Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

[Supporting Information]

β-Diketone Boron Difluoride Dye-Functionalized Conjugated Microporous Polymers for Efficient Aerobic Oxidative Photocatalysis

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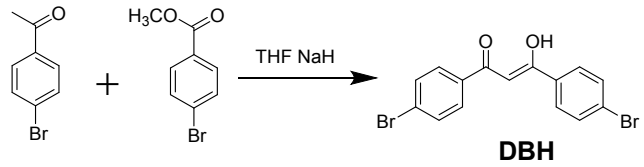
Section 1. Syntheses

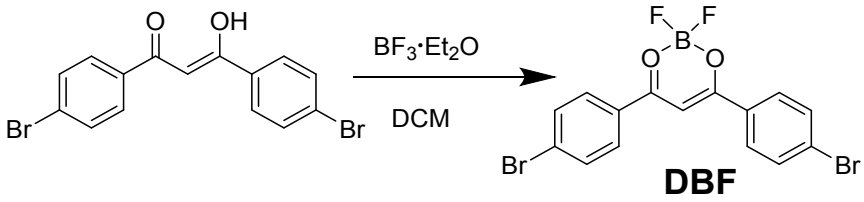
Synthesis of 1,3-Bis(4-bromophenyl)-1,3-propanedione



DBH

NaH (1.52 g, 63.3 mmol) and dried THF (10 mL) were added to a dried round flask in an ice bath. Then, the corresponding 1-(4-bromophenyl)ethanone (2.5g, 12.5 mmol) and methyl 4-bromobenzoate (3.00 g, 14 mmol) in THF solution (20mL) were added in the mixed solution. The mixture was heated to reflux for 16 h. After cooling to room temperature, the reaction mixture was neutralization by 1M hydrochloric acid. The organic layer was separated and washed two times by brine solution and dried by anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure and the residue was recrystallized from ethyl acetate to give a pure product. Yield: 6.82 g (74% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (d, J = 8.6 Hz, 4H), 7.65 (d, J = 8.6 Hz, 4H), 6.79 (s, 1H).[1]

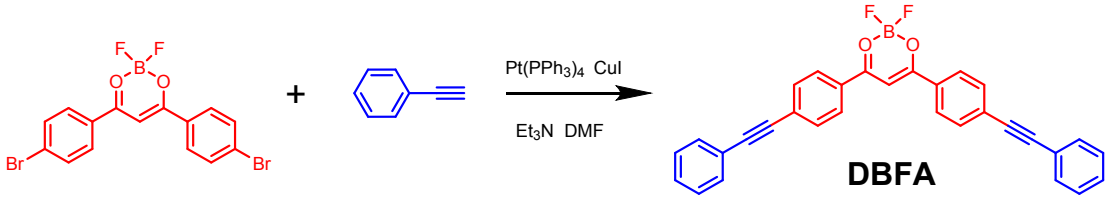
Synthesis of Boron,difluoro[1,3-bis(*p*-bromophenyl)-1,3-propanedionato]



DBF

Under a nitrogen atmosphere, 1,3-bis(4-bromophenyl)-1,3-propanedione (0.764 g, 2 mmol), BF_3. Et_2O (1.3 ml, 10 mmol) and anhydrous dichloromethane (30 ml) were added to a dried round flask. Then the mixture was refluxed for 2 h. After cooling to room temperature, the reaction was concentrated and purified by silica gel column chromatography to obtain a pale yellow solid. yield: 0.782 g (92% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (m, 4H), 7.75 (m, 4H), 7.15 (m, 1H).[2]

Synthesis of Model



DBFA

The synthesis was carried out by Sonogashira−Hagihara cross-coupling reaction. Under nitrogen protection, in a 25 mL Schlenk tube were added boron complex DBF (0.375 mmol, 160 mg), ethynylbenzene (23 mg, 0.75 mmol), $Pd(PPh_3)_4$ (0.0259 mmol,30 mg,), CuI (15 mg,0.078 mmol), dry DMF (2.5 mL), triethylamine (2.5 mL). The reaction mixture was stirred at 100 °C for 3 day. After removal of the solvents at

reduced pressure,the residue was washed three times with water (50 mL) and extracted into CH_2Cl_2. The organic layer was dried on $MgSO_4$, and the solvent was removed under reduced pressure. The crude mixture was then purified by column chromatography to yield the product as a light yellow solid. Yield: 157 mg (89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.84 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 4H), 7.65 (d, *J* = 7.8 Hz, 4H), 7.56 (s, 4H), 7.38 (s, 6H), 6.88 (d, *J* = 2.7 Hz, 1H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 183.76, 133.79, 130.80, 127.42, 126.13, 121.70, 91.59, 87.77.

Synthesis of TPB-B-CMP

DBF (0.75 mmol), TEB (0.5 mmol), $Pd(PPh_3)_4$ (60 mg, 0.052 mmol), and CuI (30 mg, 0.16 mmol) were added into a 50 mL flame-dried Schlenk tube with the mixed dry N,N-dimethyl formamide (DMF) (5 mL) and triethylamine (5 mL). The reaction suspension was degassed and then stirred at 100 °C for 3 days under an inert nitrogen atmosphere. After cooling to room temperature, the solid was obtained by filtration and washed with DMF, water, trichloromethane, methanol, and acetone. Further purification was carried out by Soxhlet extraction with methanol and trichloromethane successively for 24h each to give a yellow powder. yield: 0.367 g (95% yield).

Synthesis of TPA-B-CMP

The synthesis method is the same as TPB-B-CMP, with the ligand TEB replaced by TEA and give a red powder. yield: 0.327 g (92% yield).

Synthesis of TPB-NB-CMP

The synthesis method is the same as TPB-B-CMP, with the dibromide group DBF replaced by DBH and give a pale yellow powder. yield: 0.319 g (90% yield).

Section 2. TGA Curve

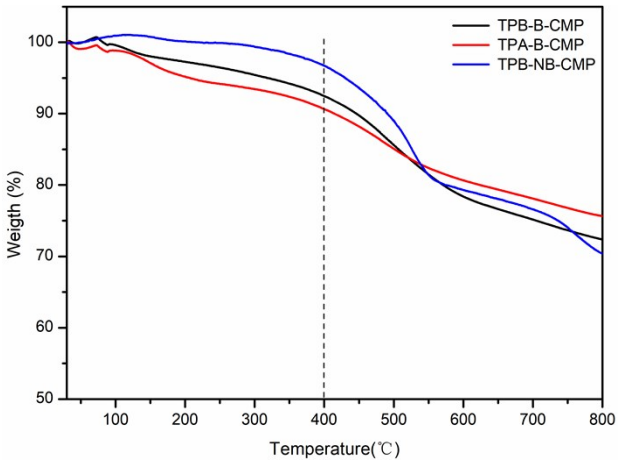


Fig. S1. TGA curve of polymer TPB-B-CMP, TPA-B-CMP, and TPB-NB-CMP.

Section3. XRD Pattern

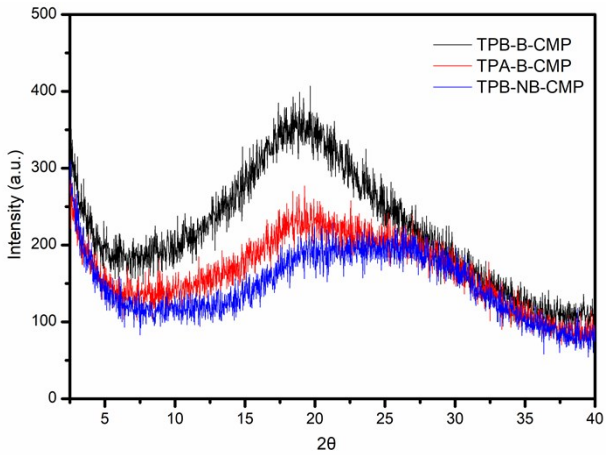


Fig. S2. PXRD of polymer TPB-B-CMP, TPA-B-CMP, and TPB-NB-CMP.

