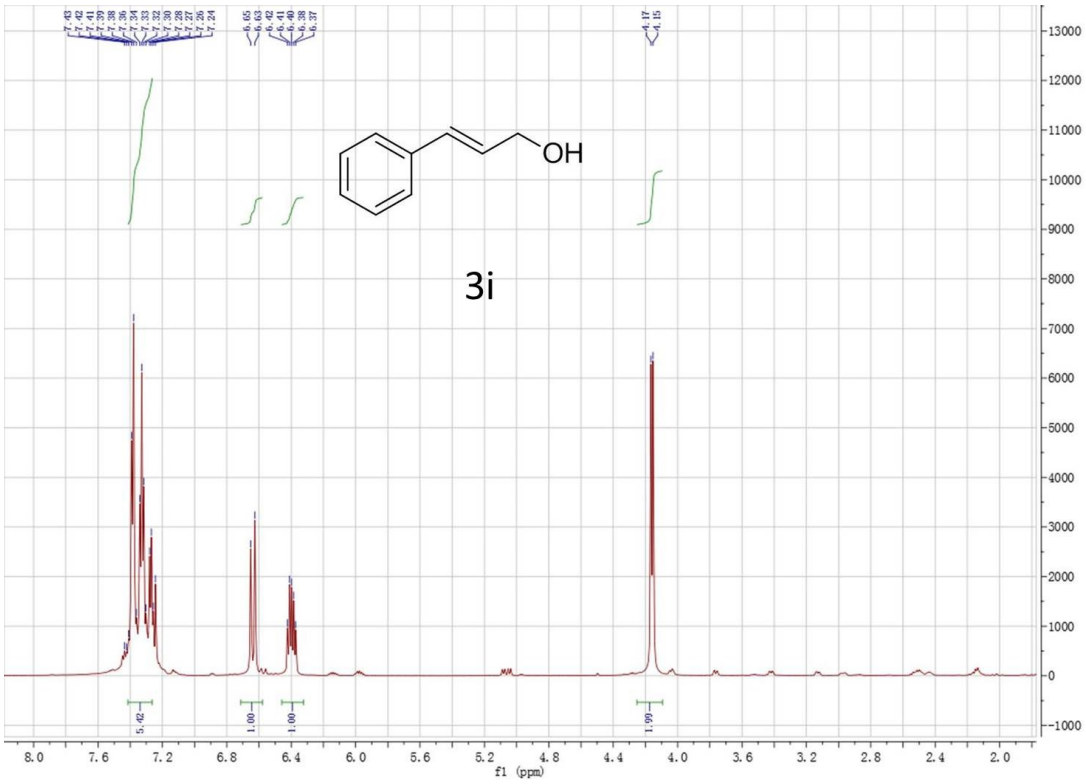

OH
O
3d
f1 (ppm)

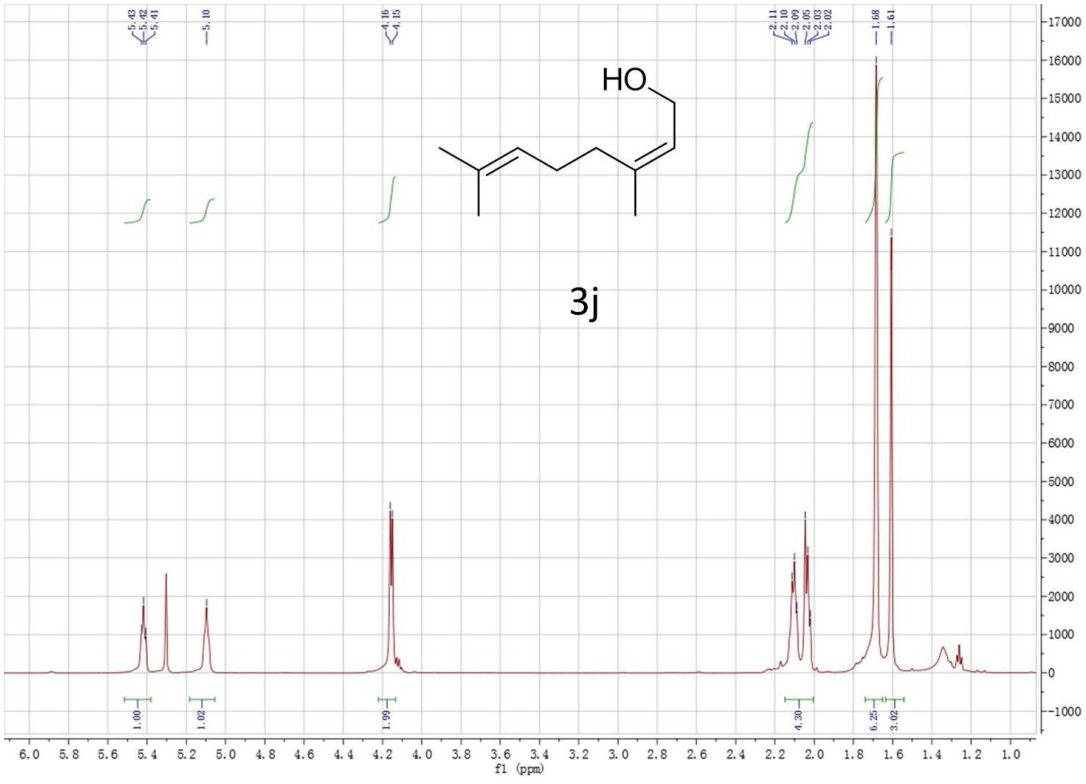

OH
2e
B (m)
7.41
A (m)
7.56
C (t)
7.34
D (s)
4.68
E (s)
2.22
f1 (ppm)

