Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information

Visible Light-Enabled Selective Depolymerization of Oxidized Lignin by an Organic Photocatalyst

*Shuyuan Li†, Zhongkai Hao†, Kaixuan Wang†, Min Tong, Yanan Yang, Huating Jiang, Yao Xiao, Fang Zhang**

The Education Ministry Key Lab of Resource Chemistry, Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, China

Corresponding author: zhangfang@shnu.edu.cn

Table of Contents

Table of Contents S-1
Experimental Procedures S-2
Chemicals S-2
Preparation of perylene diimide (PDI) organic photocatalyst S-2
Photocatalytic Depolymerization Experiments. S-2
Depolymerization of oxidized Lignin model compounds S-2
Depolymerization of oxidized Lignin model compounds and organosolv Lignin in flow reactor S-2
Extraction of Lignin S-3
Lignin Oxidation S-3
Characterization S-3
Further Optimization Studies S-4
NMR spectra of the compounds S-14

Experimental Procedures

Chemicals. 3,4,9,10-Perylenetetracarboxylic dianhydride, 2,6-Diisopropylaniline and imidazole were purchased from Sigma-Aldrich company. Acetonitrile, hydrochloric acid and nitric acid were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai. N, N-Diisopropylethylamine (DIPEA), formic acid and 1,3,5-trimethylbenzene were purchased from Aladdin Company. Formic acid-d_2 (DCOOD) and Acetonitrile-d_3 (CD_3CN) were purchased from Acros Company. The chemical reagents were directly used for the experiments without any further purification. Different lignin models and organosolv lignin were synthesized according to the literature.[3, 20]

Preparation of perylene diimide (PDI) organic photocatalyst. 3,4,9,10-Perylenetetracarboxylic dianhydride (1.0 g), 2,6-Diisopropylaniline (2.0 mL) and imidazole (7.5 g) were mixed and then was heated to 190°C for 24 h. After cooling to room temperature, 50 mL ethanol and 60 mL 2.0 mol/L HCl were successively added into the flask and stirred for another 3.0 h. The precipitate was washed by 100 ml ethanol/HCl (2.0 mol/L) and water for three times, respectively, and subsequently was dried at 80°C in vacuum for 12 h. The final photocatalyst was obtained by silica column chromatography as a red solid. (see 1H NMR spectrum in Supporting Information). 1H NMR (400 MHz, $CDCl_3$) : δ 8.80 (d, J = 8.0 Hz, 4H), 8.75 (d, J = 8.1 Hz, 4H), 7.55-7.47 (m, 2H), 7.36 (d, J = 7.8 Hz, 4H), 2.76 (hept, J = 6.7 Hz, 4H), 1.19 (d, J = 6.8 Hz, 24H)

Photocatalytic Depolymerization Experiments.

Depolymerization of oxidized Lignin model compounds. A 10 mL round-bottomed flask was charged with 0.50 mmol lignin model compound, 2.5 mmol% of catalyst PDI and 5.0 mL CH_3CN. It was filled with nitrogen gas, and then 9.0 equivalents of DIPEA and HCOOH were injected by using disposable needle. After irradiated by Xenon lamp (>420 nm) as the visible light source at 25°C for 8.0 h, the products were extracted with methanol, followed by analysis on HPLC (Agilent HPLC 1260) equipped with an ZORBAX Eclipse XDB-C18 column (4.6×250mm 5-Micron) with toluene as the internal standard. The reproducibility is checked by repeating each result at least three times and is found to be within ±5%.

Depolymerization of oxidized Lignin model compounds and organosolv Lignin in flow reactor. The home-made photocatalytic continuous flow reactor was assembled by a Corning Advanced Flow Micro-reactor with five pieces of square glass panels (1.0 mm internal diameter, 0.45 mL internal volume), 6×4 W blue light-emitting diodes light source and a high pressure peristaltic micro-pump (TAUTO TBP-1002T). In a typical run, the reaction mixture (containing a certain amount of the lignin model or organosolv lignin, PDI, DIPEA and HCO_2H) was prepared in a 50 ml glass vial, sparged with N_2 for 30 min, shielded from lights with aluminum foil and then pumped into the photoreactor using a peristaltic pump at a settled flow rate. The reaction mixture from the photochemical reactor output was collected in a shielded glass vial and concentrated in vacuo. The depolymerization rate was obtained by HPLC analysis and the depolymerization products were determined by GC-MS analysis.

Extraction of Lignin. To birch sawdust (20 g) was added 1,4-dioxane (144 mL) followed by 2N HCl (16 mL) and the mixture was heated to a gentle reflux under a N_2 atmosphere for 1 h. The mixture was then allowed to cool and the lignin containing liquor was collected by filtration. The collected liquor was partially concentrated in vacuo to give a gummy residue which was taken up in acetone/water (V:V=9:1, 250 mL) and precipitated by addition to rapidly stirring water (250 mL). The crude lignin was collected by filtration and dried under vacuum. The dried crude lignin was taken up in acetone/methanol (V:V=9:1) and precipitated by dropwise addition to rapidly stirring Et_2O (200 mL). The precipitated lignin was collected by filtration and dried under vacuum to give a purified birch lignin. This lignin was used in subsequent experiments without further processing.

Lignin Oxidation. To a solution of lignin (0.5 g) in 2-methoxyethanol (2.8 mL) and 1,2-dimethoxyethane (4.2 mL) solution was added 50 mg of DDQ followed by 22 mg of tBuONO. The reaction mixture was placed under an O_2 atmosphere (balloon) and stirred at 80 ^{o}C for 14 h. The oxidized lignin was isolated by precipitation in Et_2O (70 mL) and filtering, dried under vacuum to give an oxidized birch lignin.