Section 4. SEM Image

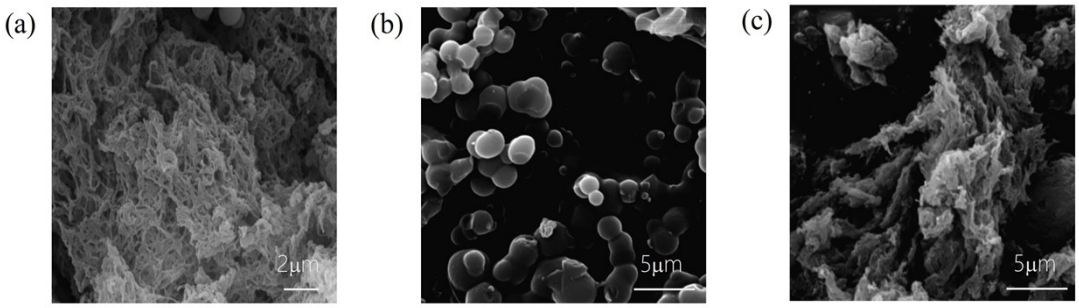


Fig. S3. SEM images of polymer TPB-B-CMP(a), TPA-B-CMP(b), and TPB-NB-CMP (c).

Section 5. Mott-Schottky curve

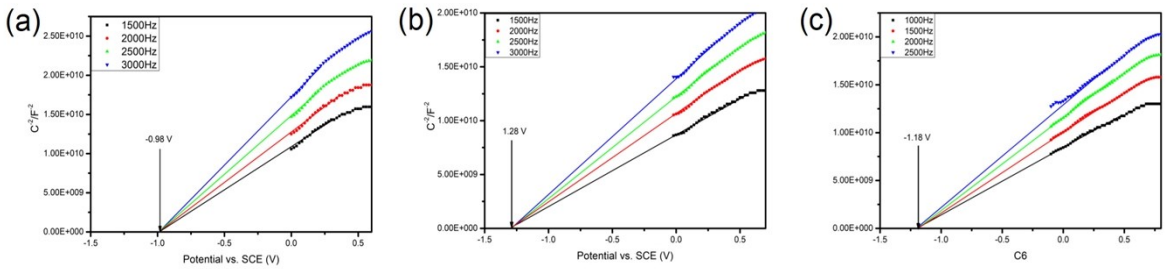


Fig. S4. Mott-Schottky curves of TPB-B-CMP (a), TPA-B-CMP (b) and TPB-NB-CMP (c) at different frequencies.

Section 6. Photocatalytic mechanism

Fig. S5 WP-TEC-1020HSL photochemical reaction system.

Table S1. Selected catalysts and their catalytic efficiency for amines into imines.

Photocatalyst	Yield (%)	Substrate (mmol)	Photocatalyst (mg)	T (h)	Light	Ref
TPB-B-CMP	97	0.5	3.3	18	10W blue LED	this work
TPA-B-CMP	99	0.5	3	18	10 W blue LED	this work
TPB-NB-CMP	77	0.5	3	18	10 W blue LED	this work
pTCT-2P	98	0.4	2.7	6	26 W white CFL	[3]
CzBDP	75	1	1.95	15	9 W CFL	[4]
C-CMP	94	1.0	20	4	150W Xe lamp	[5]
CF-HCP	91	0.2	5.0	6	30 W green LED lamp	[6]

Table S2. Selected catalysts and their catalytic efficiency for photocatalytic hydroxylation of boric acid.

Photocatalyst	Yield (%)	Substrate (mmol)	Photocatalyst (mg)	T (h)	Light	Ref
TPB-B-CMP	96	0.5	6.6	48	10W blue LED	this work
TPA-B-CMP	99	0.5	6	48	10 W blue LED	this work
TPB-NB-CMP	72	0.5	6	48	10 W blue LED	this work
PCP-MF	94	0.5	10	10	White LED lamp	[7]
BBO-COF	99	0.2	21.2	96	18 W white LED	[8]
LZU-190	99	0.2	21.2	48	20 W white LEDs	[9]
CPOP-29	98	0.5	10	48	23 W white LED lamp	[10]

EPR measurements of TEMP-^{1}O2:

2 mg photocatalyst was dispersed in 0.1 M TEMP (3 ml in CH_3CN), and the solution was continuously irradiated for 30 min with a blue lamp (λ=460-465 nm) before measurement.

UV-Vis measurements of N, N, N', N'-tetramethyl-p-phenylenediamine (NTPD):

In a typical experimental procedure, two standard solutions of N, N, N', N'-tetramethylp-phenylenedi-amine (NTPD) were prepared separately in acetonitrile. The TPA-B-CMP (2 mg) was added to one of the solutions and both the solutions were stirred for 1h under constant irradiation by visible light (10 W LED). Observe the absorption band in the 450-650 nm range.

Table S3. Quenching experimental data

Reaction	Entry	Scavengers	Yield
Photocatalytic of benzylamine [a]	1	KI [c]	7%
	2	NaN_3 [d]	99%
	3	Benzoquinone [e]	46%
Photocatalytic of boric acid [b]	4	KI [c]	3%
	5	NaN_3 [d]	99%
	6	Benzoquinone [e]	55%

[a] Benzylamine (0.5 mmol), photocatalyst (2.44mg, 1 mmol%), CH_3CN(5mL), scavengers (1mmol) 10W blue LED (460-465nm), room temperature (RT), 18 h; conversion was determined by ^{1}H NMR. [b] Phenylboronic acid (0.5 mmol), photocatalyst (2.44 mg, 1 mmol%), DMF (5 mL), scavengers (1 mmol), air, 10W blue LED (460-465nm), room temperature (RT), 48 h; conversion was determined by ^{1}H

NMR. [c] hole scavenger. [d] $^1O_2$ scavenger. [e] $O_2^{\bullet-}$ scavenger.

Section 7. Stability and cycling

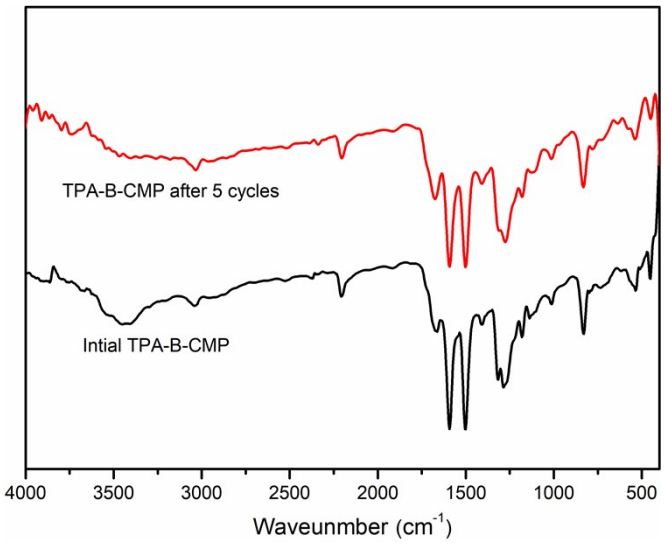


Fig. S6. Initial infrared spectrum of TPA-B-CMP and spectrum after five cycles.