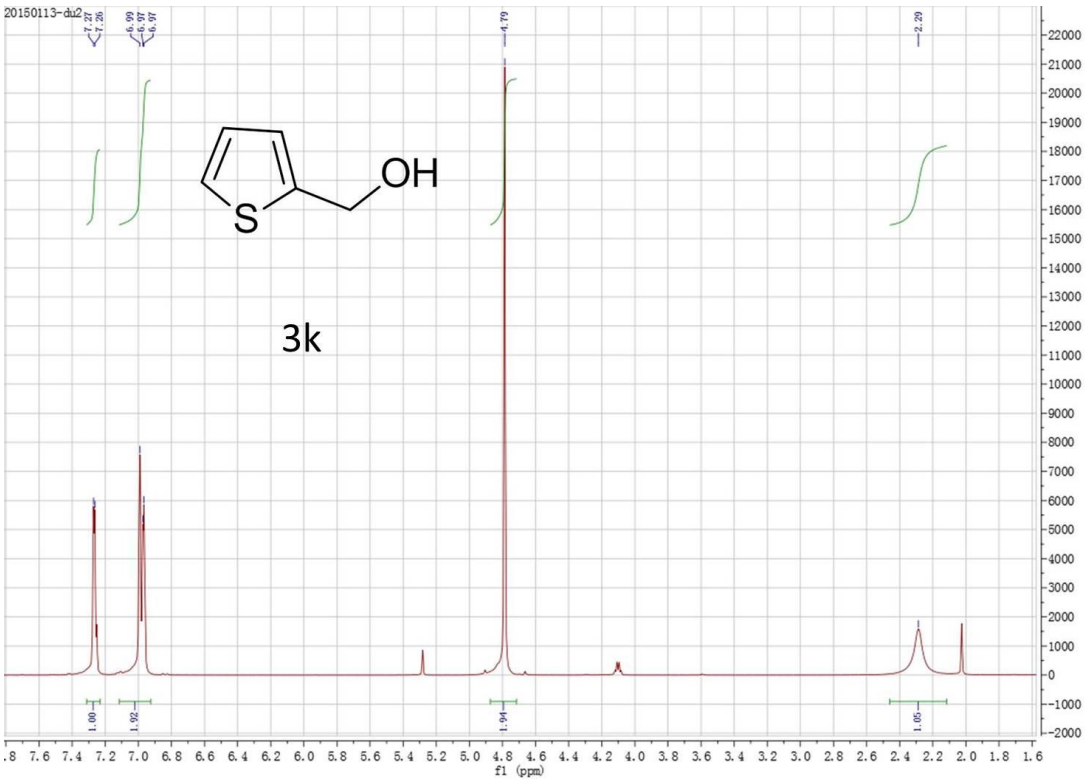

OH
O
3f
f1 (ppm)

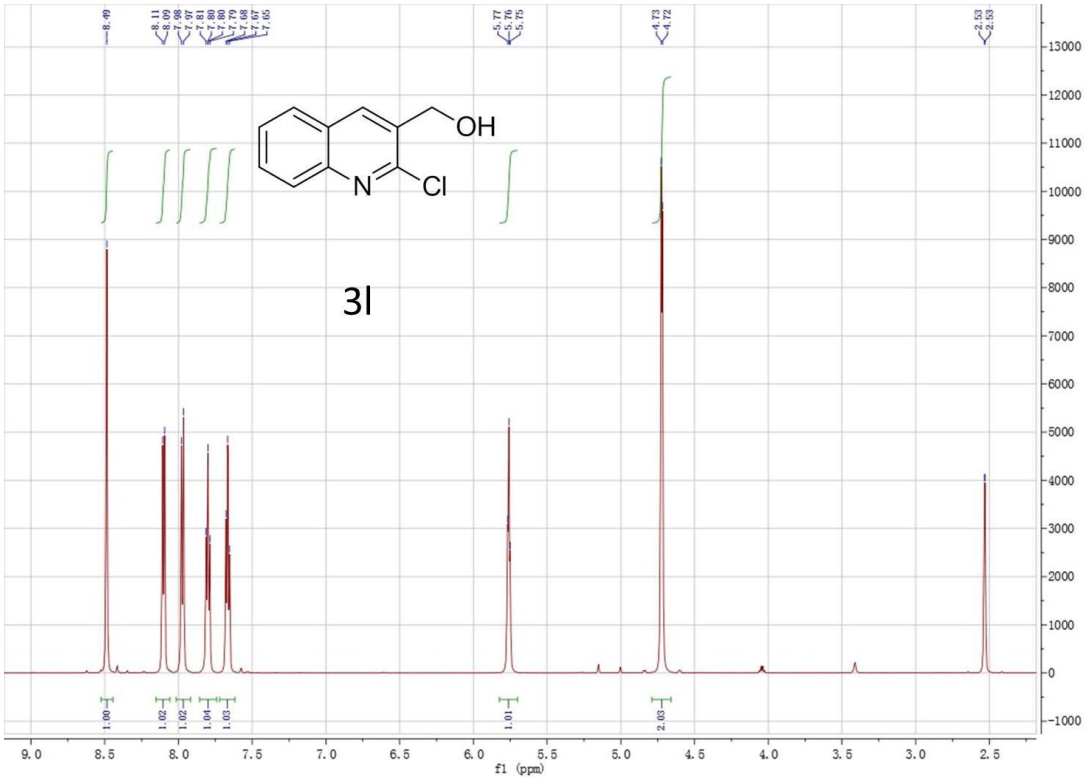

OH
3g
f1 (ppm)