Characterization. UV-Vis spectra were measured on a Shimadzu UV 2600 spectrometer. Fluorescence spectra were collected on a FLS920 fluorescence spectrophotometer. NMR spectra were acquired on a Bruker Ascend 400 MHz spectrometer equipped with a cryogenically cooled 5-mm TCI gradient probe with inverse geometry. The ^{13}C-^{1}H correlation (HSQC) experiments were adiabatic experiments and were carried out using the following parameters: acquired from 11 to 0 ppm in F2 (1H) with 1098 data points (acquisition time 100 ms), 210 to 0 ppm in F1 (^{13}C) with 420 increments (F1 acquisition time 8 ms) of 72 scans with a 0.5 s interscan delay; the d24 delay was set to 0.89 ms (1/8J, J = 145 Hz). The total acquisition time for a sample was 5.0 h. Processing used typical matched Gaussian apodization (GB = 0.001, LB = -0.3) in F2 and squared cosinebell and one level of linear prediction (32 coefficients) in F1. The GC/MS system consisted of an Agilent GC 7900 with the quadrupole-Orbitrap mass spectrometer. Electron impact ionization was used for all analyses. The oven was held at 80^{o}C for 1.0 min and then increased to 300^{o}C at 20^{o}C/min after a 0.50 μL splitless injection of sample diluted in chloroform. Text Paragraph.

Further Optimization Studies

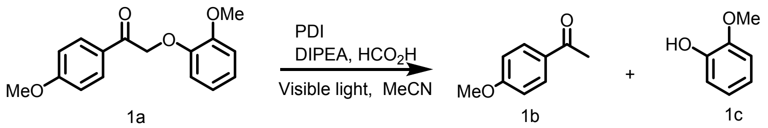
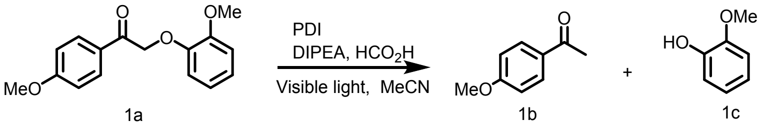


Table S1. Depolymerization performances of (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) by using different amounts and types of base and hydrogen source.[a]

Entry	Base	Doses of base (equiv.)	Hydrogen source	Doses of hydrogen source (equiv.)	Conversion (%)	Yield 1b (%)	Yield 1c (%)
1	TEA	2.0	HCOOH	2.0	10	8.3	0.69
2	DIPEA	2.0	Hantzsch ester	2.0	26	25	14
3	DIPEA	2.0	HCOOH	2.0	28	24	20
4	DIPEA	3.0	HCOOH	3.0	29	26	25
5	DIPEA	6.0	HCOOH	3.0	31	29	29
6	DIPEA	3.0	HCOOH	6.0	33	30	27
7	DIPEA	6.0	HCOOH	6.0	57	50	53
8*	DIPEA	6.0	HCOOH	6.0	trace	trace	trace
9	DIPEA	9.0	HCOOH	6.0	69	57	59
10	DIPEA	9.0	HCOOH	9.0	>99	99	99

[a] Reaction conditions: model molecule (0.50 mmol), PDI (5.0 mol%), MeCN (5.0 mL), Xenon lamp (>420 nm), 25°C, N_2, 10 h, * no light.

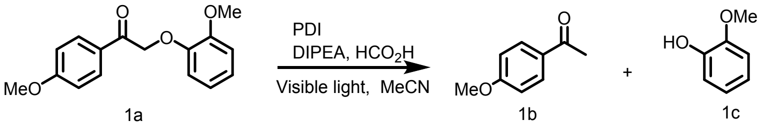
Table S2. Depolymerization performances of (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) under different time by using organocatalyst PDI. [a]



Entry	Time (h)	PDI (mol%)	DIPEA (equiv.)	HCO_2H (equiv.)	Conversion (%)	Yield 1b (%)	Yield 1c (%)
1	1	2.5	9.0	9.0	8.4	7.0	7.3
2	2	2.5	9.0	9.0	24	21	21
3	3	2.5	9.0	9.0	44	40	40
4	4	2.5	9.0	9.0	60	58	59
5	5	2.5	9.0	9.0	77	73	74
6	6	2.5	9.0	9.0	89	87	88
7	7	2.5	9.0	9.0	97	95	95
8	8	2.5	9.0	9.0	>99	99	99

[a] Reaction conditions: model molecule (0.50 mmol), MeCN (5.0 mL), Xenon lamp (>420 nm), 25°C, N_2.

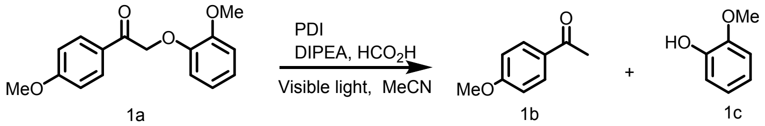
Table S3. Depolymerization performances of oxidized β-O-4 model molecule (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) with different flow rates. [a]



Entry	Flow rates (mL/min)	Time (min)	Conversion (%)	Yield 1b (%)	Yield 1c (%)
1	0.5	55	69	66	66
2	1.0	55	81	77	79
3	6	55	76	71	65
4	8	55	72	69	63
5	10	55	71	67	69

[a] Reaction conditions: model molecule (3.0 mmol), PDI (2.50 mol%), HCOOH (9.0 equiv.), DIPEA (9.0 equiv.), MeCN (30 mL), Blue LEDs, 25°C, N_2.

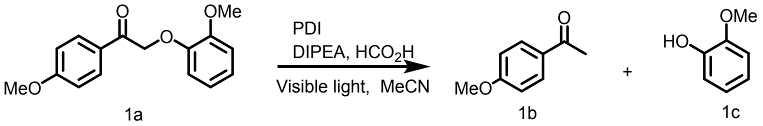
Table S4. Depolymerization performances of oxidized β-O-4 model molecule (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) with different amounts of PDI.[a]



Entry	Dose of PDI	Time (min)	Conversion (%)	Yield 1b (%)	Yield 1c (%)
1	1.25	55	89	84	86
2	2.50	55	81	77	79
3	3.50	55	64	42	61
4	5.00	55	55	37	45

[a] Reaction conditions: model molecule (3.0 mmol), 1.0 mL/min, HCOOH (9.0 equiv.), DIPEA (9.0 equiv.), MeCN (30 mL), Blue LEDs, 25°C, N_2.

