Electronic Supplementary Information for

Covalent Triazine Frameworks Catalytically Oxidative Cleavage of Lignin Models and Organosolv Lignin

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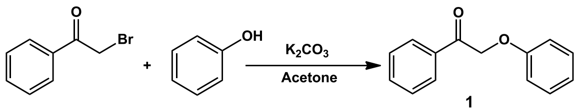
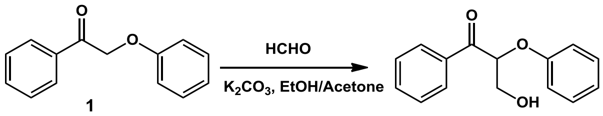
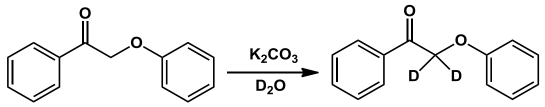


2-phenoxyacetophenone **1** was prepared by the literature procedures.[1] A 500 mL bottle was charged with phenol (6.9 g，73 mmol) and K_2CO_3 (10.4 g，75 mmol) in acetone (150 mL) and stirred at RT for 30 min. To this solution, 2-bromoacetophenone (14.0 g, 70 mmol) was added, the resulting suspension was stirred at RT for 24 h, after which the suspension was filtered and concentrated *in cacuo*. The solid was dissolved in ethyl acetate and washed with NaOH aqueous (5%, 30 ml) and water (30 ml). The organic phase was dried over anhydrous Na_2SO_4. The crude product was recrystallized from ethanol to give 2-phenoxyacetophenone as a white solid. Spectral data were in accordance with those previously reported. For the other methoxy substituted 2-phenoxyacetophenone, the preparation procedure was the same as described above except using different starting materials.



According to the literature.[2] A solution of 2-phenoxyacetophenone **1** (848.0 mg, 4.00 mmol) and HCHO (aqueous solution, 36 wt%, 0.6 mL, 7.3 mmol) in EtOH/acetone (1:1, 20 mL) was treated with K_2CO_3 (0.6 g, 4.3 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was then evaporated and the residue was diluted with ethyl acetate and washed with water and brine. The organic phase was concentrated and the resulting crude materials were purified by column chromatography with hexanes/EtOAc (15:1 to 1:1) to give the product.

Procedure for the synthesis of the deuterated compounds



According to the literature.[1] 2-phenoxyacetophenone (0.50 g 2.36 mmol) was added to a vial with anhydrous K_2CO_3 (0.126 g, 0.92 mmol) and 5 mL of D_2O. The vial was caped. The reaction ran at 100 °C for 24 h. The D_2O was decanted and replaced by fresh one. The reaction was maintained for additional 24 h at 100 °C. Then the solid was washed to remove the K_2CO_3 residues. Finally, the solid was dried under vacuum to give deuterated compounds as a light yellow solid.

Synthesis of ethylbenzene hydroperoxide

Ethylbenzene hydroperoxide was synthesized by thermal oxidation method. Typically, 30 mL ethylbenzene was added into a 100 mL Teflon insert reactor. Then the reactor was charged with 0.8 MPa of O_2 and heated to 130 ^{o}C kept for 3 h under magnetic stirring. When the reaction was complete, the reaction mixture first reacted with NaOH in water, leading to an aqueous solution of the peroxide sodium salt, which was neutralized by $NaHCO_3$ followed by extraction with n-hexane and acetonitrile.

Extraction of Lignin[3]

To birch sawdust (20 g) was added 1,4-dioxane (144 mL) followed by 2N HCl (16mL) 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 collect 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 Oxidations[3]

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 *t*BuONO. The reaction mixture was placed under an O_2 atmosphere (balloon) and stirred at 80 °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.

Catalytically oxidative cleavage of oxidized lignin

0.1g of oxidized lignin with 10 mL of methanol and 40 mg of CTF-pDCB-1 catalyst were added into a 60 mL Teflon insert reactor. Then the reactor was charged with 0.5 MPa of O_2 and heated to 180 ^{o}C kept for 8 h under magnetic stirring. After the reaction was complete, the reaction mixture was centrifuged, solid catalyst was washed several times with methanol and the liquid was all collected and evaporated. DMSO-*d6* and internal sample pyrazine was added to determine the 2D HSQC NMR spectrum.

1. M. Wang, L. H. Li, J. M. Lu, H. J. Li, X. C. Zhang, H. F. Liu, N. C. Luo and F. Wang, *Green Chem.*, 2017, **19**, 702-706.
2. J. Zhang, Y. Liu, S. Chiba and T. P. Loh, *Chem. Commun.*, 2013, **49**, 11439-11441.
3. C. S. Lancefield, O. S. Ojo, F. Tran and N. J. Westwood, *Angew. Chem., Int. Ed.*, 2015, **54**, 258-262.

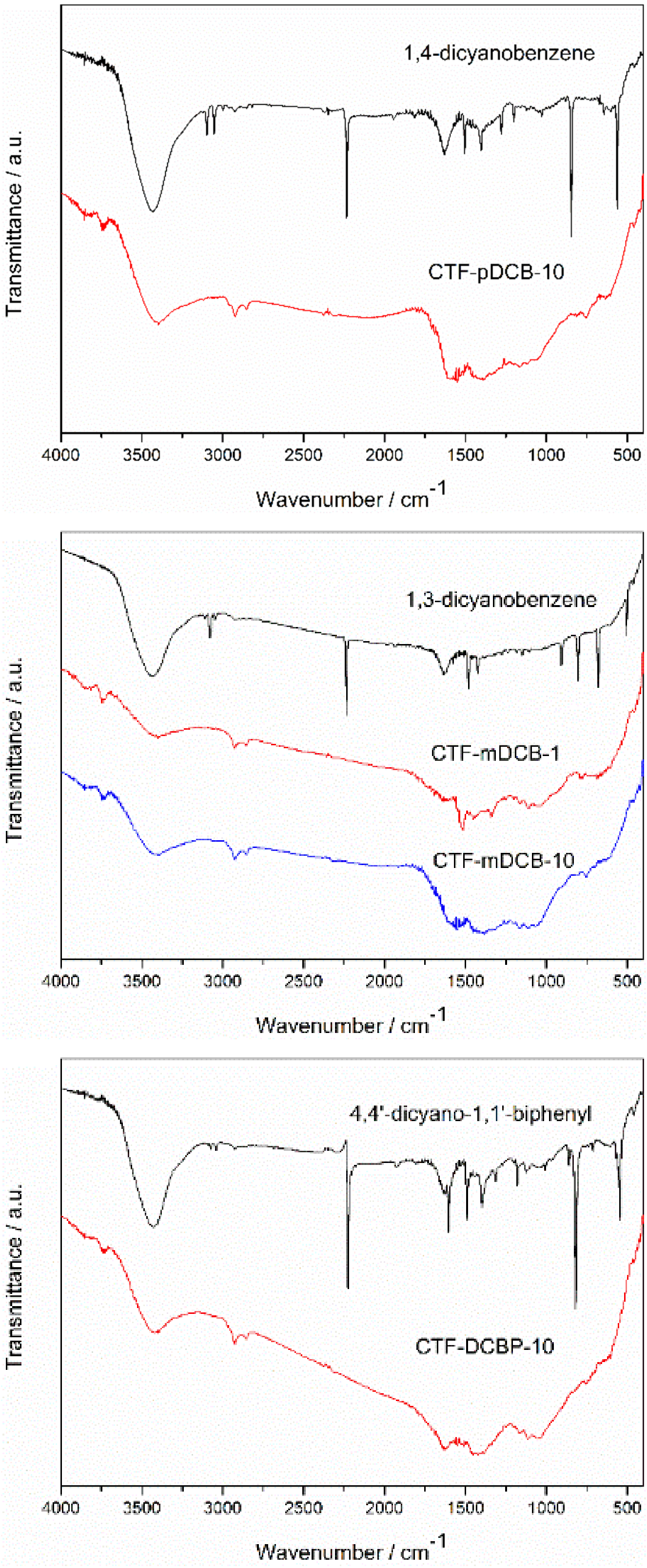


Fig. S1 FT-IR spectra of the monomers and the corresponding CTFs.