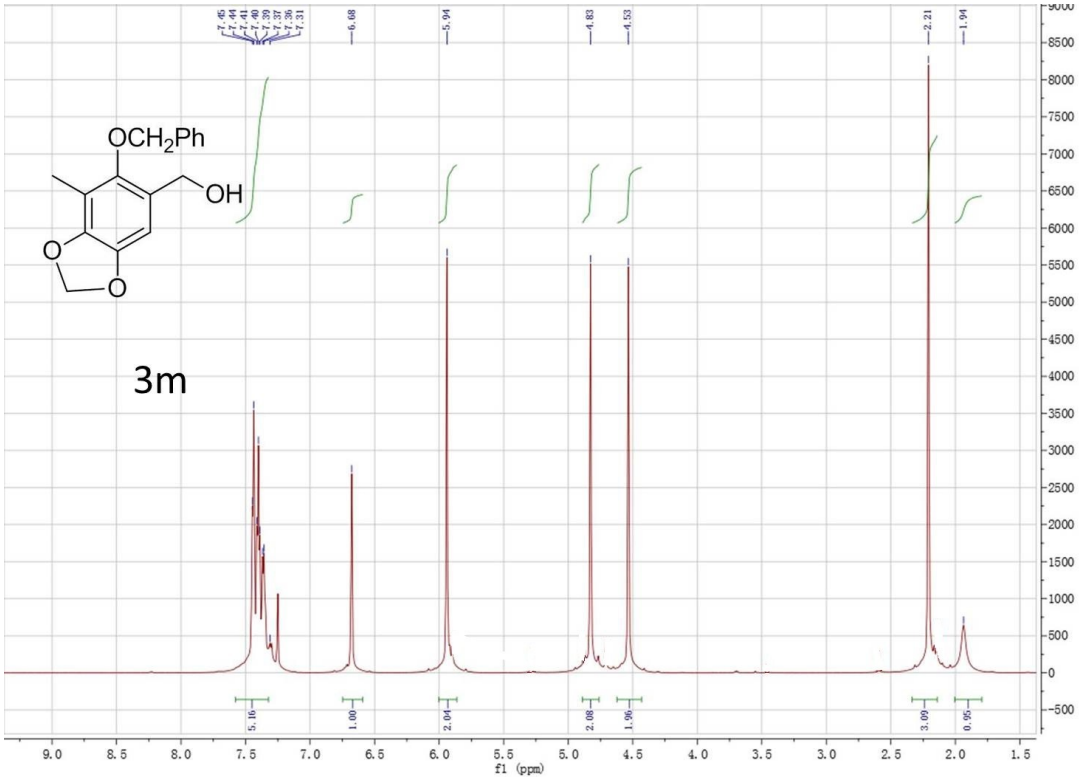

OH
3h
f1 (ppm)

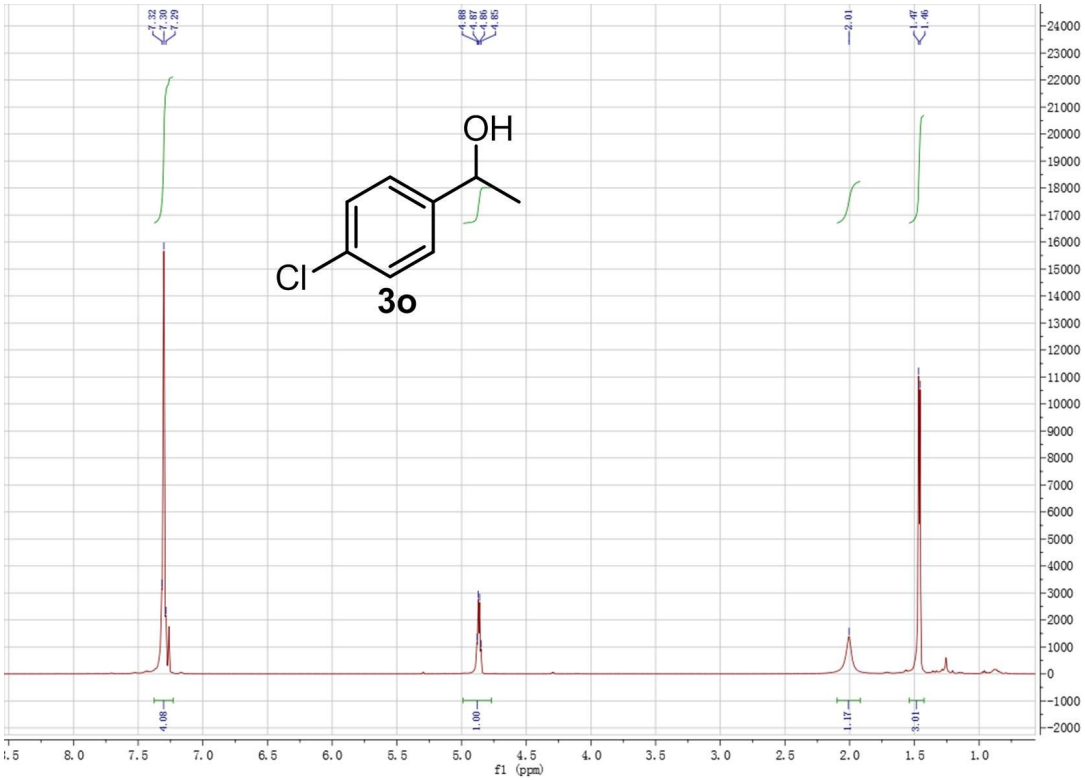

OH
3i
f1 (ppm)

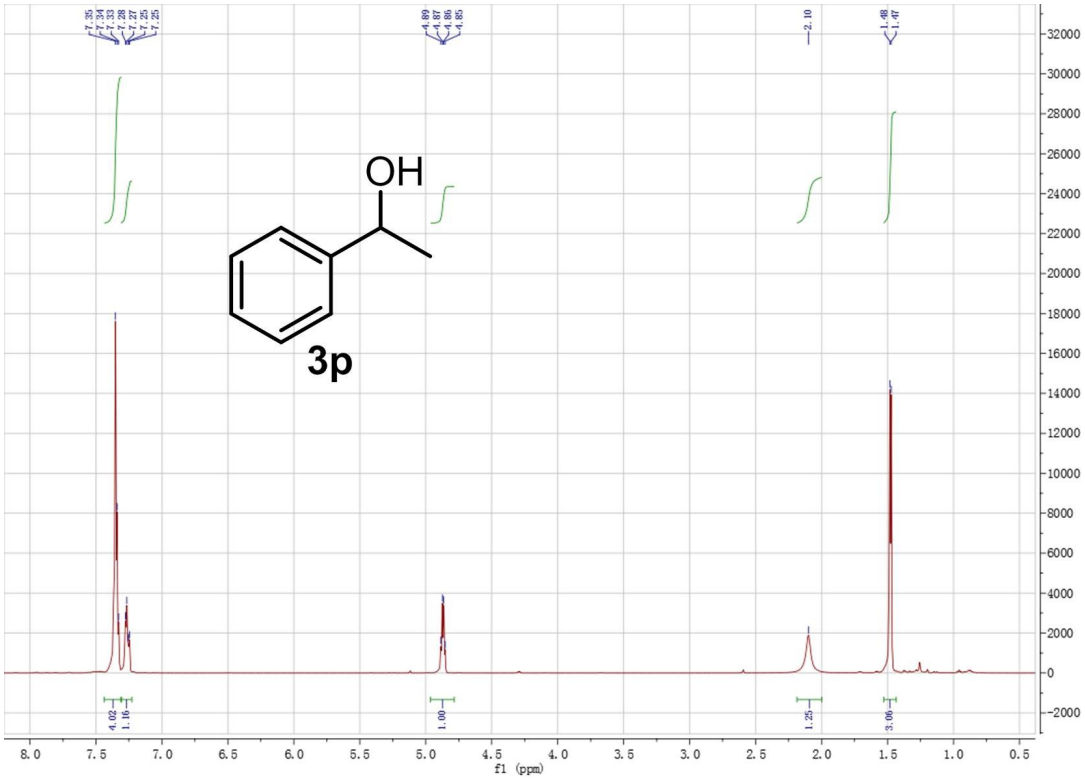

HO
3j
f1 (ppm)