Table S5. Depolymerization performances of oxidized β-O-4 model molecule (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) with different amounts of the additives of HCOOH and DIPEA. [a]



Entry	Time (min)	DIPEA (equiv.)	HCO_2H (equiv.)	Conversion (%)	Yield 1b (%)	Yield 1c (%)
1	55	6.0	6.0	>99	98	97
2	55	6.0	9.0	85	73	78
3	55	9.0	9.0	89	84	86

[a] Reaction conditions: model molecule (3.0 mmol), MeCN (30 mL), 1.0 mL/min, PDI (1.25 mol%), Blue LEDs, 25°C, N_2.

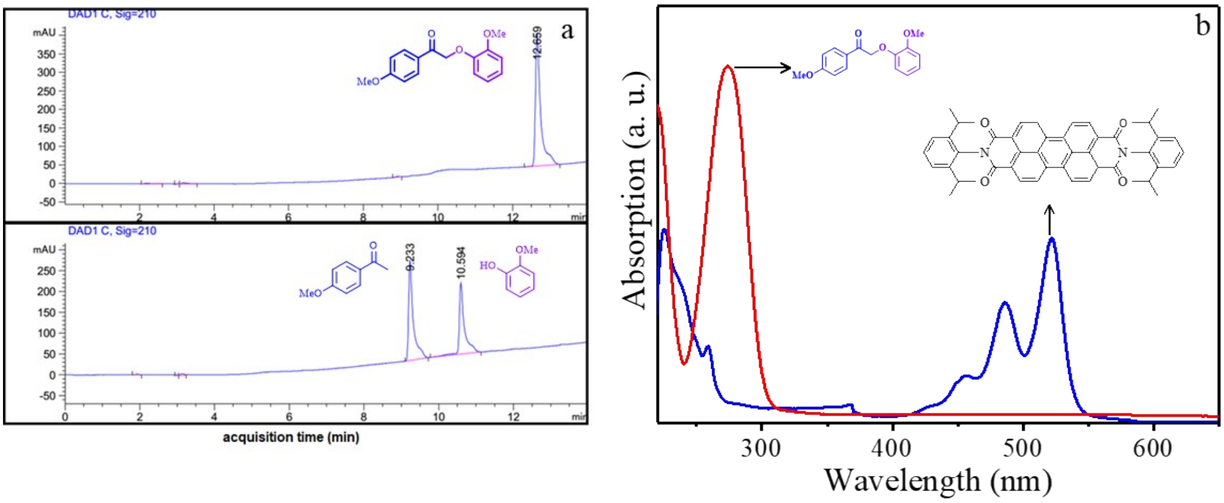


Figure S1. HPLC spectra of model molecule and depolymerization products (a), UV-Vis spectra of PDI and model molecule (b).

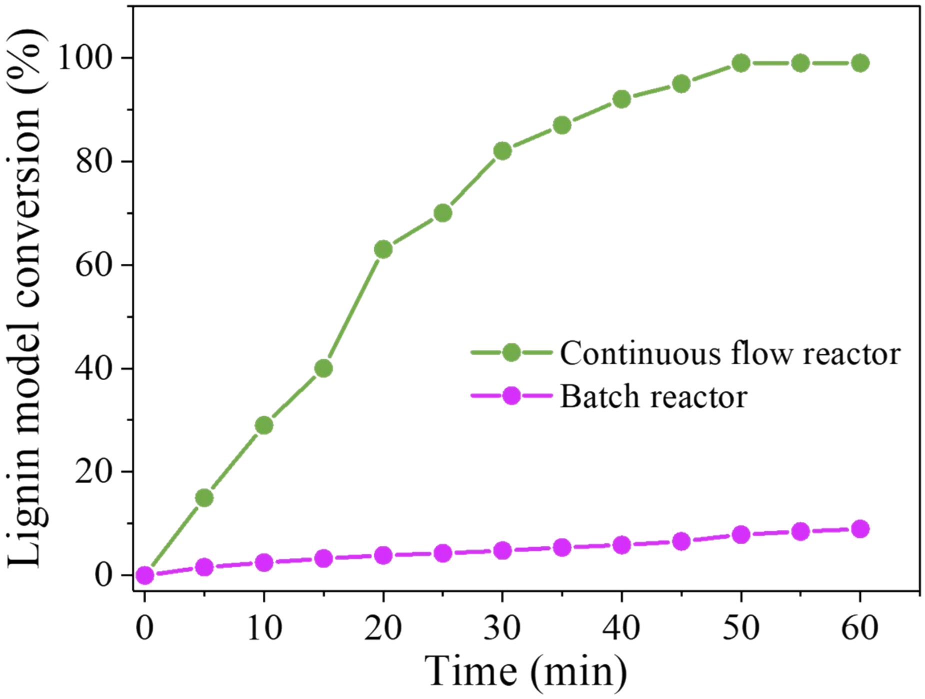


Figure S2. Time profile of the depolymerization performances of oxidized β-O-4 model molecule (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) with different photocatalytic reactor.