Section 8. Liquid NMR Spectra of Some Compounds

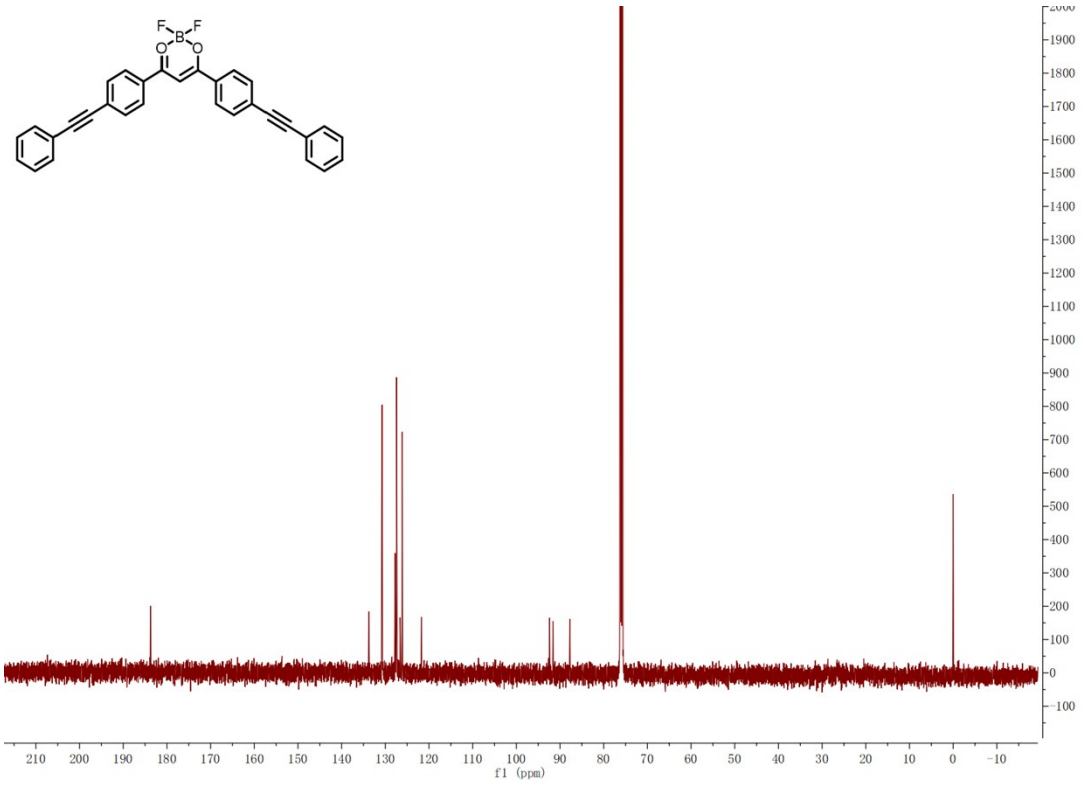
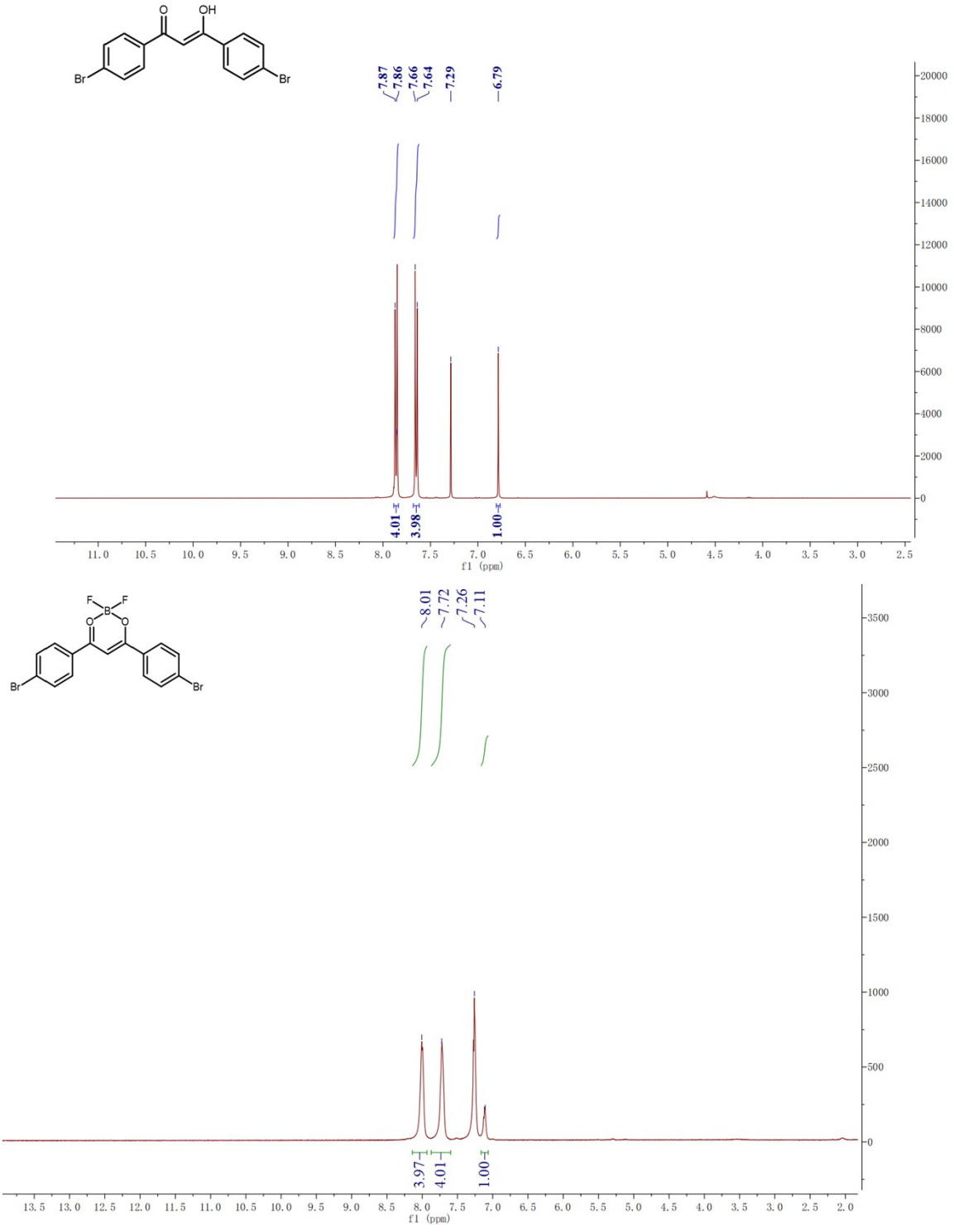
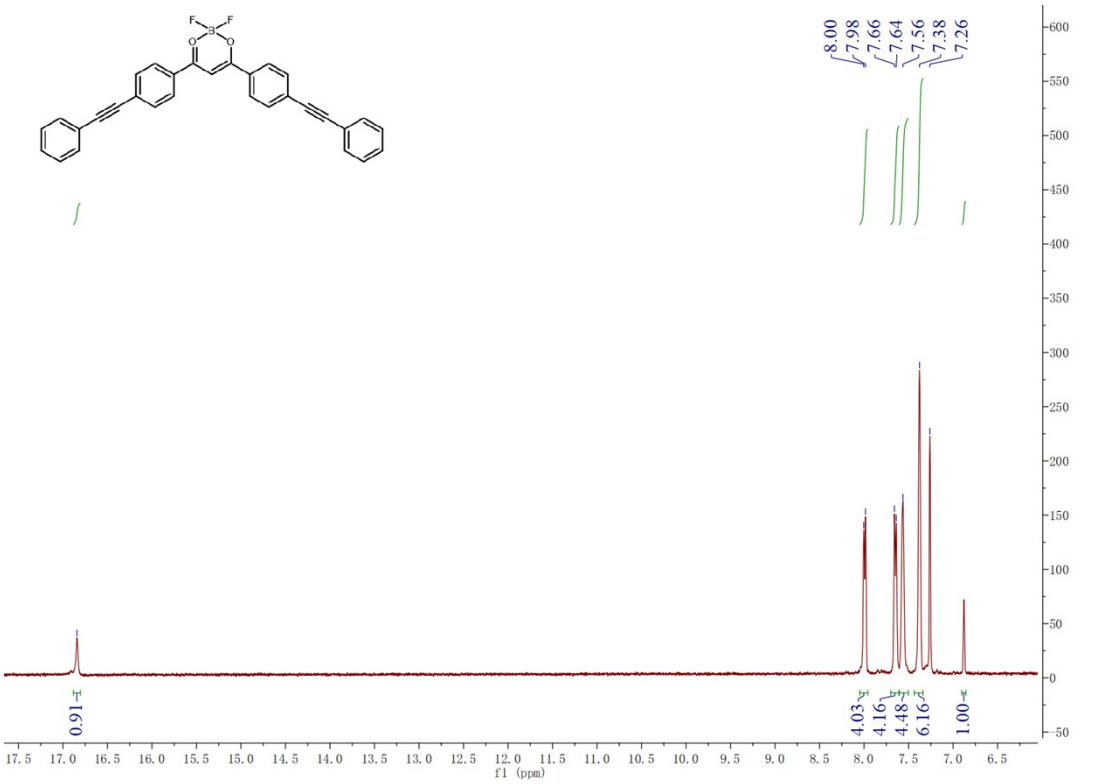