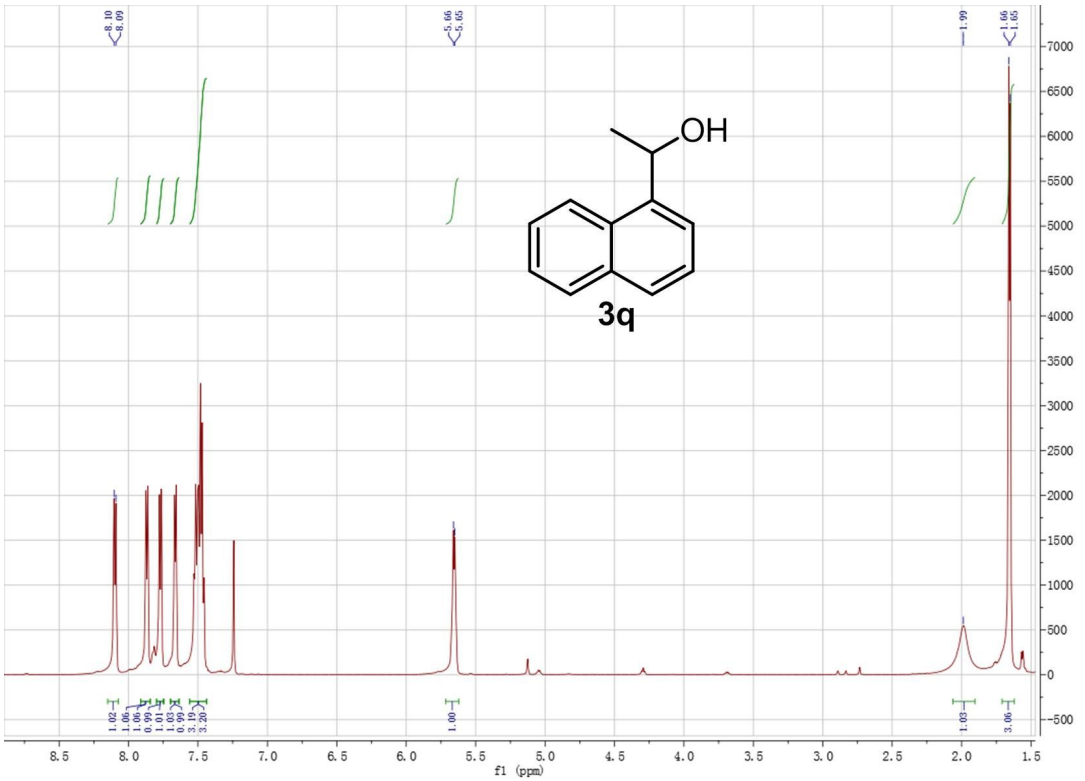

20150113-du2
OH
S
3k
f1 (ppm)

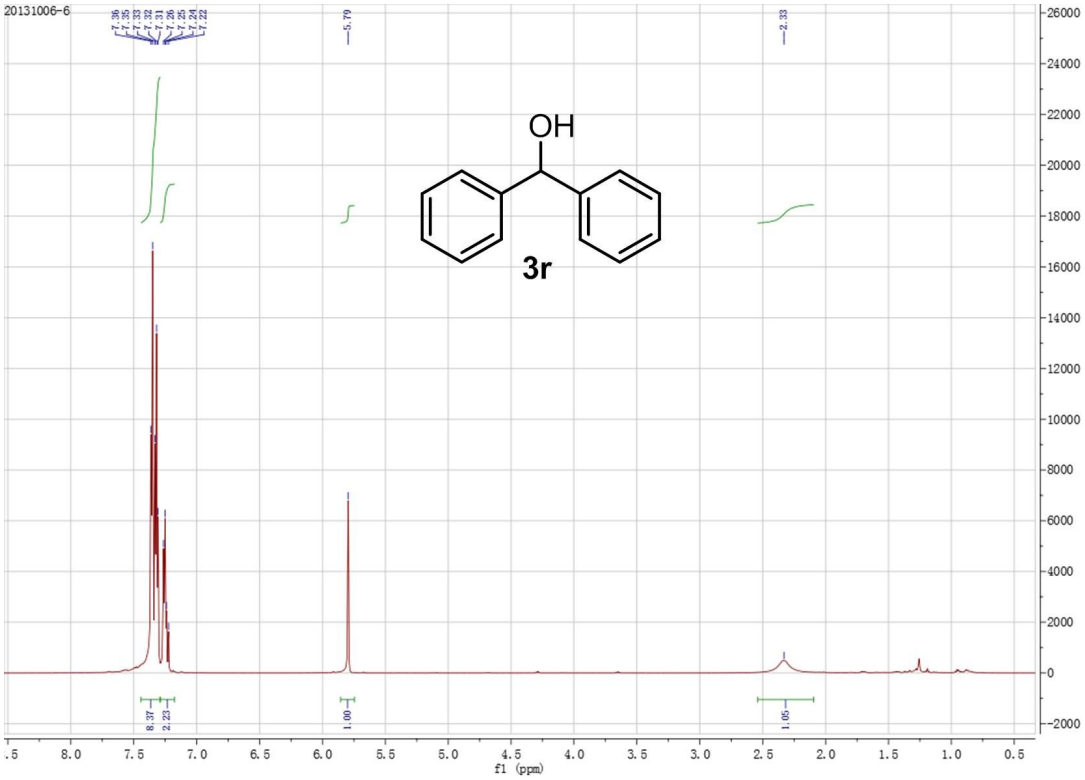

OH
N
Cl
3l
f1 (ppm)