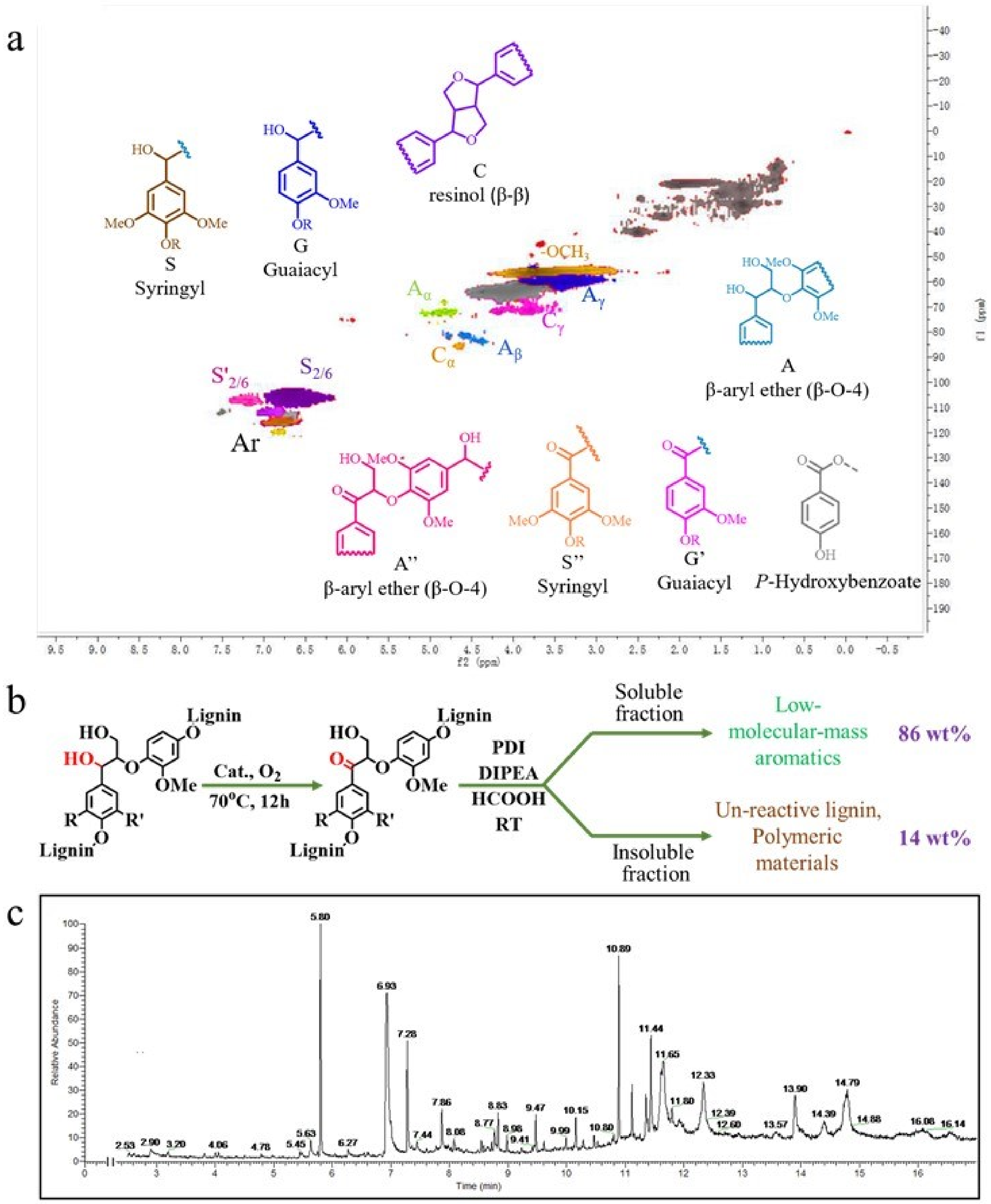


Figure S3. 2D HSQC NMR spectra (in $CDCl_3$) of extracted lignin (a), Scheme of PDI photocatalytic depolymerization of authentic lignin (b), GC-MS spectra of the depolymerization products (c).

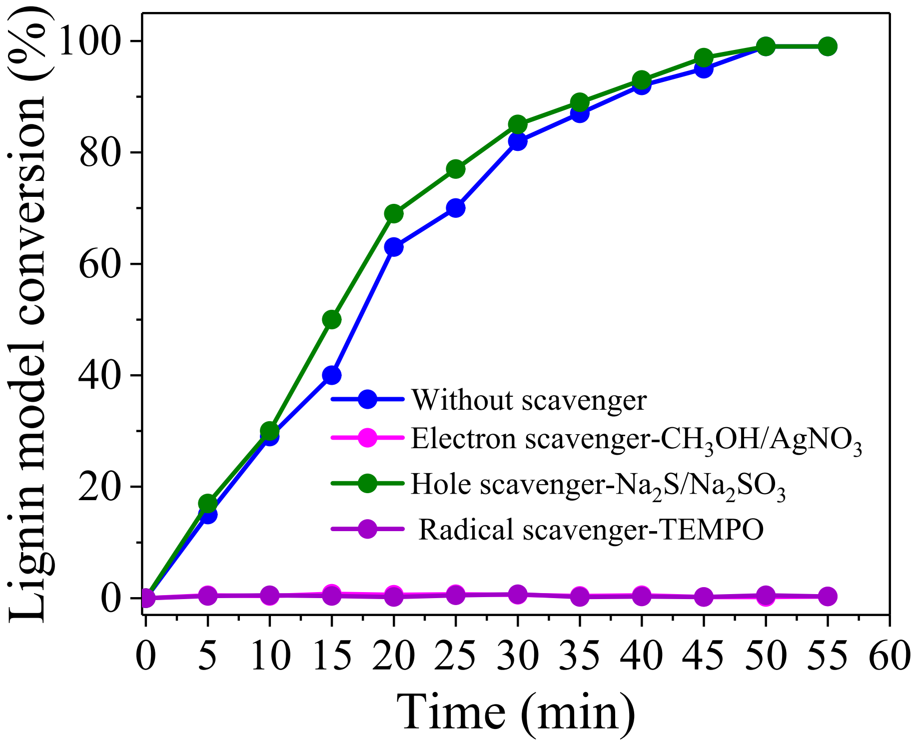


Figure S4. Time profile of the depolymerization rate of oxi-dized β-O-4 model molecule by using PDI catalyst with different scavengers.