Fig. S7. ^{13}C NMR Spectra of DBFA

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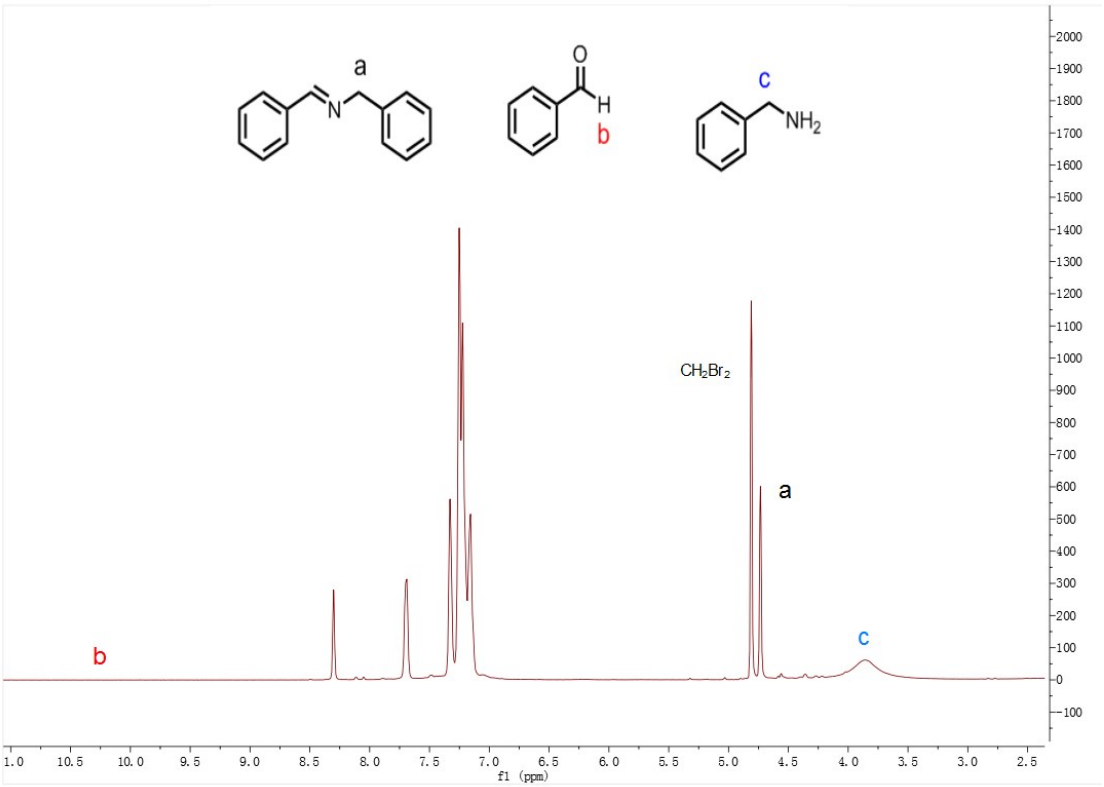
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b
c
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CH2Br2
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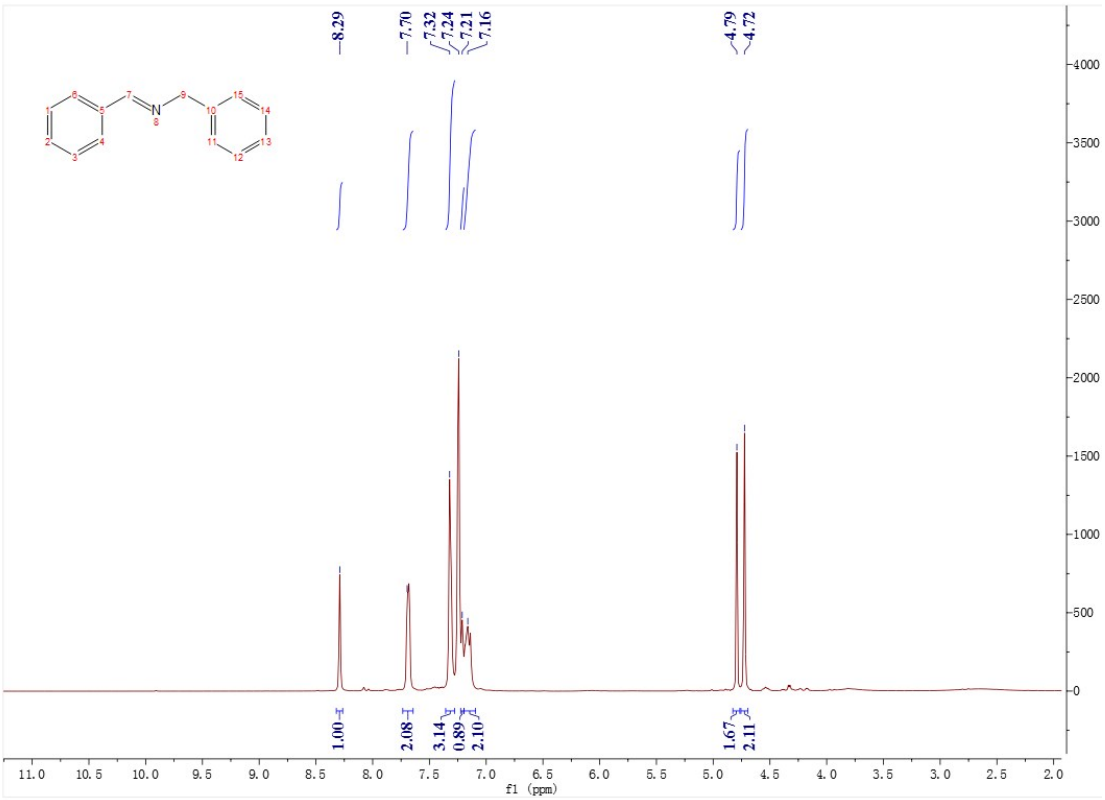