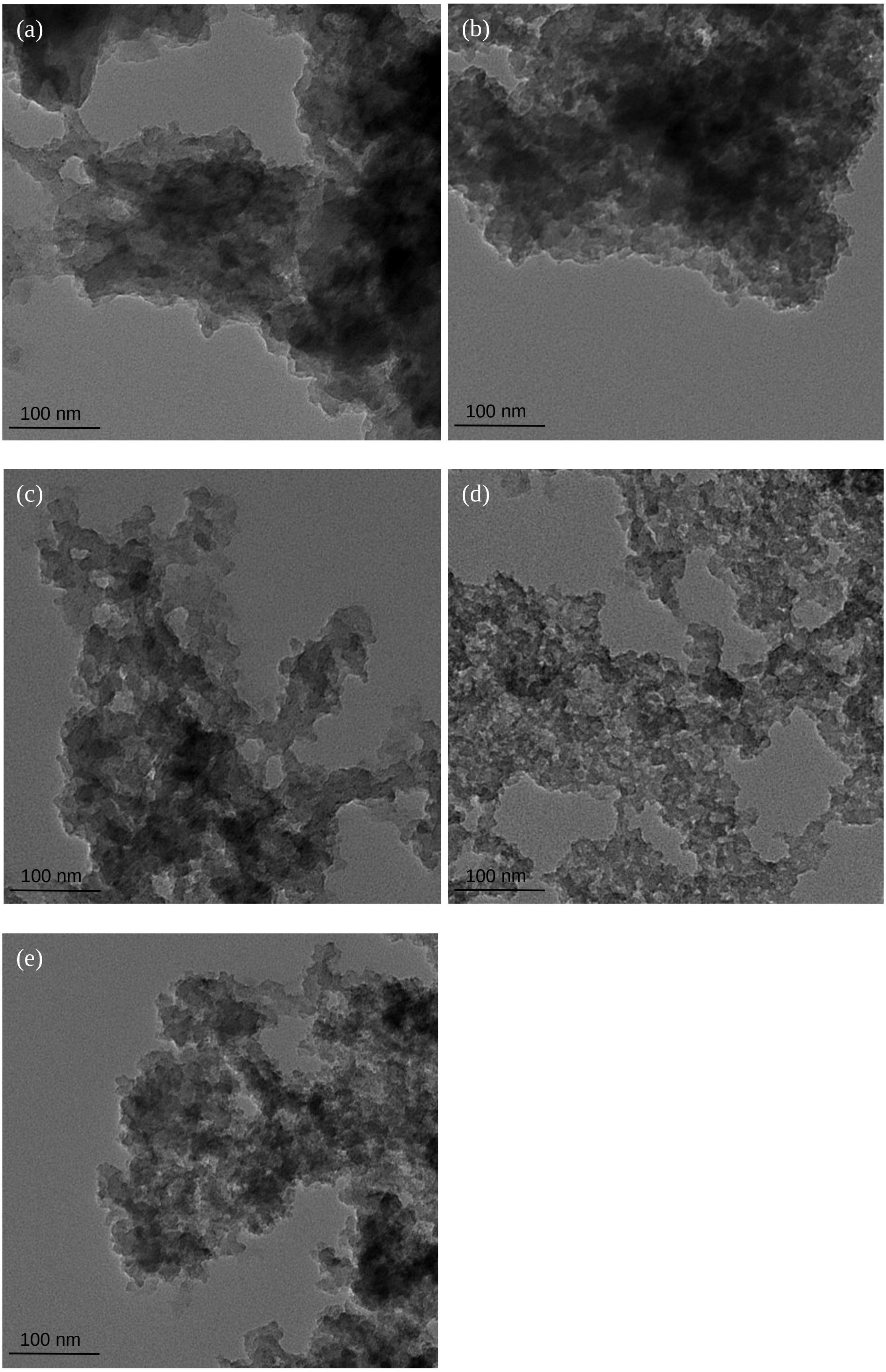


Fig. S2 TEM of (a) CTF-pDCB-1, (b) CTF-mDCB-1, (c) CTF-pDCB-10, (d) CTF-mDCB-10 and (e) CTF-DCBP-10.

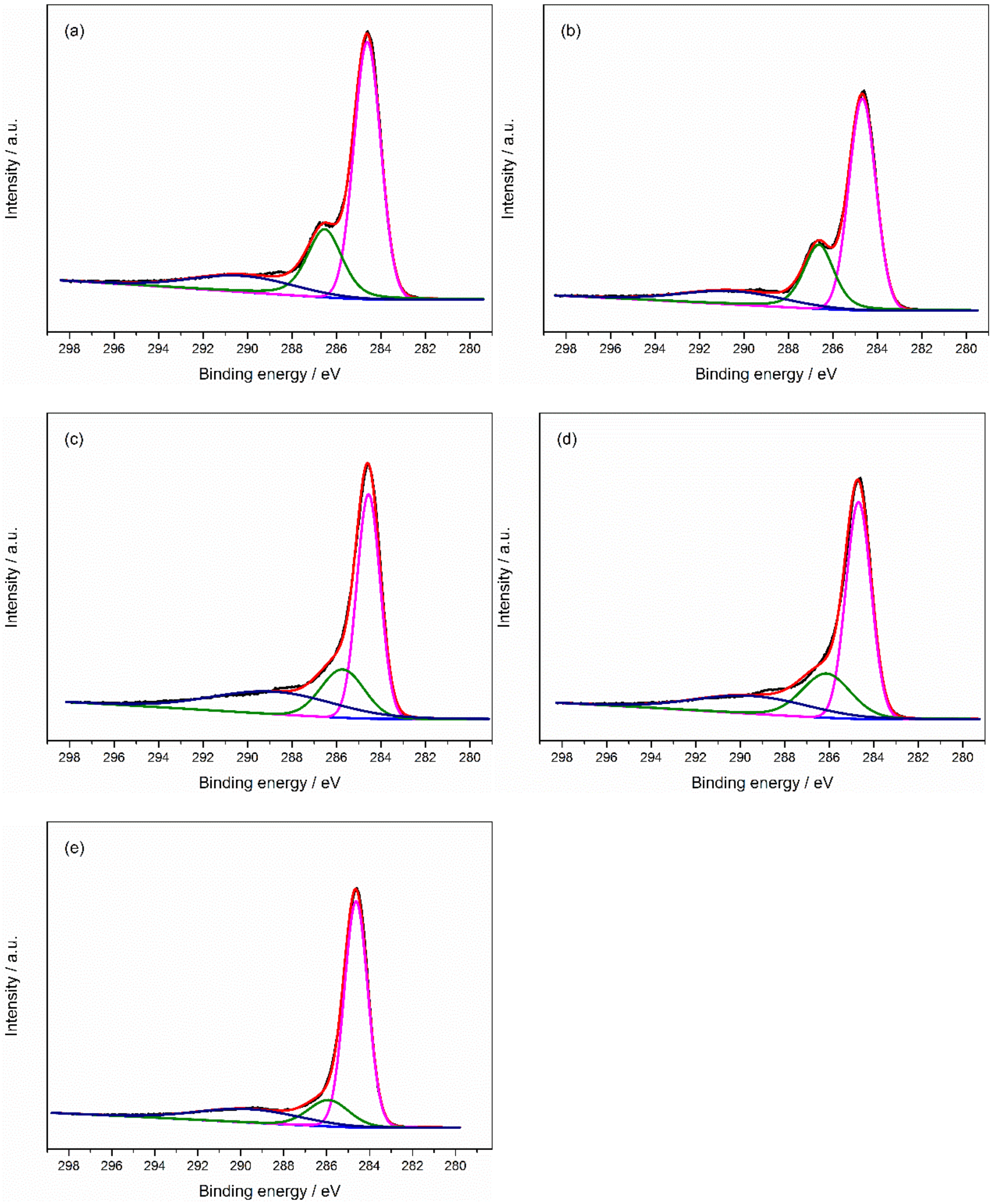


Fig. S3 C 1s peak of (a) CTF-pDCB-1, (b) CTF-mDCB-1, (c) CTF-pDCB-10, (d) CTF-mDCB-10 and (e) CTF-DCBP-10 at high resolution.