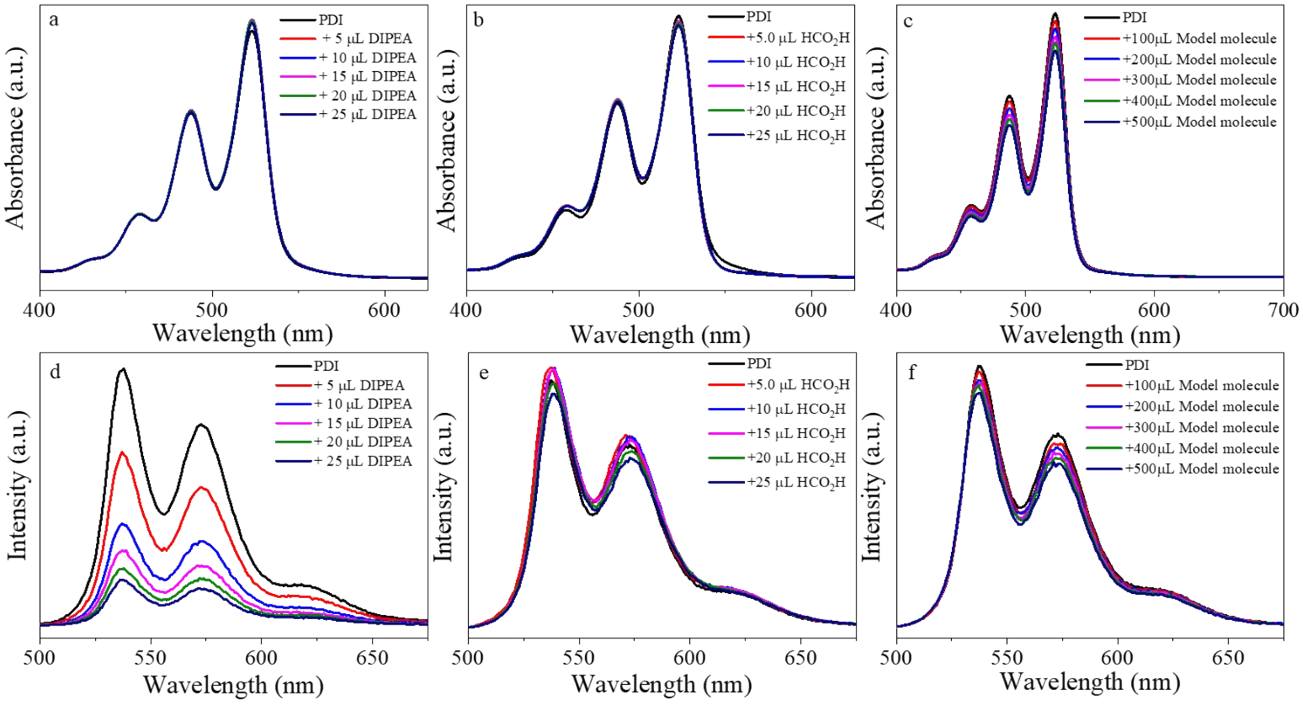


Figure S5. UV-Vis (a-c) and fluorescence (d-f) spectral of PDI with different additives. (DIPEA: N, N-Diisopropylethylamine, Model molecule: (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone)).