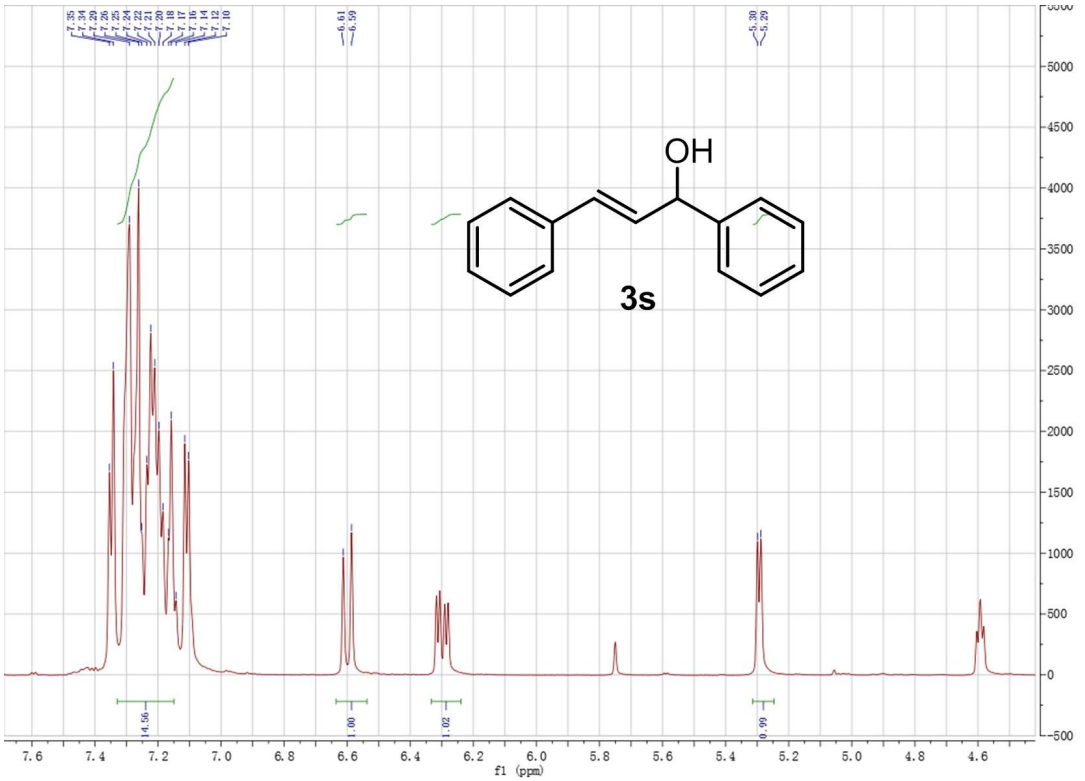

OCH2Ph
OH
O
O
3m
f1 (ppm)

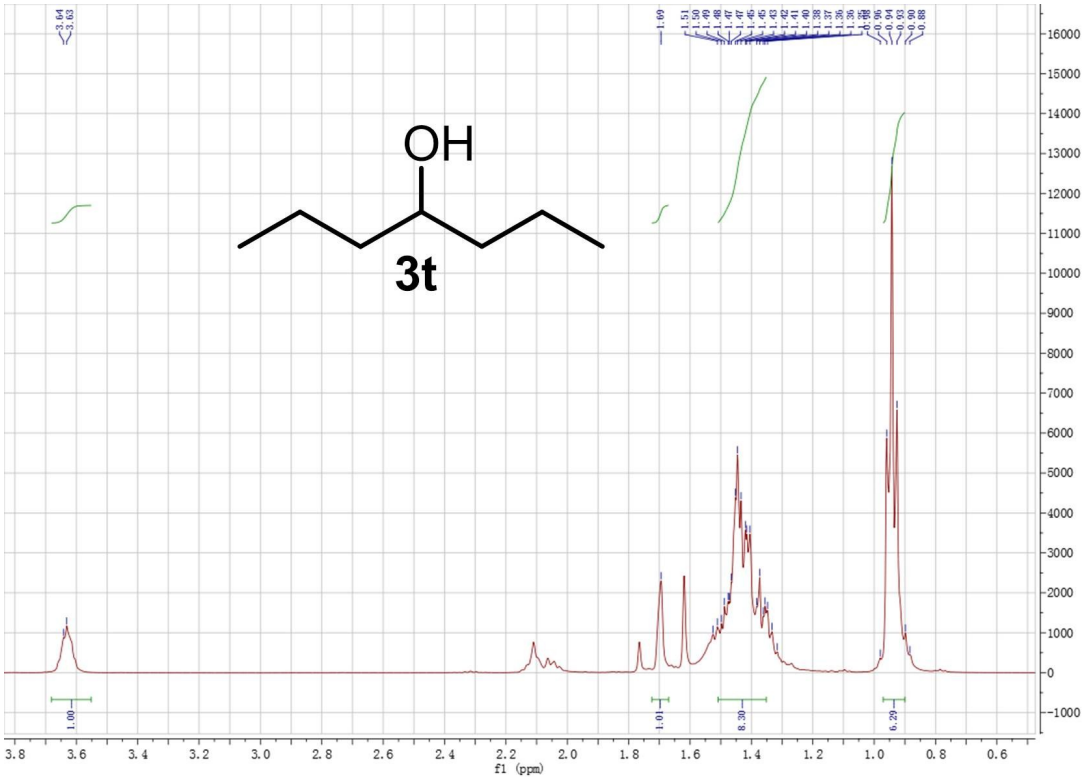

OH
Cl
3o
f1 (ppm)