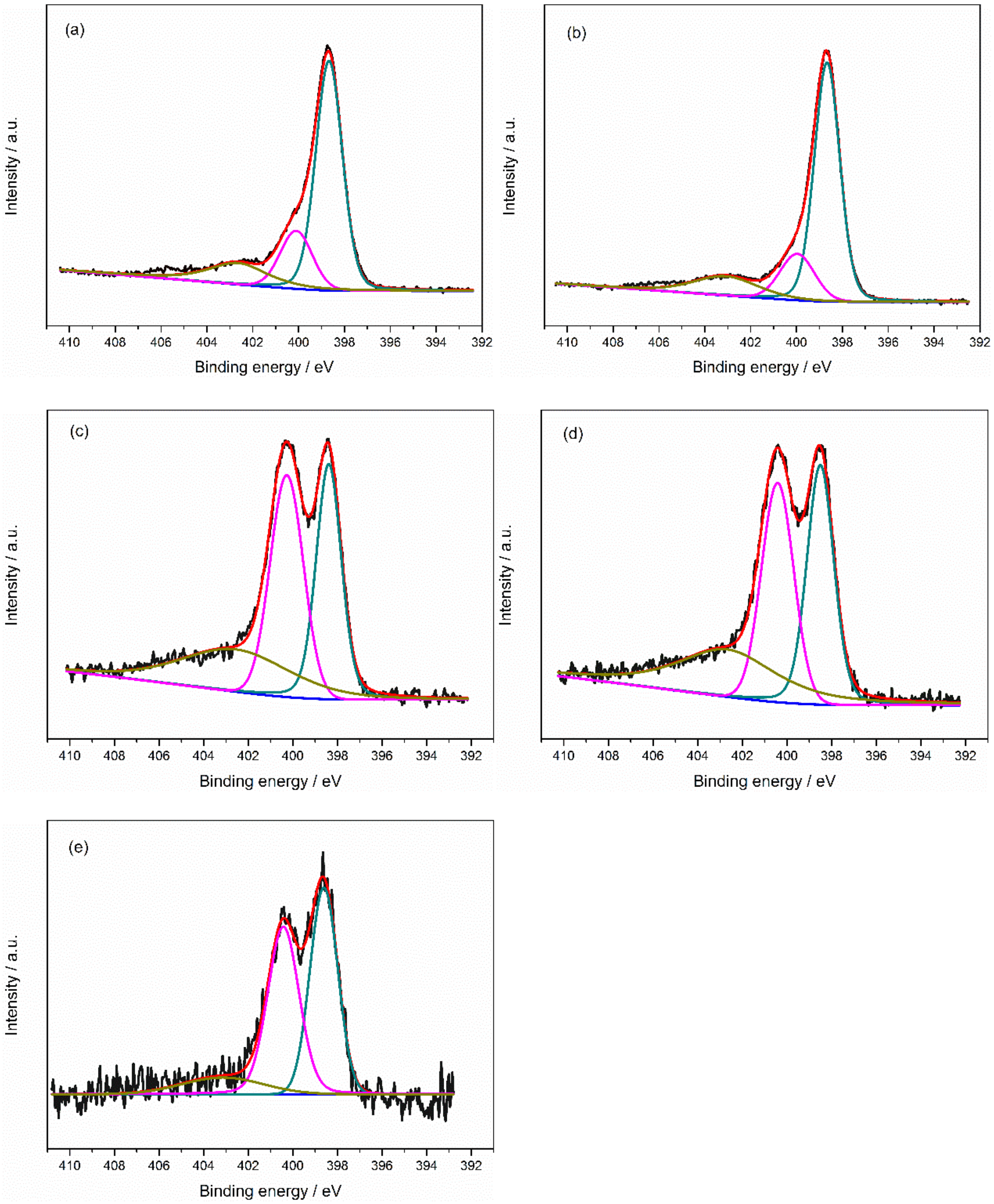


Fig. S4 N 1s peak of (a) CTF-pDCB-1, (b) CTF-mDCB-1, (c) CTF-pDCB-10, (d) CTF-mDCB-10 and (e) CTF-DCBP-10 at high resolution.

Table S1 The content of different types of C [a]

Entry	Sample	C-C (%)	C-N (%)	C-O (%)
1	CTF-pDCB-1	60.5	24.8	14.7
2	CTF-mDCB-1	60.4	24.9	14.7
3	CTF-pDCB-10	52.0	20.7	27.3
4	CTF-mDCB-10	55.6	23.4	21.0
5	CTF-DCBP-10	68.2	14.4	17.4

[a] Determined by XPS.

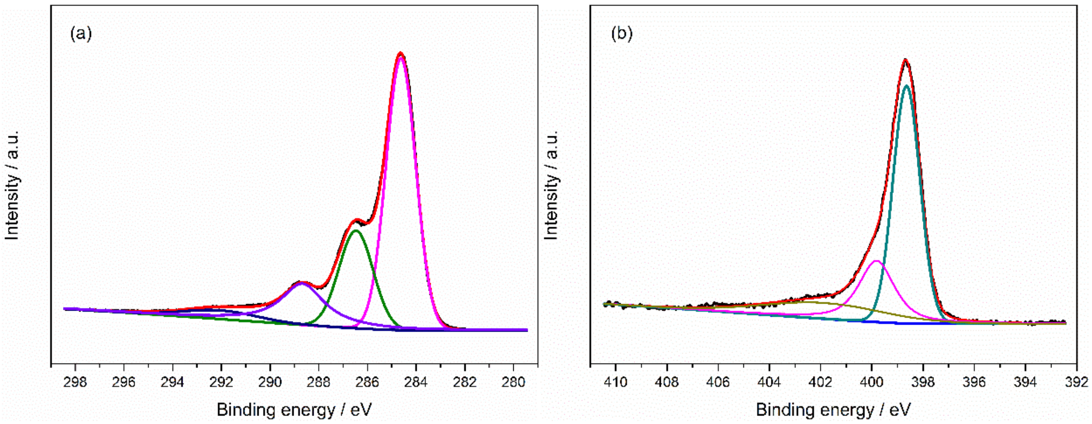
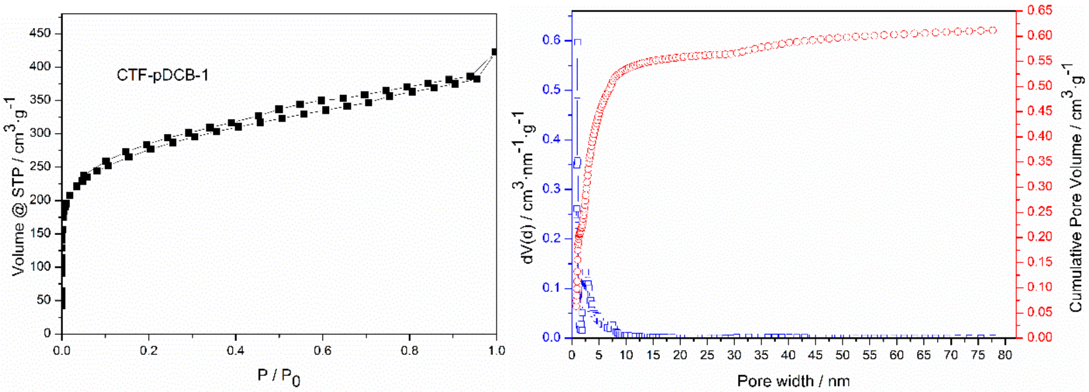
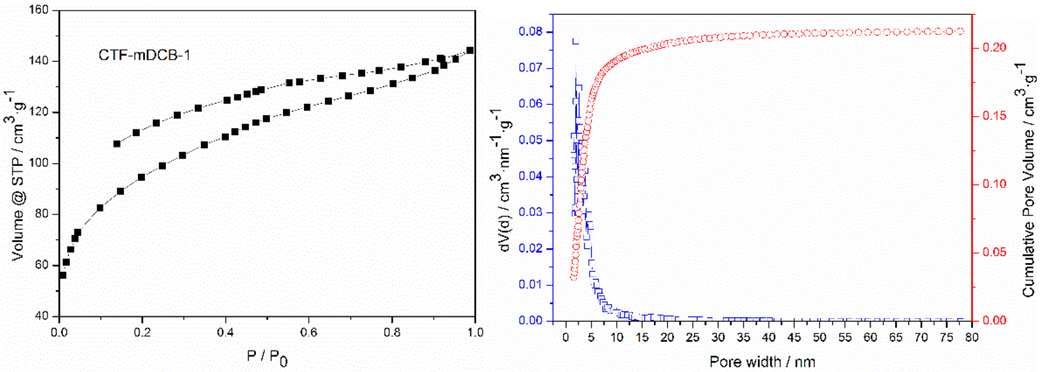
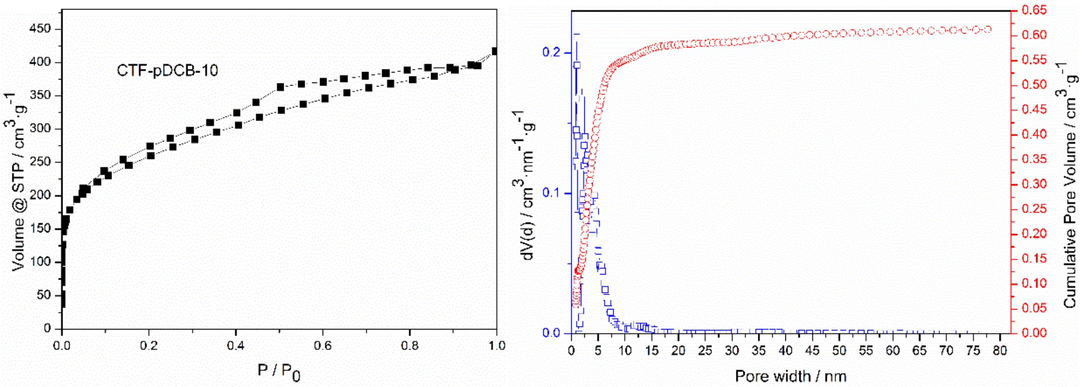
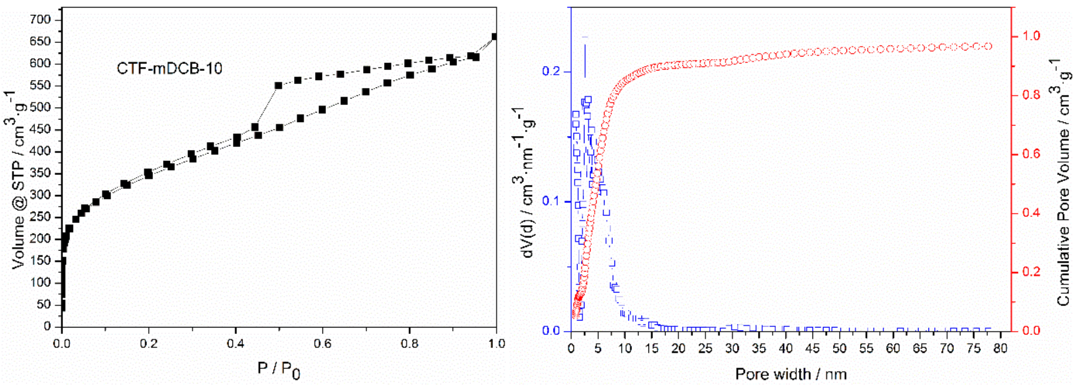


Fig. S5 (a) C 1s peak and (b) N 1s peak of CTF-pDCB-1 after reaction at high resolution.