NMR spectra of the compounds

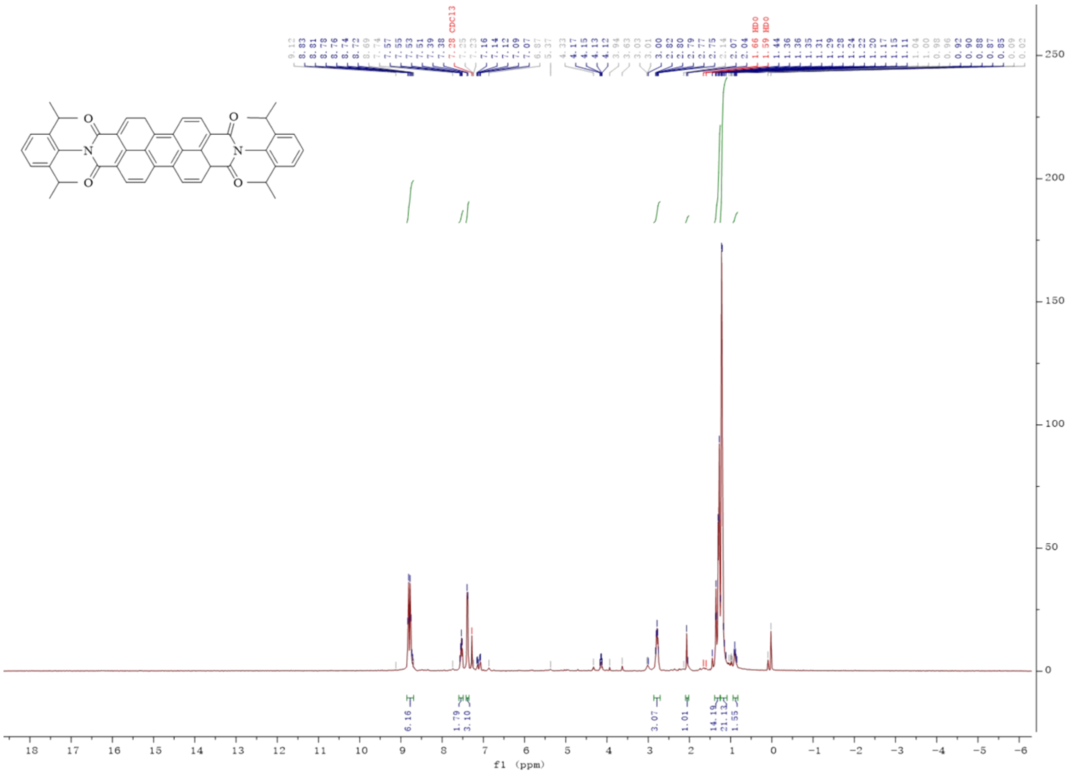


Figure S6. ^{1}H NMR spectra of PDI

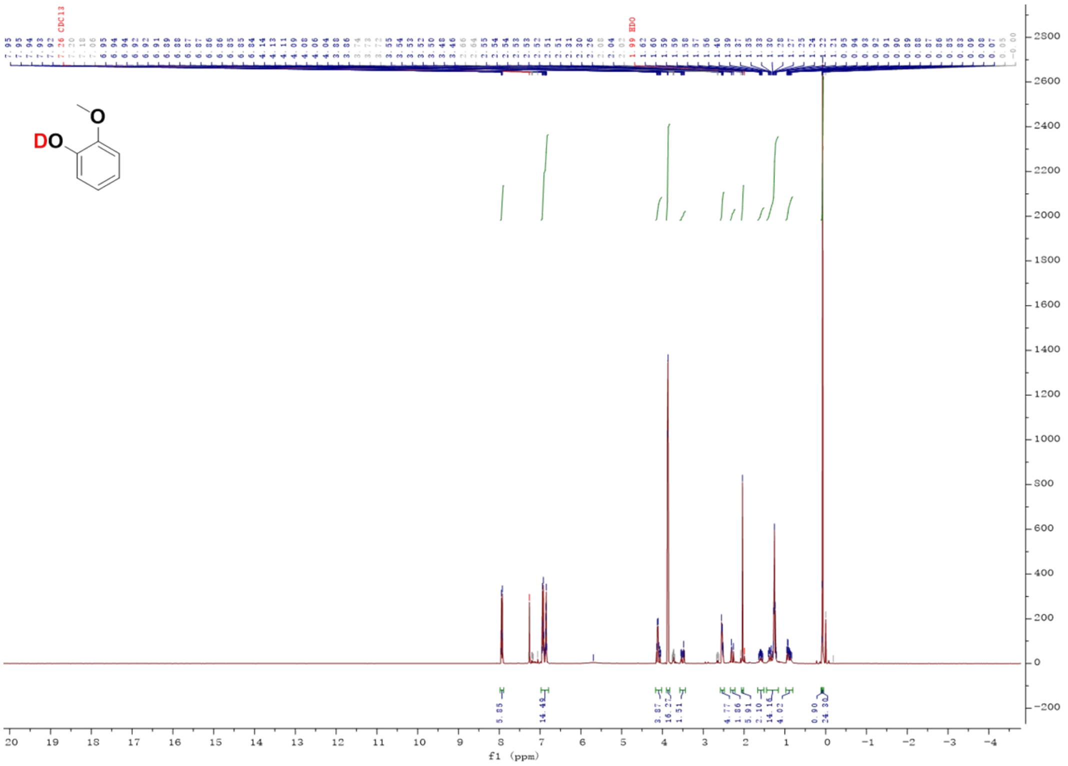


Figure S7. ^{1}H NMR spectra of duterium guaiacol.

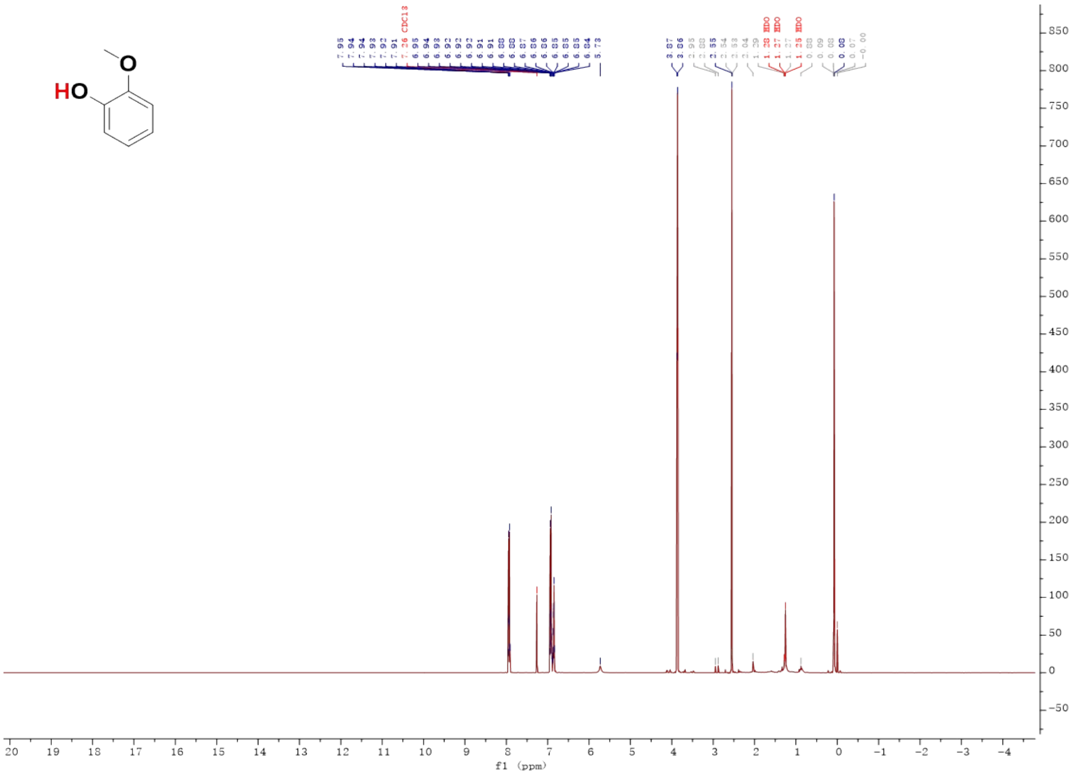


Figure S8. ^{1}H NMR spectra of guaiacol.