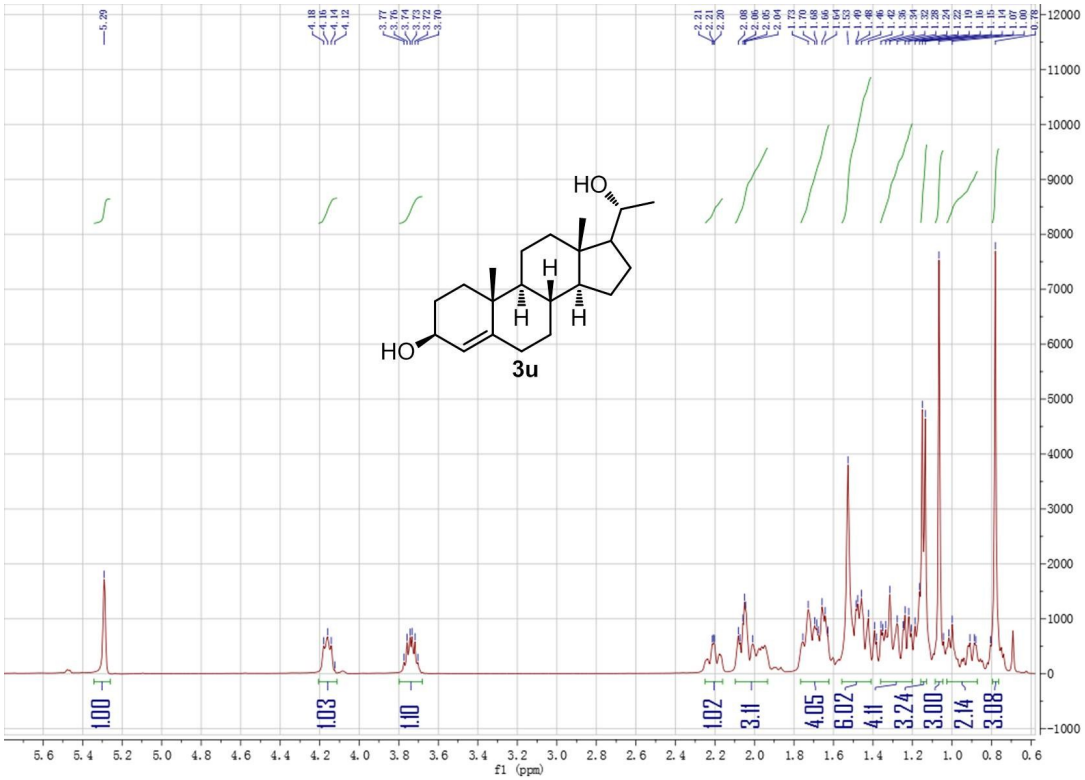

OH
3p
f1 (ppm)

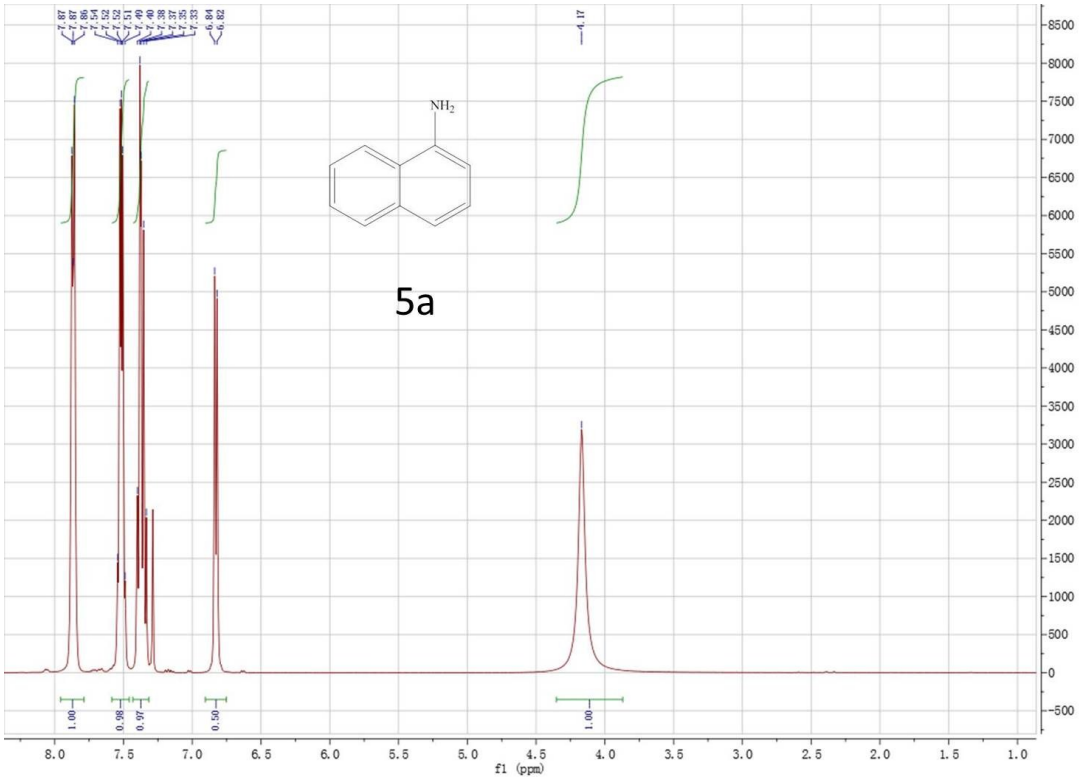

OH
3q
f1 (ppm)

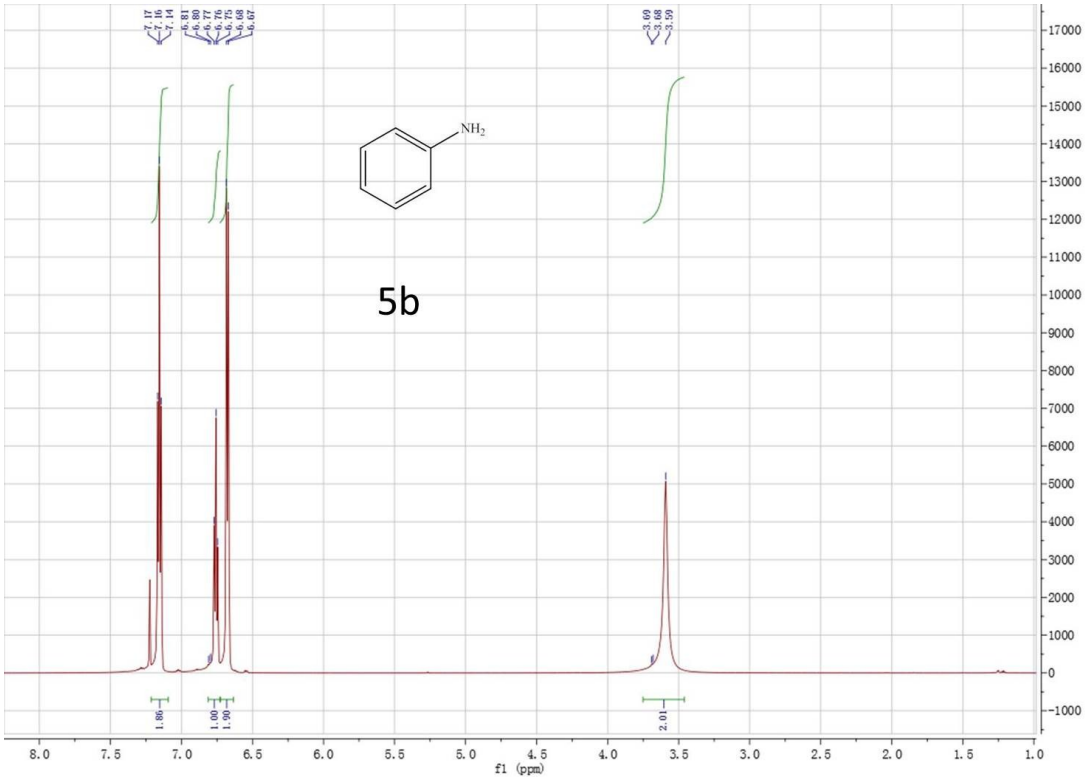

20131006-6
OH
3r
f1 (ppm)