CTF-pDCB-1
Volume @ STP / cm^3·g^{-1}
0
50
100
150
200
250
300
350
400
450
P / P$_0$
0.0
0.2
0.4
0.6
0.8
1.0
dV(d) / cm^3·nm^{-1}·g^{-1}
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Cumulative Pore Volume / cm^3·g^{-1}
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
Pore width / nm
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80


CTF-mDCB-1
Volume @ STP / cm^3·g^{-1}
40
60
80
100
120
140
160
P / P$_0$
0.0
0.2
0.4
0.6
0.8
1.0
dV(d) / cm^3·nm^{-1}·g^{-1}
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
Cumulative Pore Volume / cm^3·g^{-1}
0.00
0.05
0.10
0.15
0.20
Pore width / nm
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80


CTF-pDCB-10
Volume @ STP / cm^3·g^{-1}
0
50
100
150
200
250
300
350
400
450
P / P$_0$
0.0
0.2
0.4
0.6
0.8
1.0
dV(d) / cm^3·nm^{-1}·g^{-1}
0.0
0.1
0.2
Cumulative Pore Volume / cm^3·g^{-1}
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
Pore width / nm
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80


CTF-mDCB-10
Volume @ STP / cm^3·g^{-1}
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
P / P$_0$
0.0
0.2
0.4
0.6
0.8
1.0
dV(d) / cm^3·nm^{-1}·g^{-1}
0.0
0.1
0.2
Cumulative Pore Volume / cm^3·g^{-1}
0.0
0.2
0.4
0.6
0.8
1.0
Pore width / nm
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80

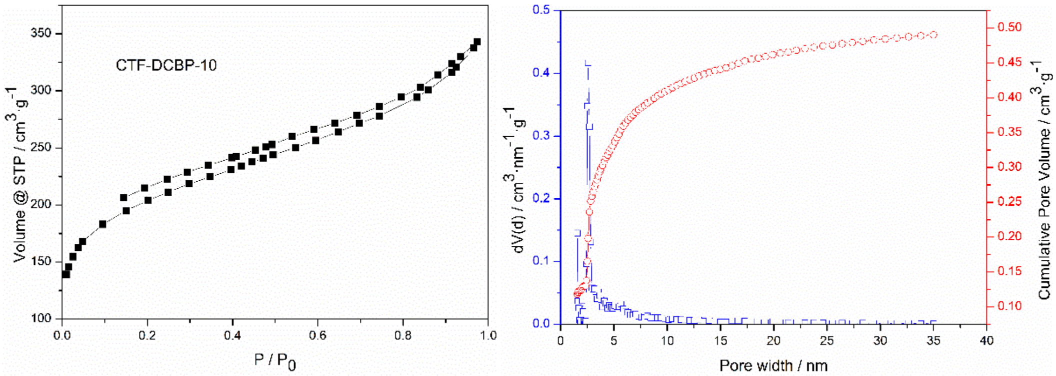


Fig. S6 The N_2 sorption isotherms and the pore size distributions of CTFs.

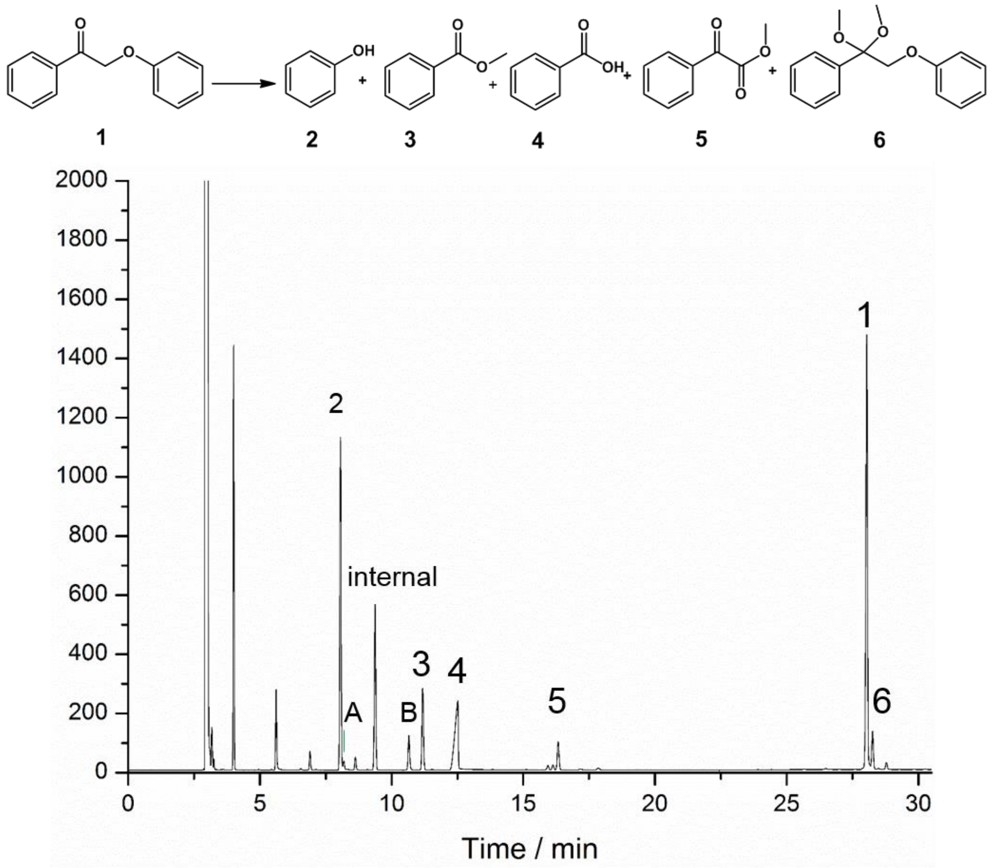


Fig. S7 The products of catalytically oxidative cleavage of lignin model compound **1**. A had the same retention time with phenyl formate and B had the same retention time with phenylglyoxal.

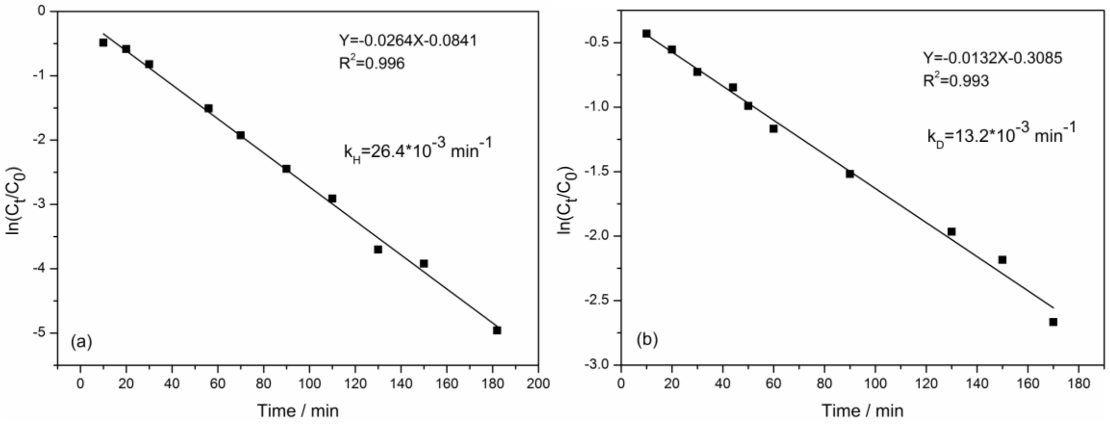


Fig. S8 The linear fit of ln(C_t/C_0) against the reaction time of (a) 2-phenoxyacetophenone, (b) Deuterium-labeling 2-phenoxyacetophenone, C_t/C_0 was defined as the ratio of the concentration at *t* and initial of the substrate. Reaction conditions: 0.4 mmol of substrate, 40 mg of CTF-pDCB-1, 5 mL of methanol, 140 ^{o}C, 0.5 MPa of O_2, internal standard: 20.3 mg of p-dichlorobenzene.