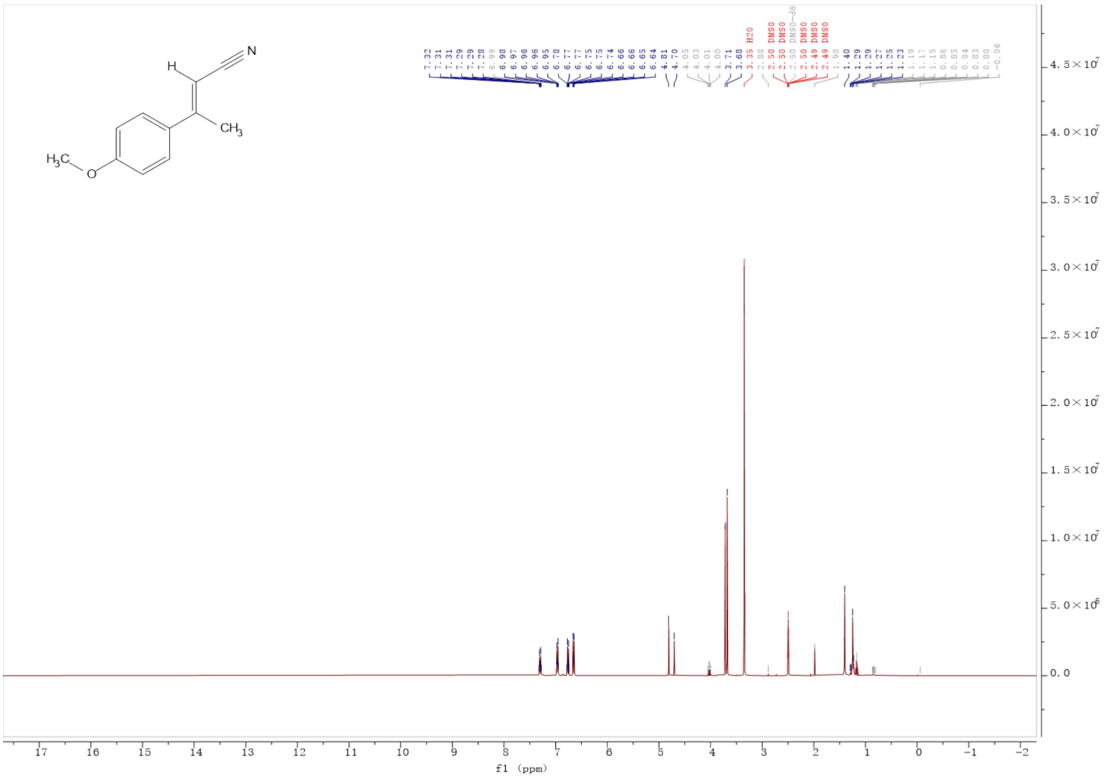
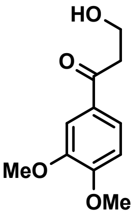
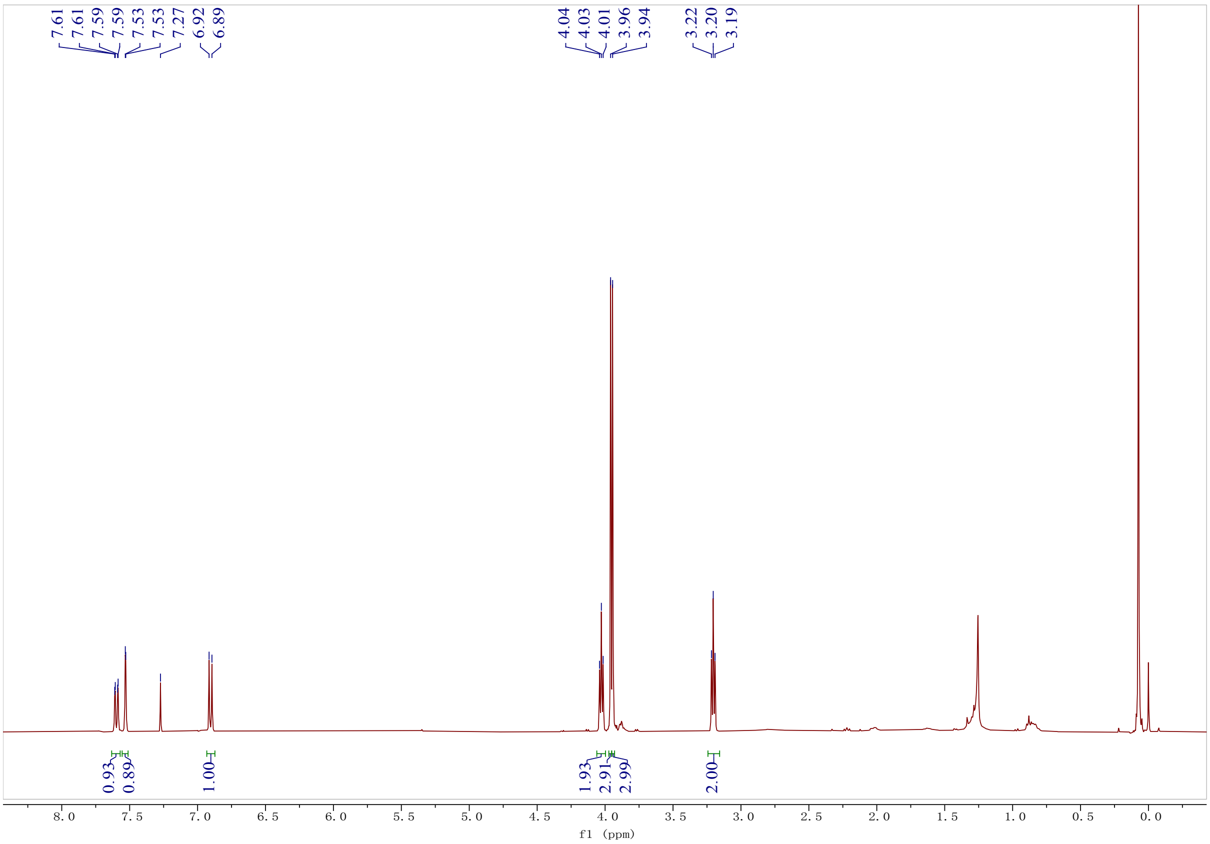
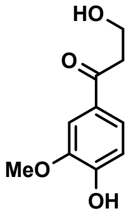


Figure S9. ^{1}H NMR spectra of α, β-unsaturated nitrile.