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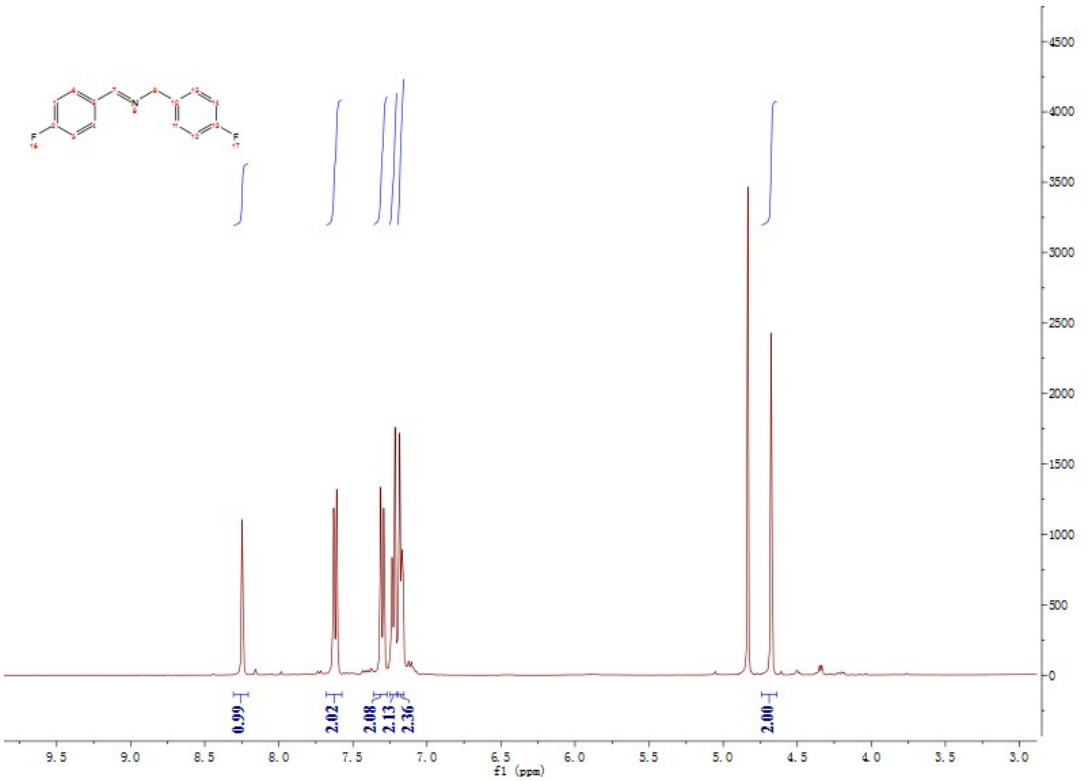
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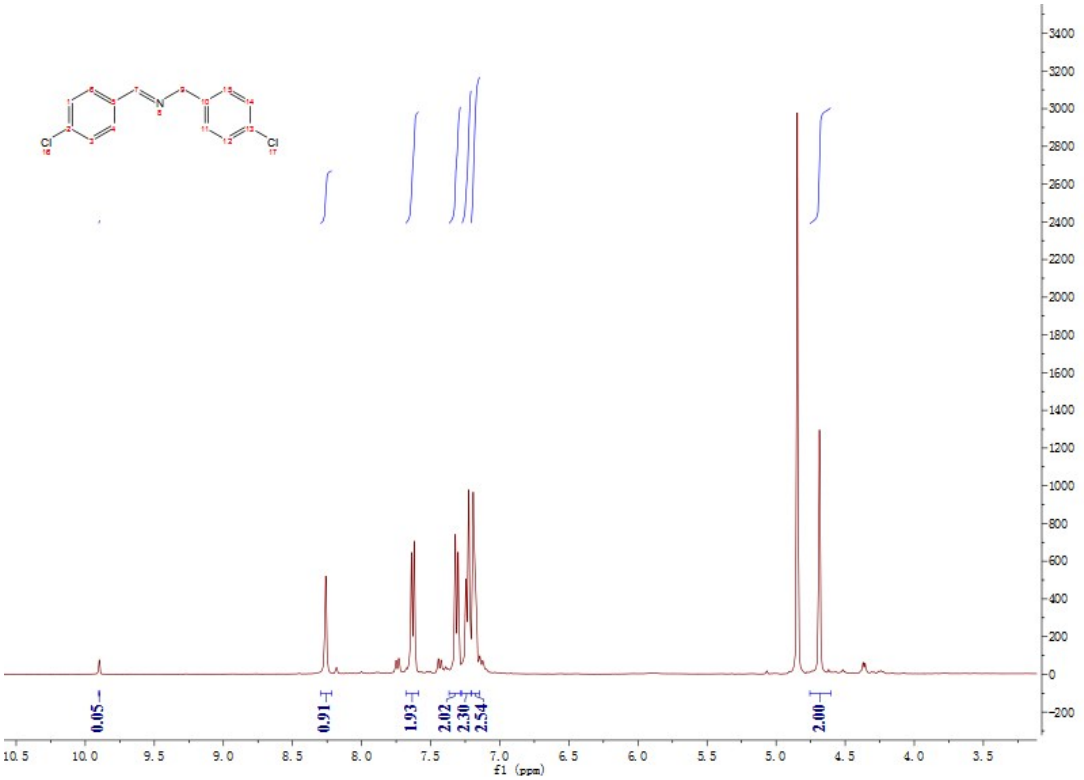
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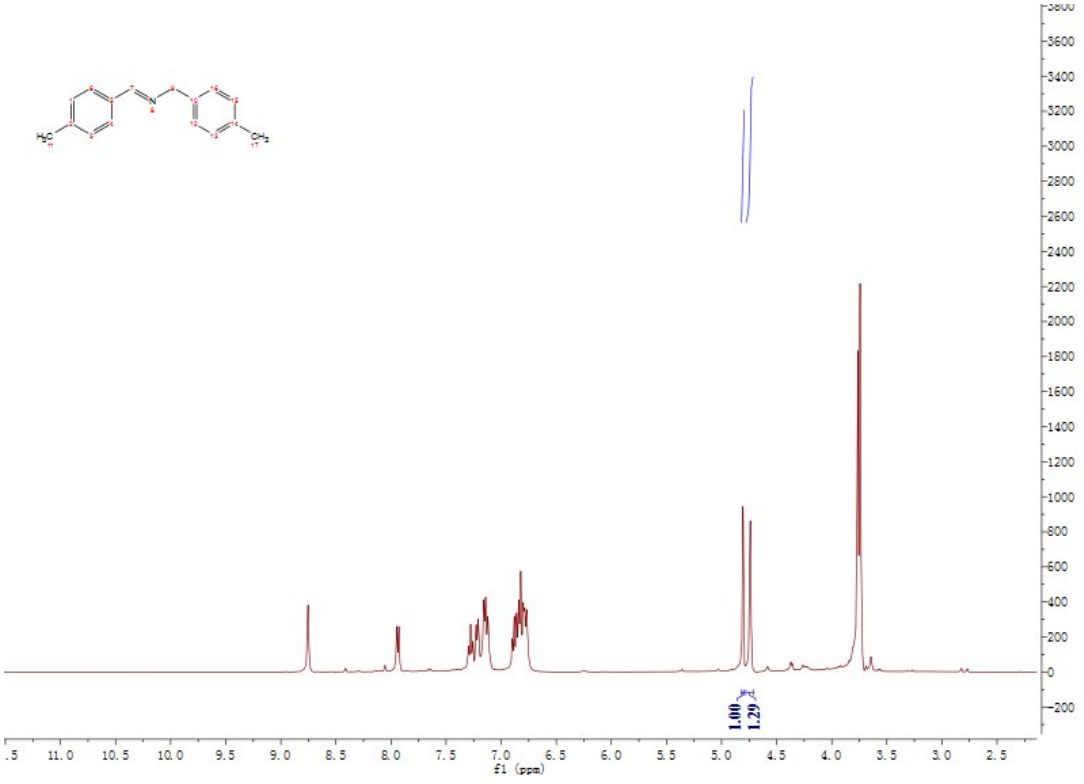
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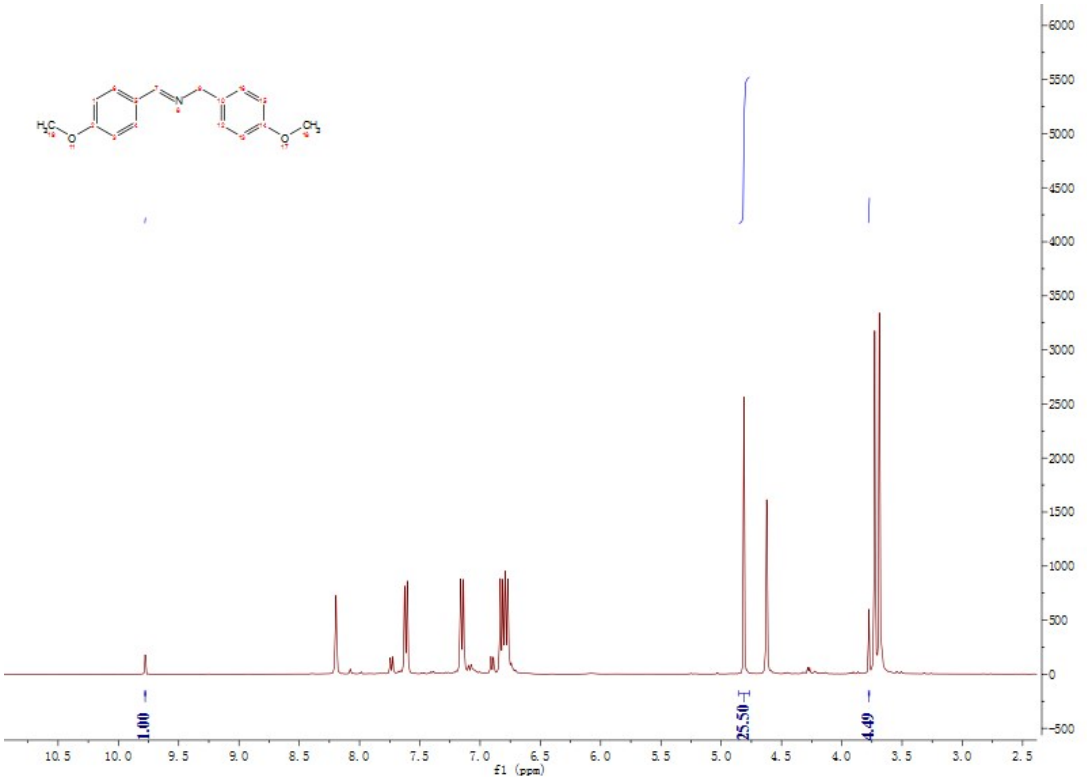