Table S2 $ZnCl_2$ as catalyst for the oxidative cleavage of lignin model compound **1** [a]

Entry	Catalyst	Conv. (%)	Product distribution (%)						Selectivity of cleavage products (%)
			2	3	4	5	6	others	
1	$ZnCl_2$	24.6	44.7	3.1	38.1	0	13.3	0.8	85.9

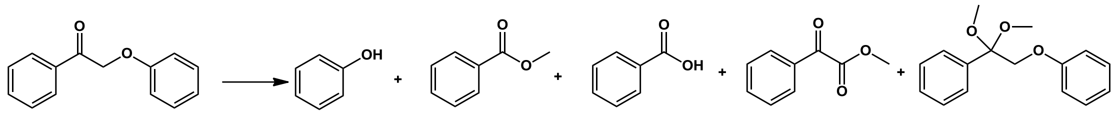
[a] Reaction conditions: 0.4 mmol of substrate, 4.4 mg of $ZnCl_2$, 5 mL of methanol, 140 °C, 2 h, 0.5 MPa of O_2. Selectivity of cleavage products was presented as the amount of (2 + 3 + 4 + 5) in product distribution. Others include some unidentified and undetected compounds that were regarded as uncleavage products.

Table S3 Different reaction atmosphere for the catalytic cleavage of lignin model compound **1** [a]

Entry	Atmosphere	Conv. (%)	Product distribution (%)						Selectivity of cleavage products (%)
			2	3	4	5	6	others	
1	N_2	25.1	30.7	3.8	0	0	49.5	16.0	34.5
2	N_2/O_2	71.3	46.8	14.3	22.9	5.4	3.2	7.4	89.4

[a] Reaction conditions: 0.4 mmol of substrate, 40 mg of CTF-pDCB-1, 5 mL of methanol, 140 °C, 2 h. Selectivity of cleavage products was presented as the amount of (2 + 3 + 4 + 5) in product distribution. Others include some unidentified and undetected compounds that were regarded as uncleavage products.

Table S4 The catalytic conversion of lignin model compound **1** over the catalysts [a]



1 2 3 4 5 6

Entry	Catalyst	Conv. (%)	Product yield (%)					Selectivity (%)	
			2	3	4	5	6	2	3+4+5
1	Blank	16.9	11.0	0.1	8.5	0	3.0	65.1	50.9
2	CTF-pDCB-1	66.8	54.4	13.6	34.2	4.8	3.0	81.4	78.7
3	CTF-mDCB-1	51.5	32.2	8.3	18.1	2.4	11.0	62.5	55.9
4	CTF-pDCB-10	74.5	63.7	12.9	35.9	9.5	3.6	85.5	78.3
5	CTF-mDCB-10	89.0	65.0	17.2	29.0	11.3	2.8	73.0	64.6
6	CTF-DCBP-10	55.6	36.4	6.6	23.8	2.4	8.3	65.5	59.0
7	Pyridine	52.2	39.7	1.8	36.8	3.0	1.3	76.1	79.7
8	Pyrimidine	27.8	17.2	0.2	15.2	0	1.8	61.9	55.4
9[b]	1,3,5-Triazine	74.5	64.2	3.9	24.2	1.4	0	86.2	39.6
10[c]	CTF-pDCB-1	>99	83.7	27.7	44.6	14.8	0	83.7	87.1

[a] Reaction conditions: 0.4 mmol of substrate, 40 mg of catalyst, 5 mL of methanol, 140 ^{o}C, 2 h, 0.5 MPa of O_2. [b] 18 mg of catalyst, [c] 60 mg of catalyst, 160 ^{o}C, 6 h.

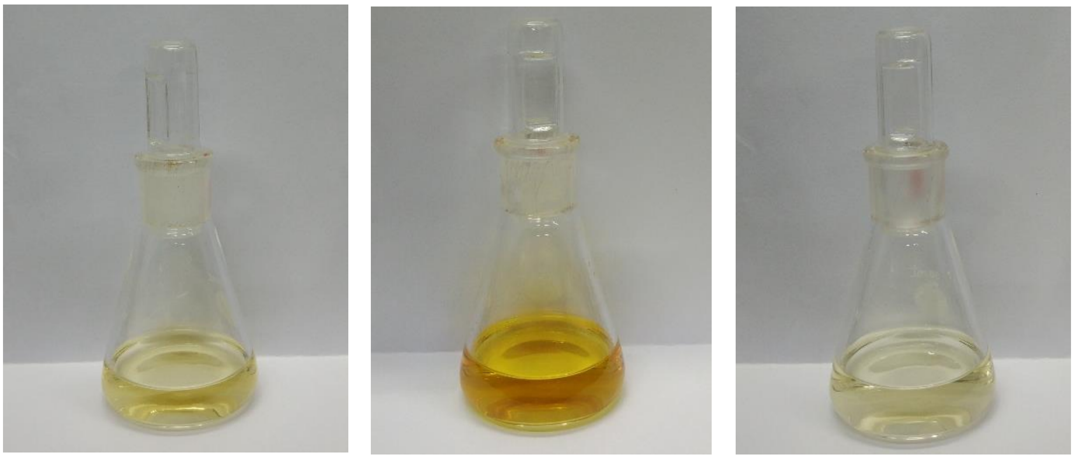


Fig. S9 The color change of the reaction solution (left) after adding the KI aqueous (middle) and titration by $Na_2S_2O_3$ (right). The color of the solution changed from canary yellow to brown with I^- oxidizing to I_2, indicating the presence of the substrate peroxide.

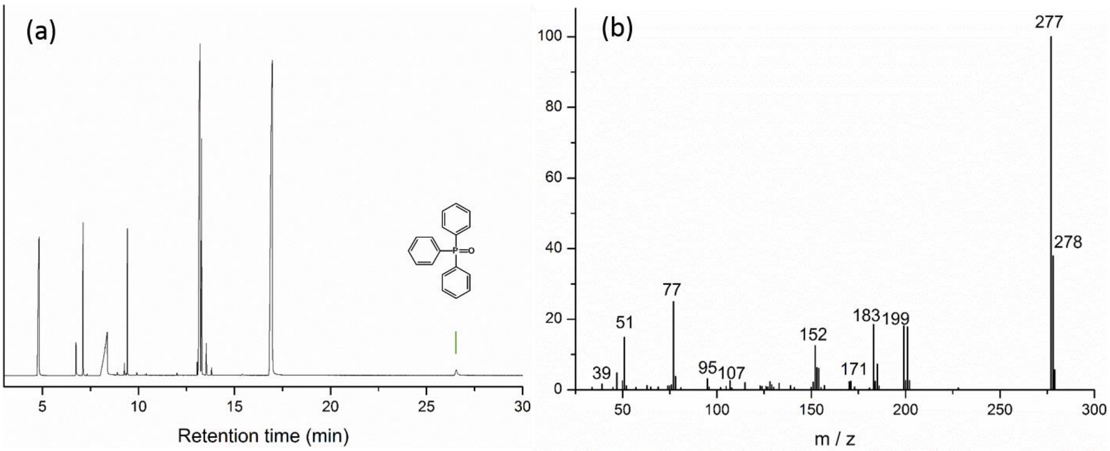
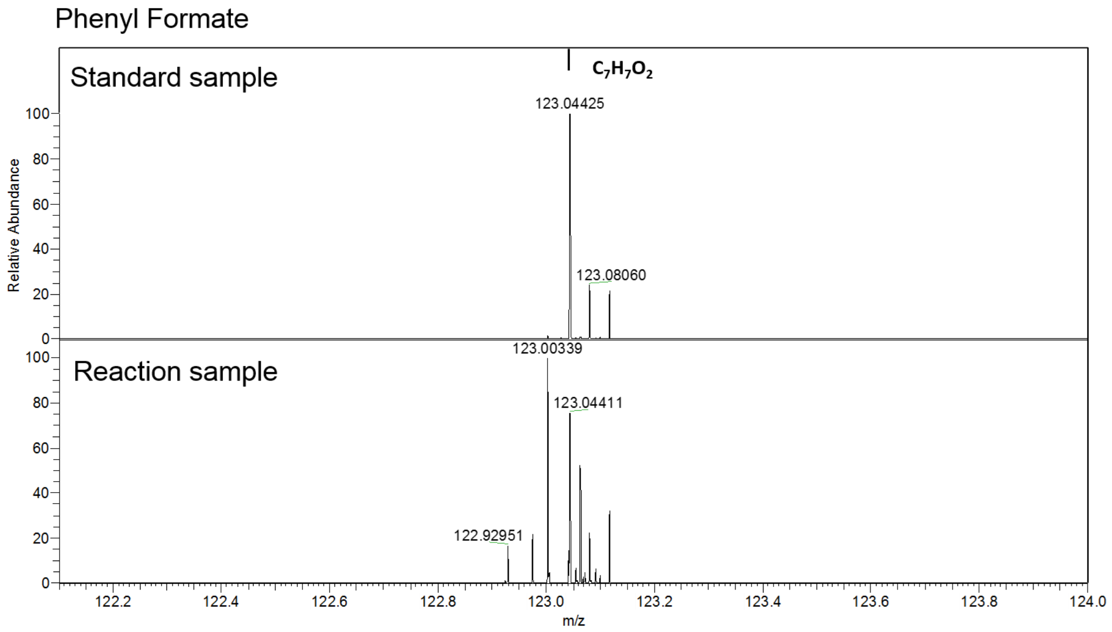
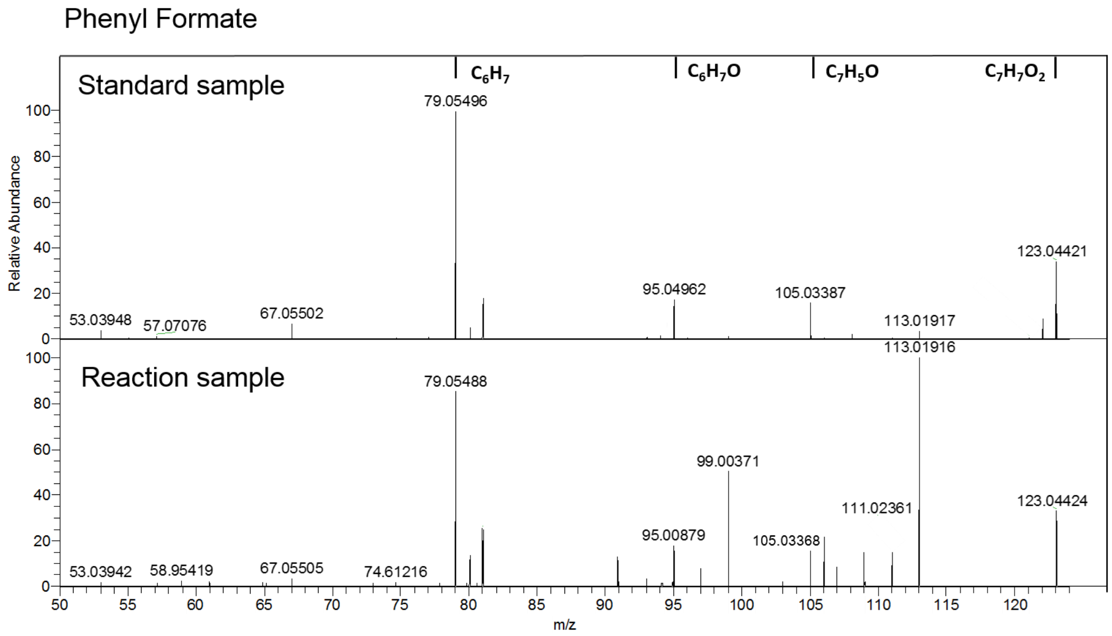