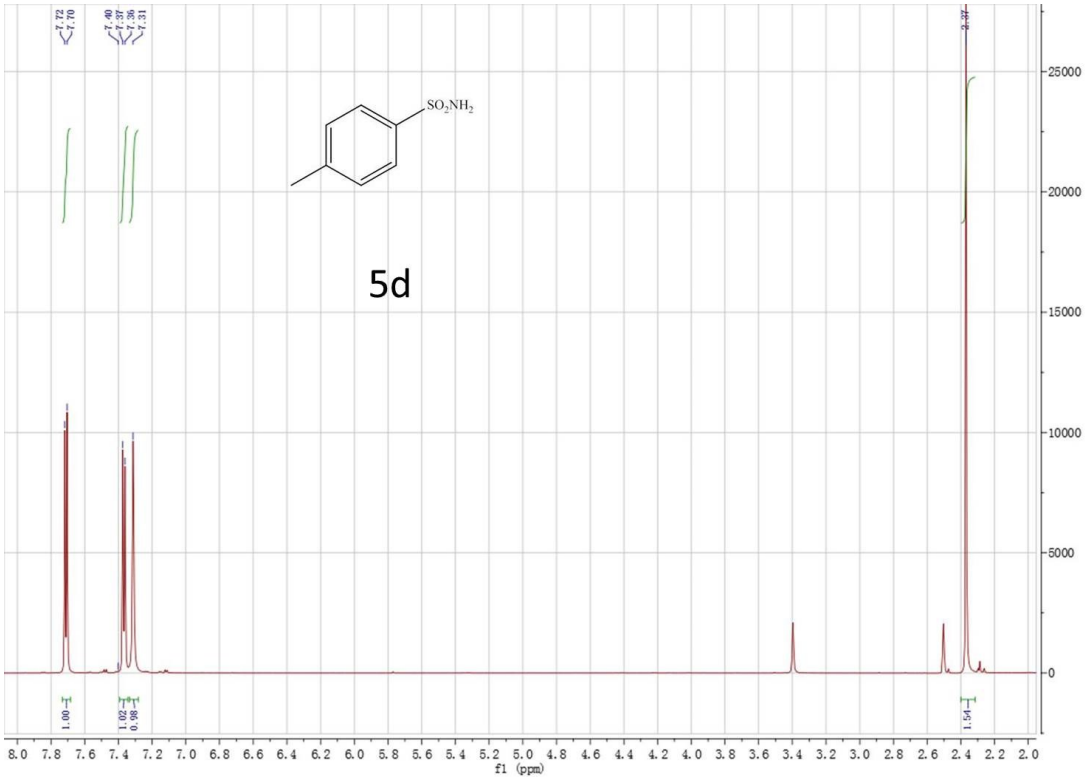

OH
3s
f1 (ppm)

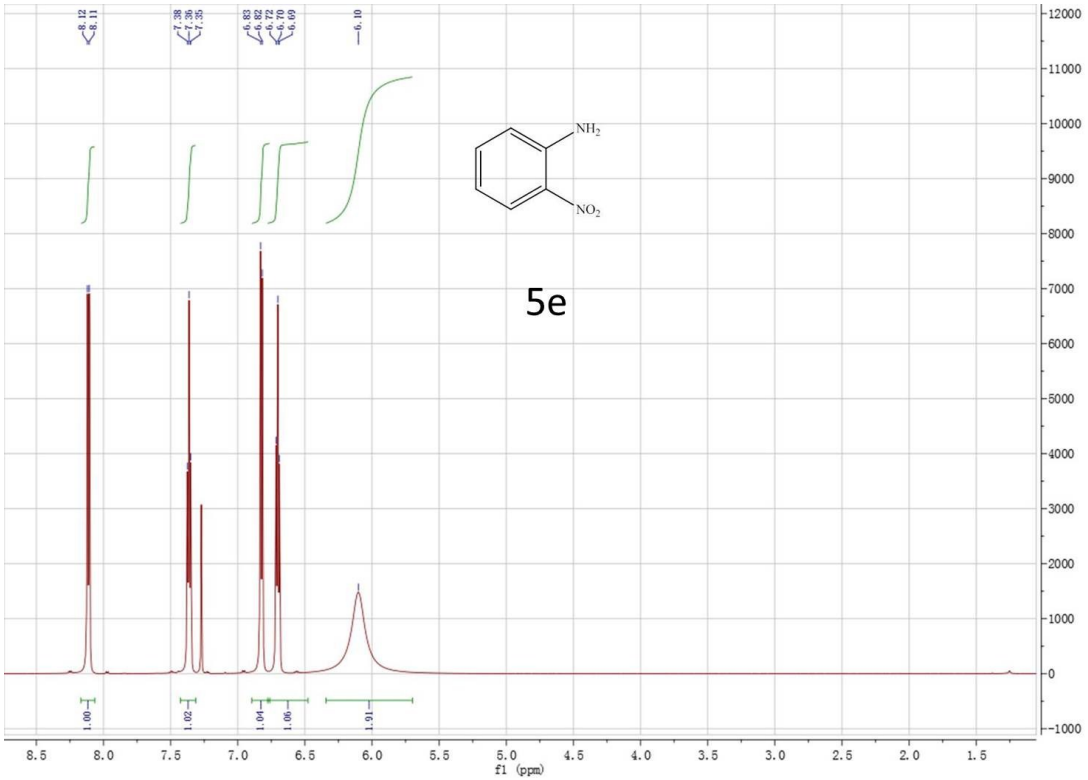

OH
3t
f1 (ppm)