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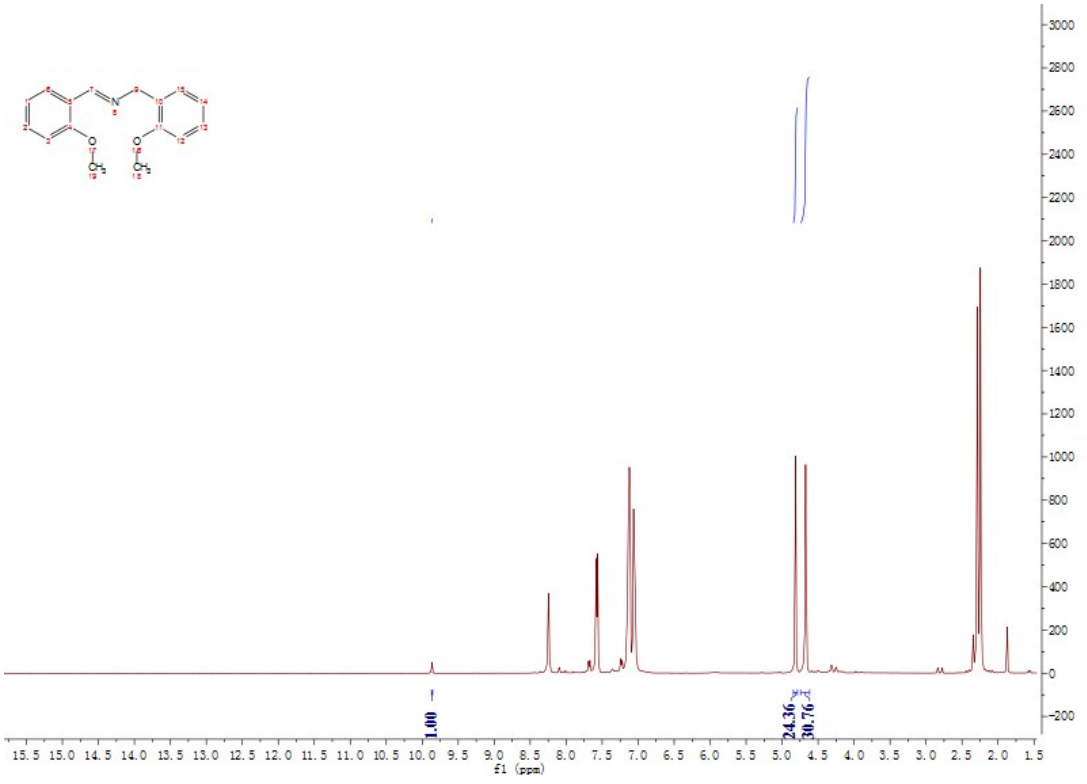
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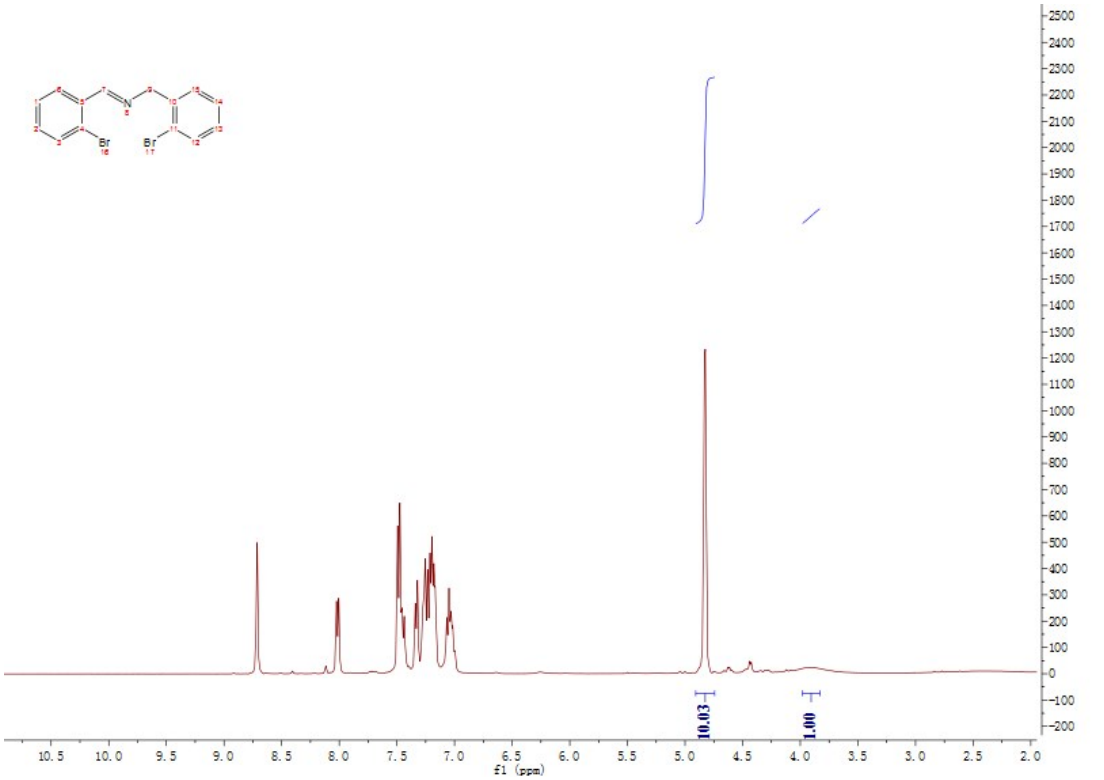
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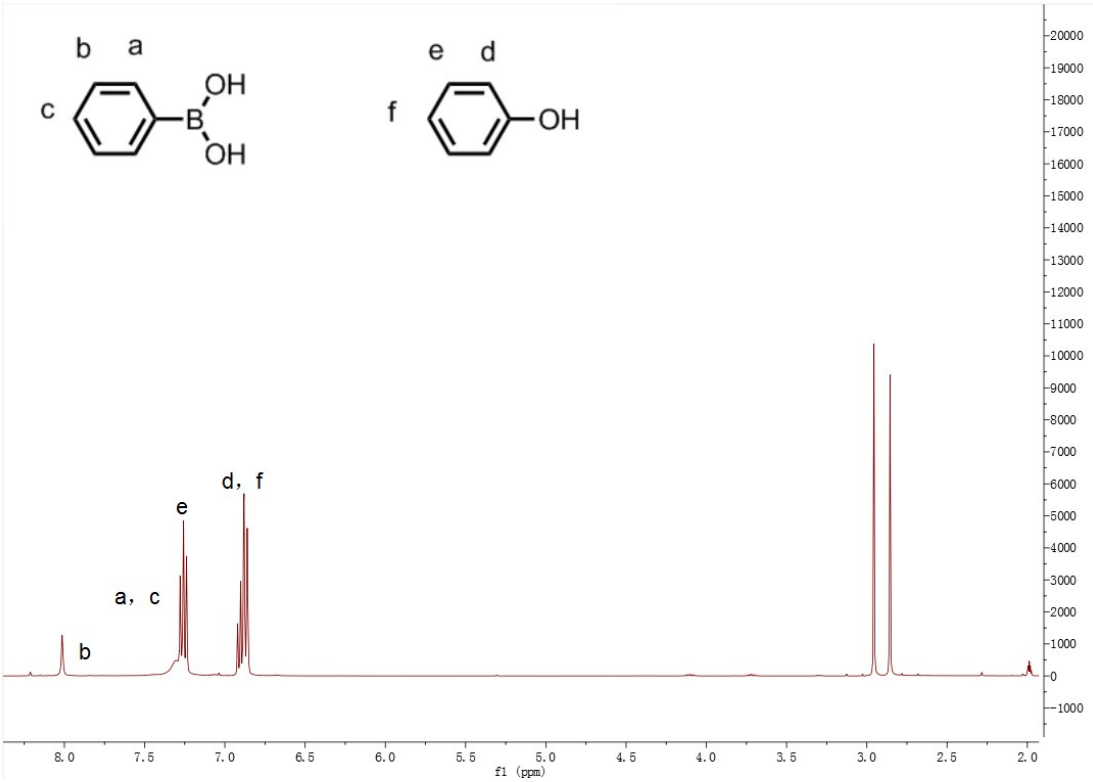