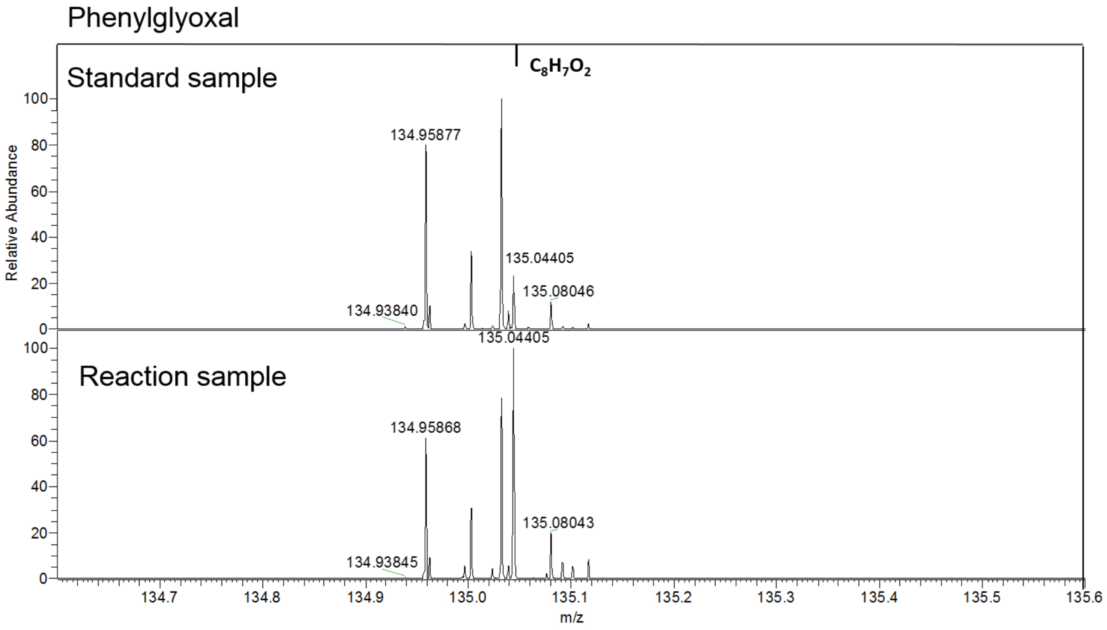
Fig. S10 (a) GC-MS spectrum of the reaction solution with triphenylphosphine added and (b) MS spectrum of triphenylphosphine oxide. Triphenylphosphine oxide was detected, indicating the peroxide was present.



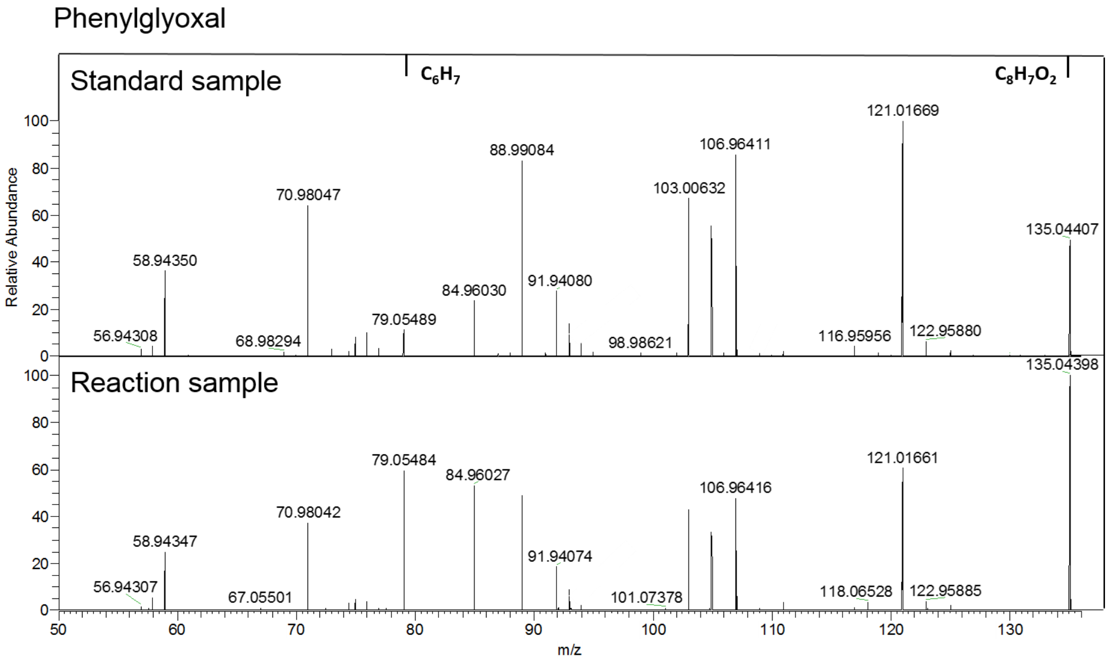
The MS spectra of standard phenyl formate and reaction sample



The MS^2 spectra of standard phenyl formate and reaction sample



The MS spectra of standard phenylglyoxal and reaction sample



The MS^2 spectra of standard phenylglyoxal and reaction sample

Fig. S11 The verification of the proposed intermediates phenyl formate and phenylglyoxal by HRMS/MS (ESI, M+H). For the reaction sample, reaction conditions: 0.4 mmol of substrate, 40 mg of CTF-pDCB-1, 5 mL of methanol, 0.5 MPa of O_2, 140 ^oC, 2 h.