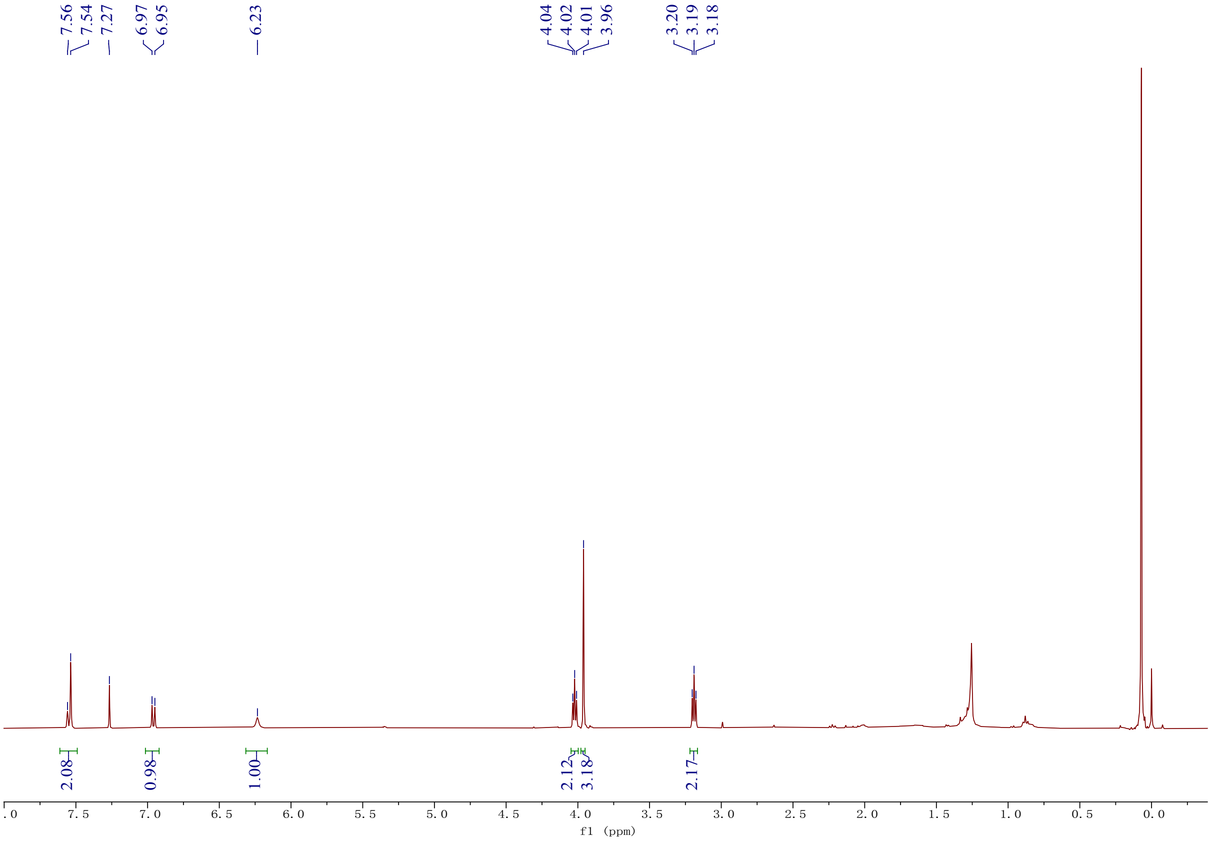


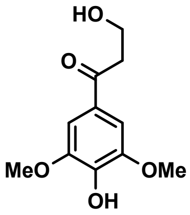
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53 (d, *J* = 1.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.03 (t, *J* = 5.3 Hz, 2H), 3.96 (s, 3H), 3.94 (s, 3H), 3.20 (t, *J* = 5.3 Hz, 2H).



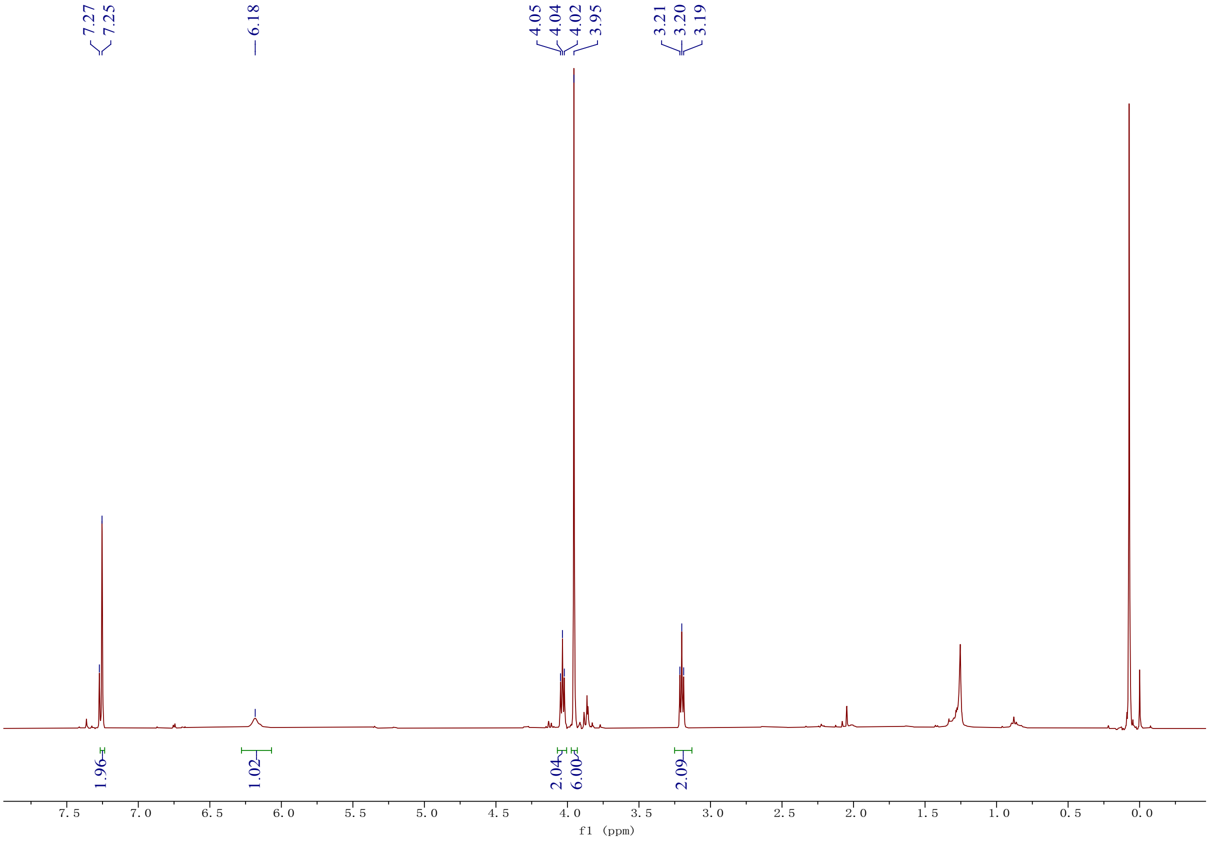


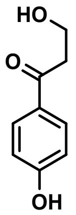
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 – 7.51 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.23 (brs, 1H), 4.02 (t, *J* = 5.3 Hz, 2H), 3.96 (s, 3H), 3.19 (t, *J* = 5.3 Hz, 2H).





^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (s, 2H), 6.18 (brs, 1H), 4.04 (t, J = 5.3 Hz, 2H), 3.95 (s, 6H), 3.20 (t, J = 5.3 Hz, 2H).





^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.35 (s, 1H), 4.02 (t, *J* = 5.3 Hz, 2H), 3.18 (t, *J* = 5.3 Hz, 2H).