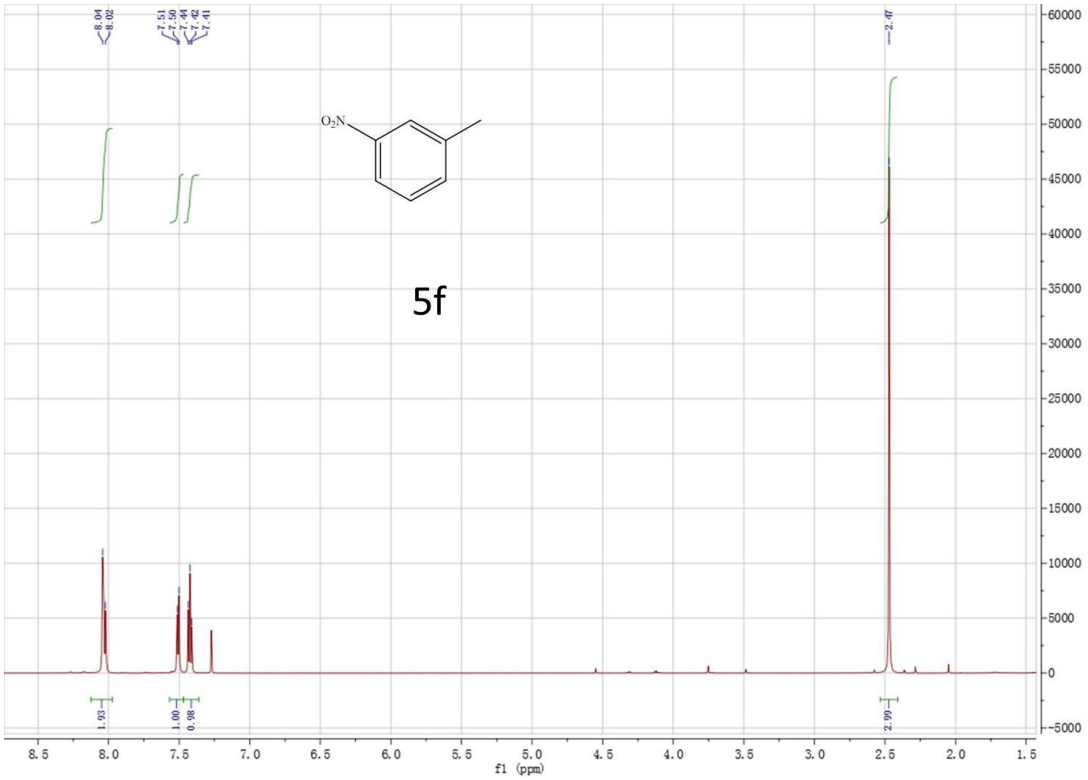

HO
H
H
H
HO
3u
f1 (ppm)

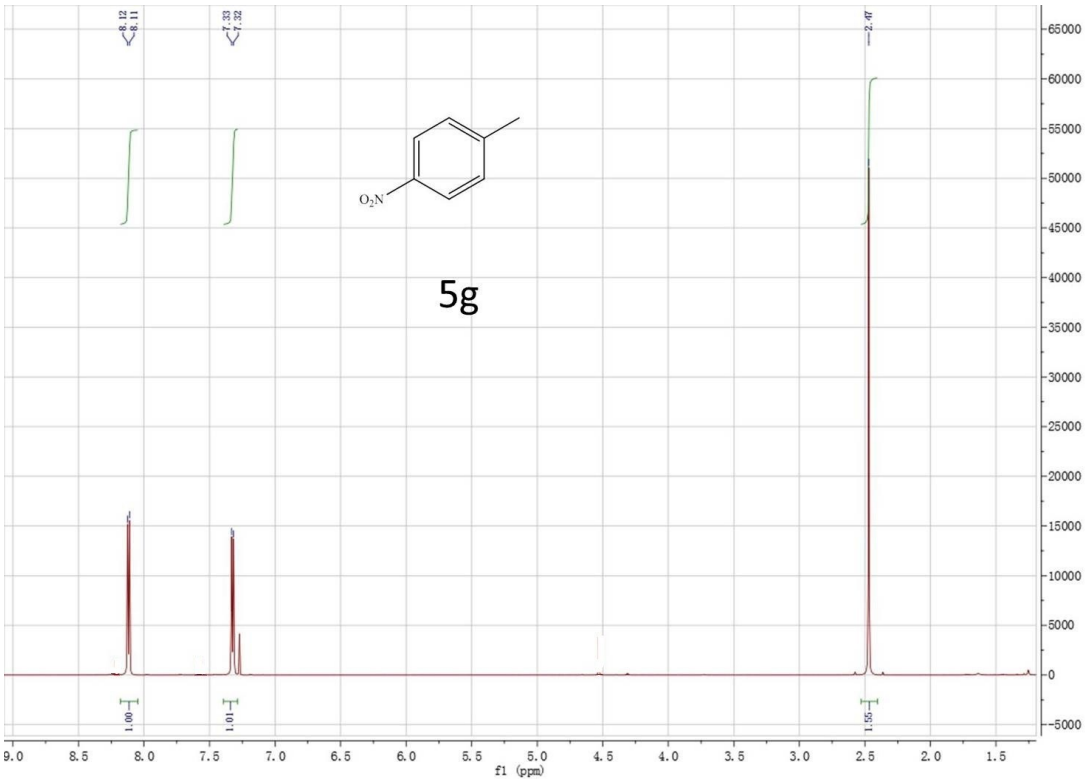

7.87
7.87
7.86
7.54
7.52
7.52
7.51
7.51
7.49
7.49
7.38
7.37
7.35
7.33
6.84
6.82
4.17
NH2
5a
1.00
0.98
0.97
0.50
1.00
f1 (ppm)


7.17
7.16
7.14
6.81
6.80
6.77
6.76
6.75
6.68
6.67
3.69
3.68
3.59
NH2
5b
1.86
1.00
1.90
2.01
f1 (ppm)


7.72
7.70
7.40
7.37
7.36
7.31
2.37
SO2NH2
5d
1.00
1.02
0.98
1.54
f1 (ppm)


8.12
8.11
7.38
7.36
7.35
6.83
6.82
6.72
6.70
6.69
6.10
NH2
NO2
5e
1.00
1.02
1.04
1.06
1.91
f1 (ppm)


8.04
8.02
7.51
7.50
7.44
7.42
7.41
2.47
O_2N
5f
1.93
1.00
0.98
2.99
f1 (ppm)


8.12
8.11
7.33
7.32
2.47
O_2N
5g
1.00
1.01
1.55
f1 (ppm)