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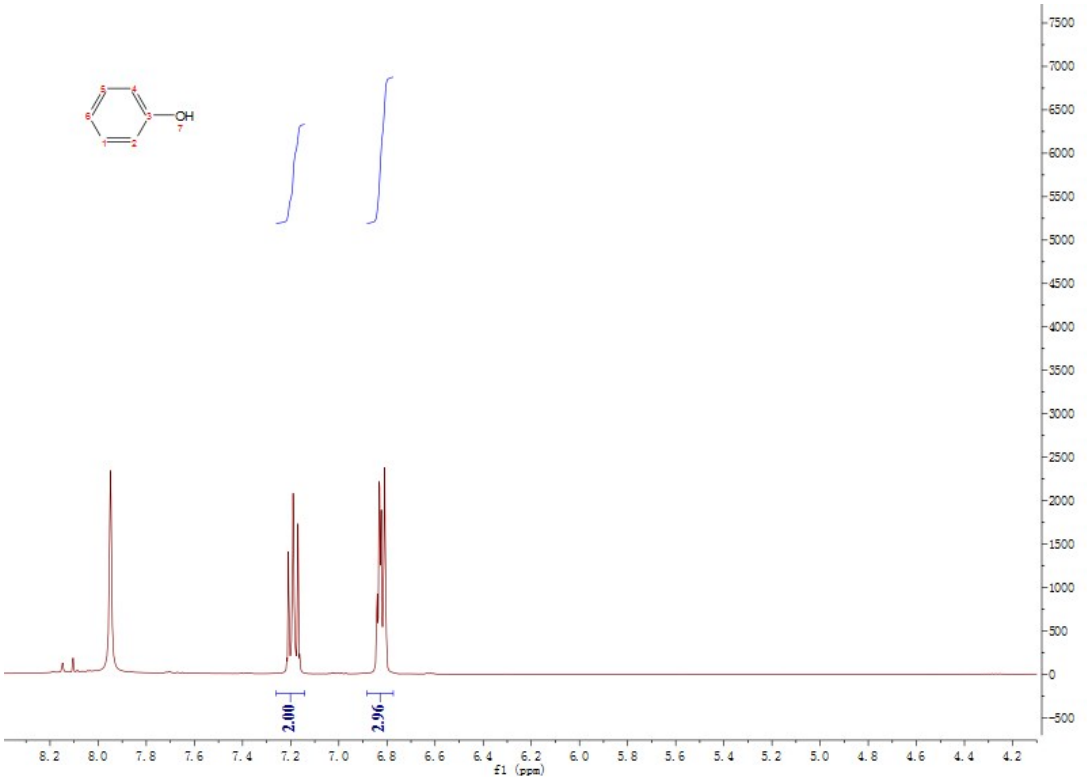
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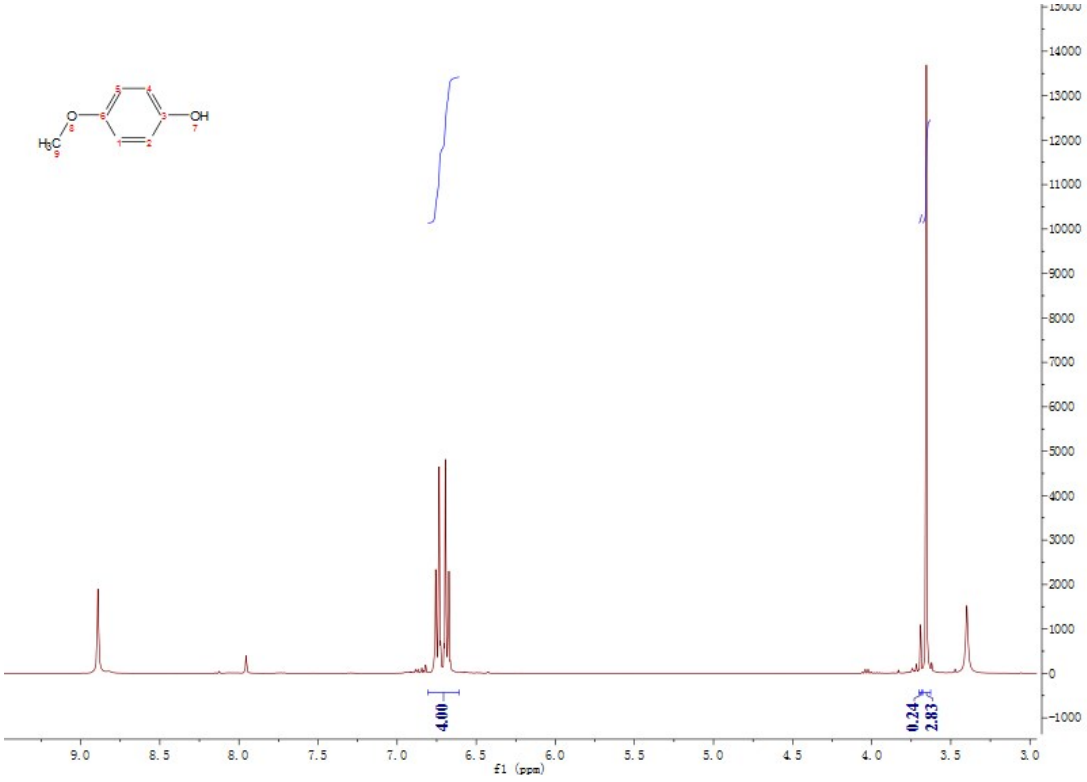
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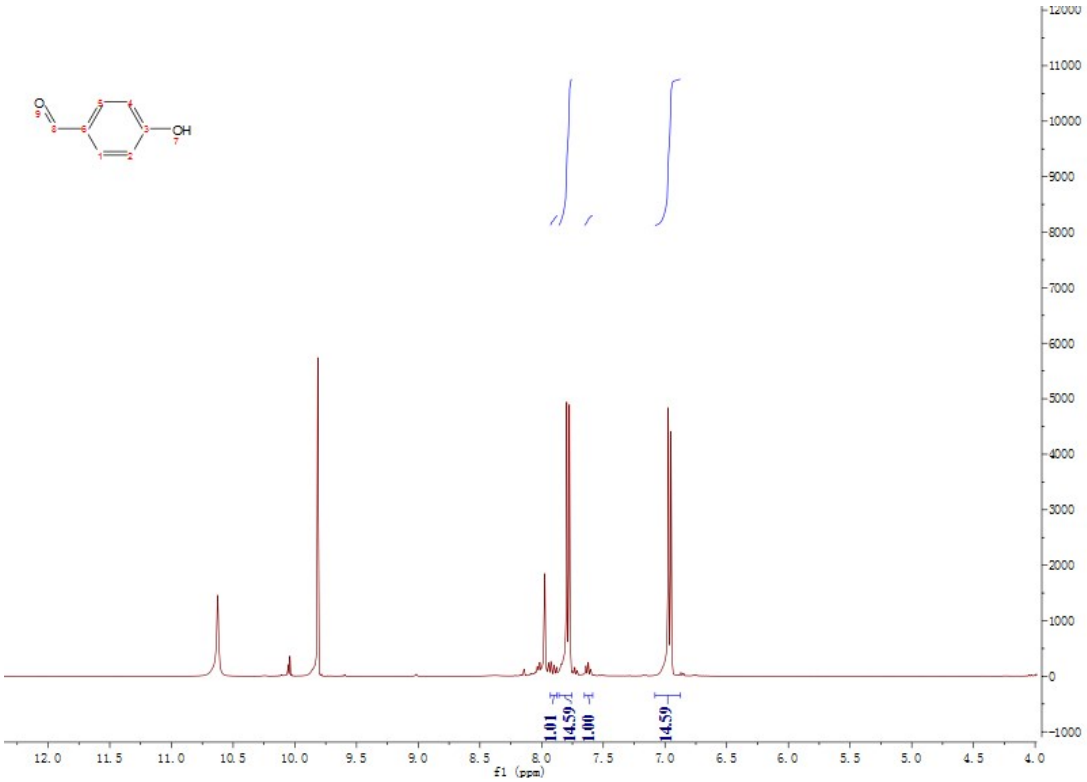
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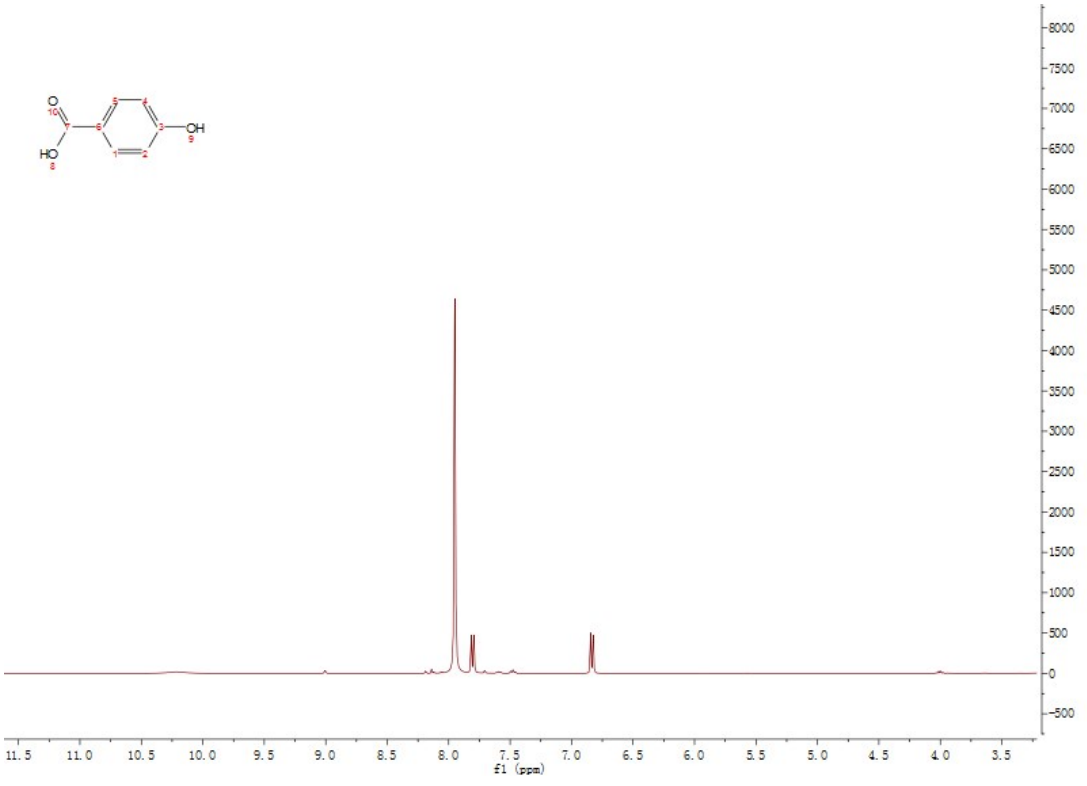