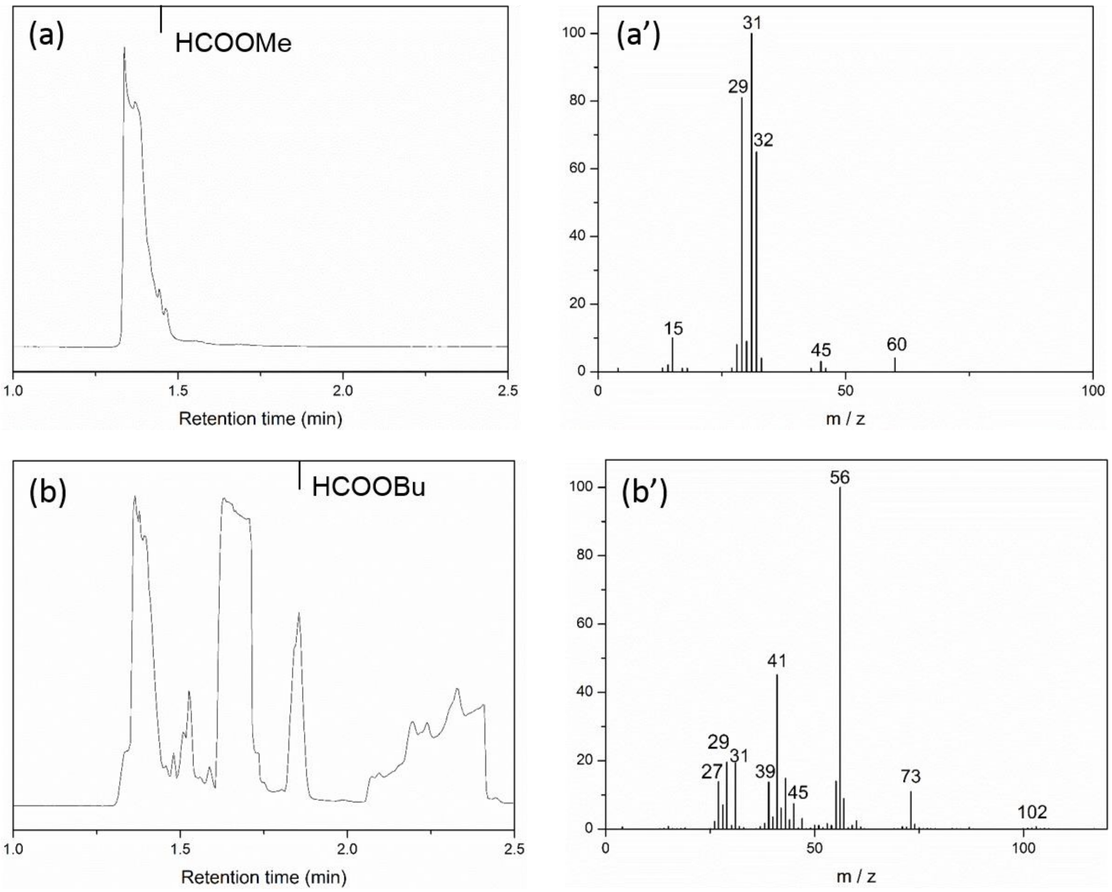


Fig. S12 GC-MS spectra of the oxidation of lignin model compound **1** (a) in methanol and (a') MS spectrum of HCOOMe，(b) in n-butanol and (b') MS spectrum of HCOOBu.

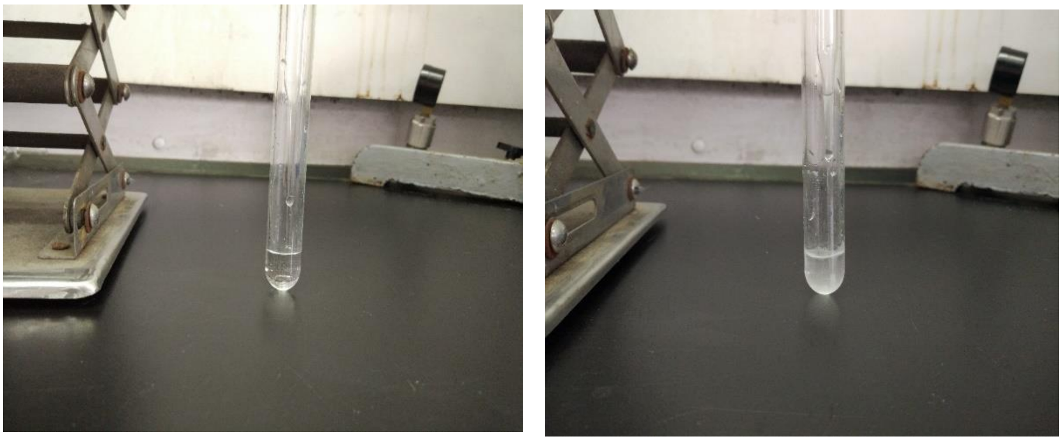


Fig. S13 Limewater images before (left) and after (right) introduction of the reaction gas phase. The limewater was cloudy, indicating the generation of CO_2 during the reaction.

Table S5 The content of the structural units [a]

	Lignin	Oxidized Lignin
Weight (mg)	40.0	40.0
$S_{2,6}$ (2H) (peak area ratio to internal)	0.43	0.11
$S'_{2,6}$ (2H) (peak area ratio to internal)	0.02	0.14
$S''_{2,6}$ (2H) (peak area ratio to internal)	0.01	
$S_{condensed}$ (1H) (peak area ratio to internal)	0.07	-
G_2 (1H) (peak area ratio to internal)	0.13	0.03
G'_2 (1H) (peak area ratio to internal)	-	0.04
Total C_9 units	0.43	0.195
β-O-4 α (1H) (peak area ratio to internal)	0.20	0.02
β-O-4 linkages per C_9 unit	46.5%	10.3%
A'(1H) (peak area ratio to internal)	0	0.04
A''(1H) (peak area ratio to internal)	0	0.06
A' linkages per C_9 unit	0	20.5%
A'' linkages per C_9 unit	0	30.8%

[a] 10.0 mg of internal (peak area=1.00),

Total C_9 units $=(S_{2,6} + S'_{2,6} + S''_{2,6}) / 2 + S_{condensed} + G_2 + G'_2$

β-O-4 linkages per C_9 unit=β-O-4 α / Total C_9 units

A' linkages per C_9 unit=A' / Total C_9 units

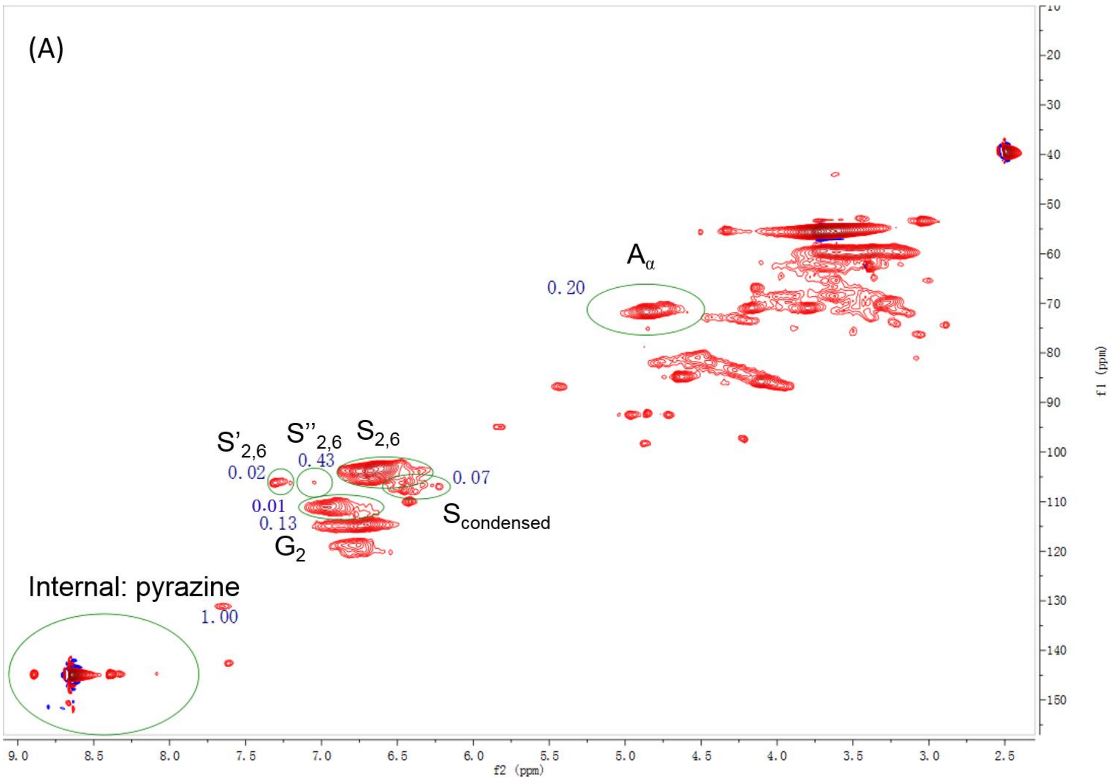
A'' linkages per C_9 unit=A'' / Total C_9 units