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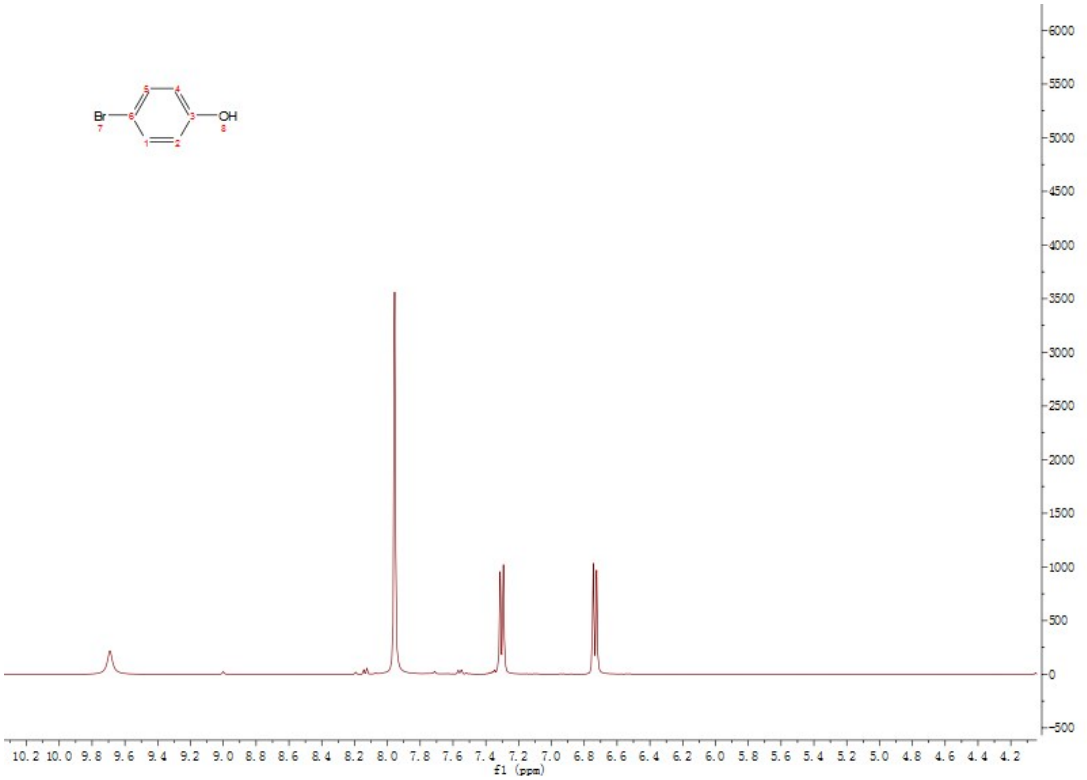
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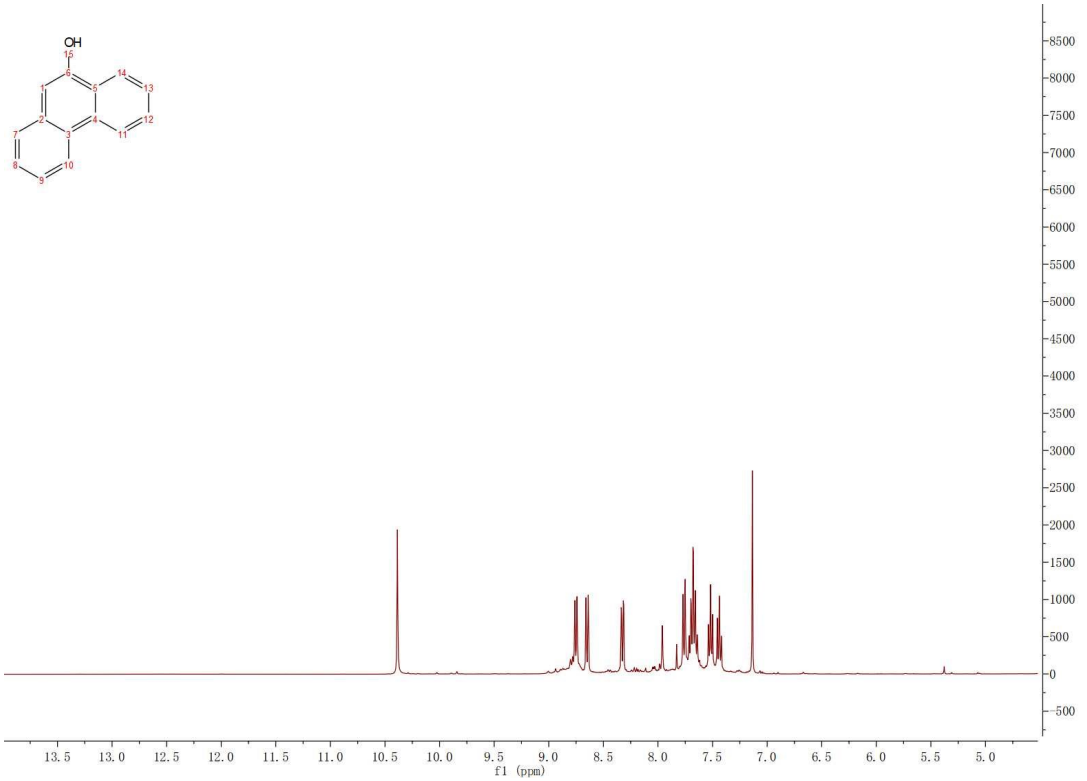
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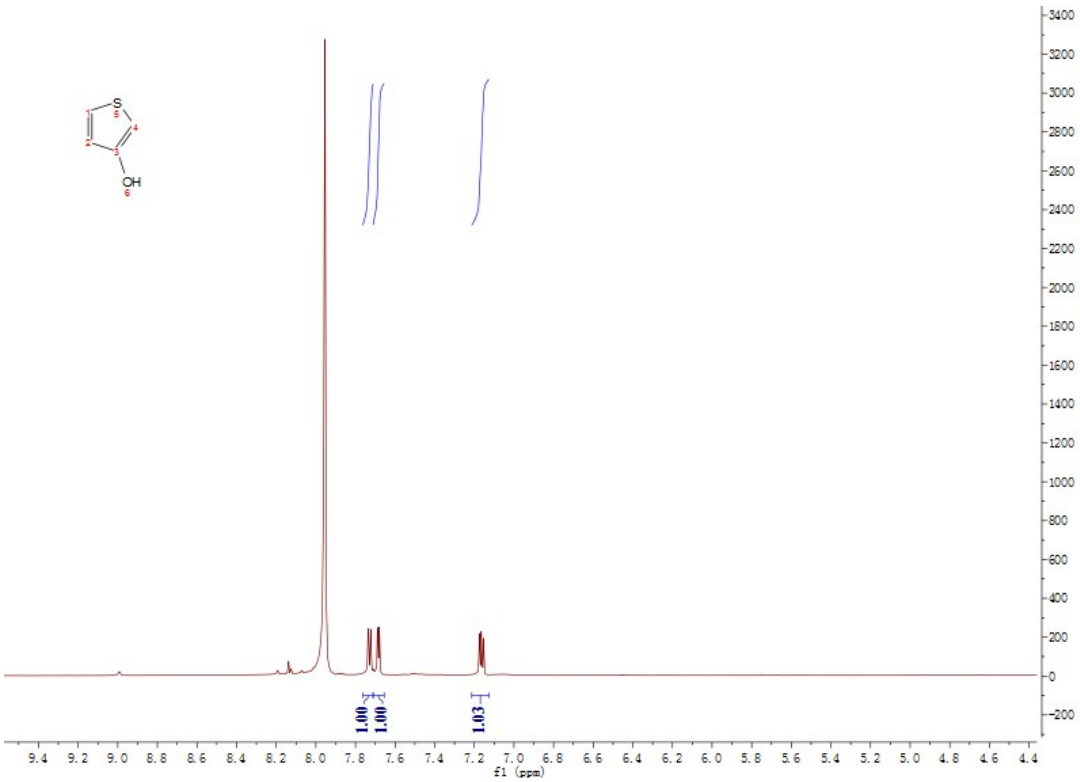

Section 10. Reference

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