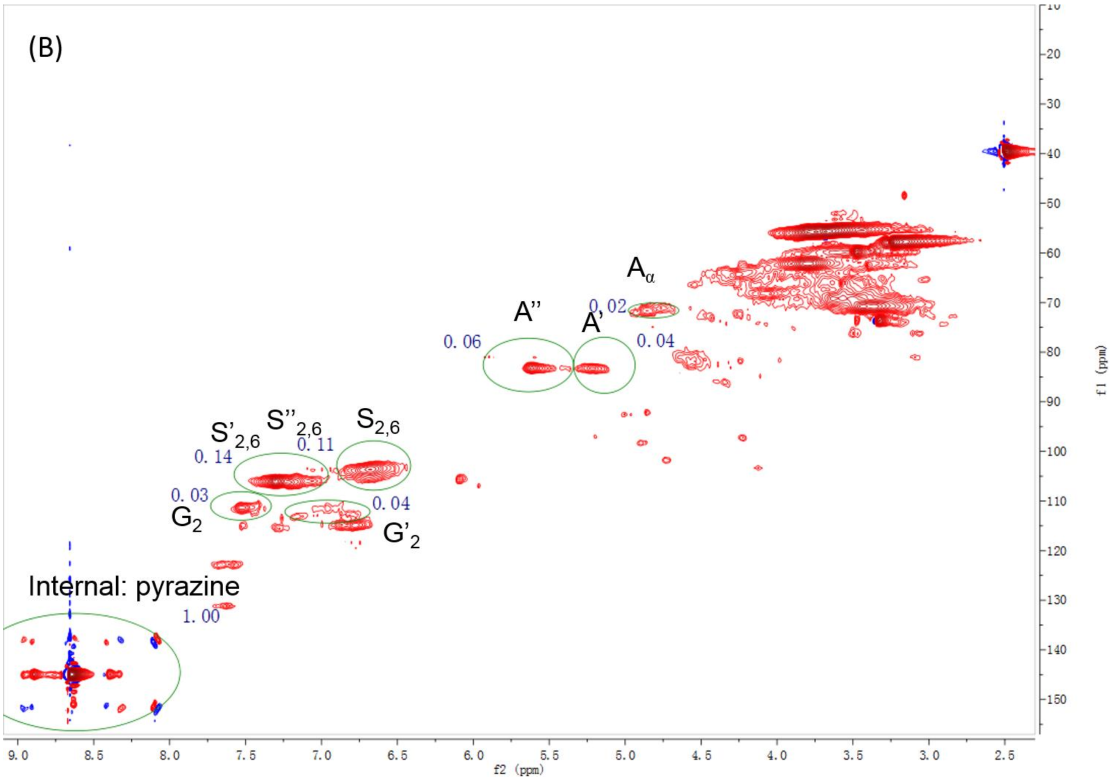
Table S6 The conversion of the β-O-4 ketone bonds [a]

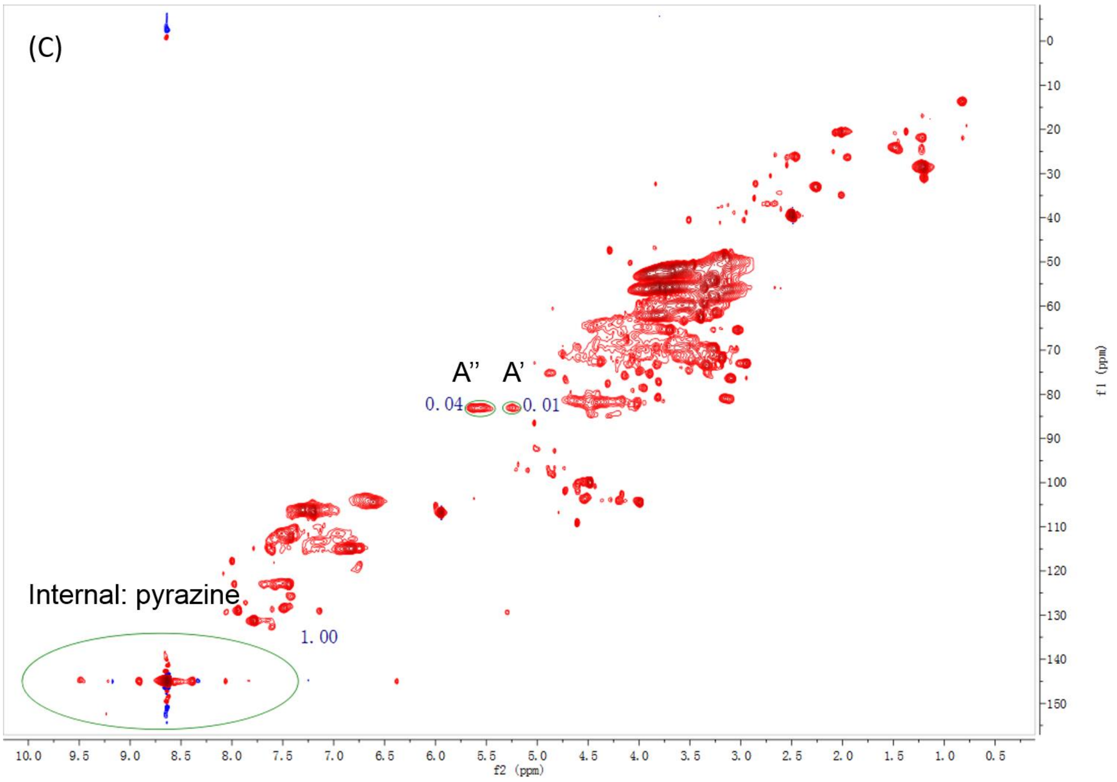
	Standard oxidized lignin	Oxidized lignin for reaction	Conversion of β-O-4 ketone bonds (%)
Weight (mg)	40.0	100.0	80.0
A' (peak area ratio to internal)	0.04	0.01	
A'' (peak area ratio to internal)	0.06	0.04	

[a] Internal: 10.0 mg of pyrazine (peak area=1.00)

After reaction: the conversion of β-O-4 ketone bonds was calculated referred to internal [(0.06 + 0.04)*(100 / 40) - (0.04 + 0.01)] / (0.06 + 0.04) / (100 / 40) = 80.0%


(A)
Aα
0. 20
S'2,6
S''2,6
S2,6
0. 02
0. 43
0. 07
0.01
0. 13
Scondensed
G2
Internal: pyrazine
1. 00
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


(B)
Aα
0. 02
A''
A'
0. 06
0. 04
S'2,6
S''2,6
S2,6
0. 14
0. 11
0. 03
G2
0. 04
G'2
Internal: pyrazine
1. 00
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150



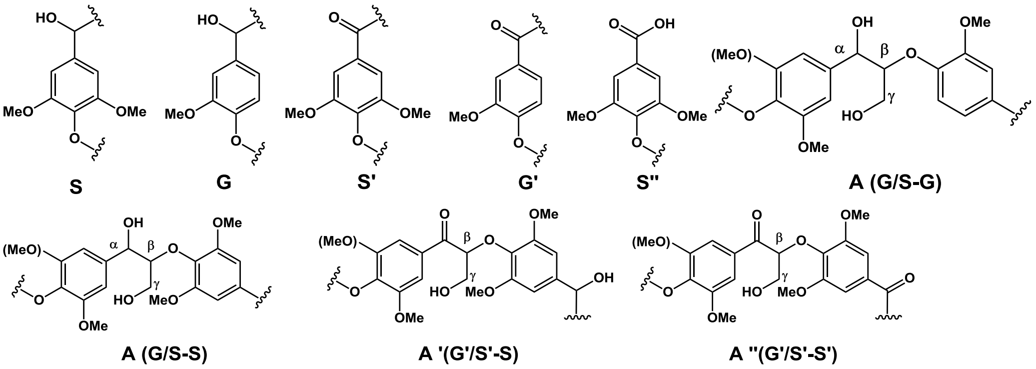
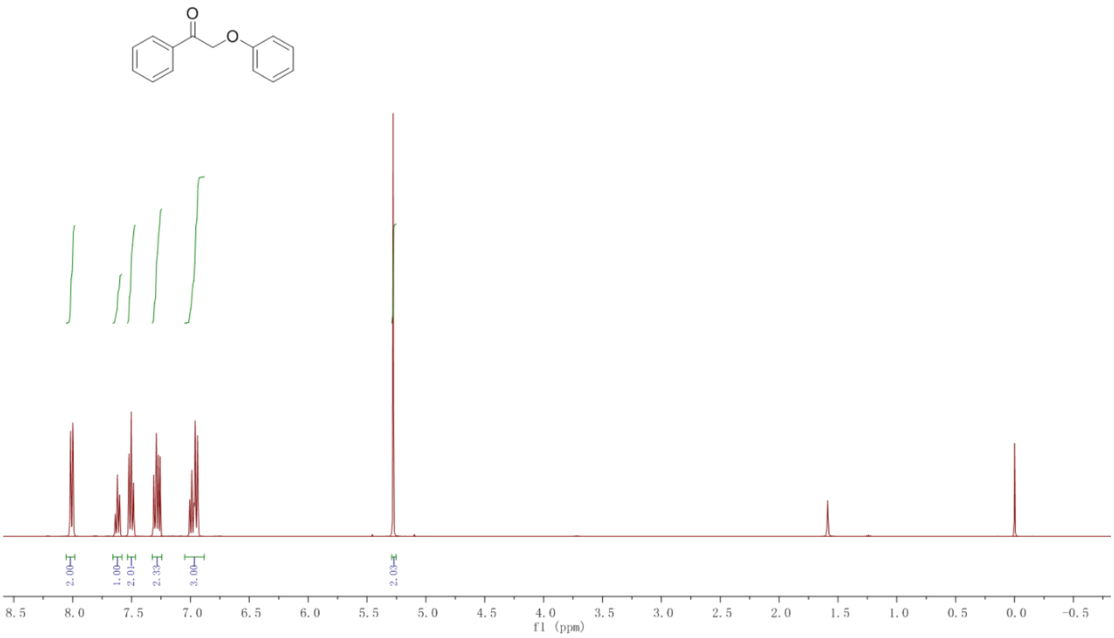


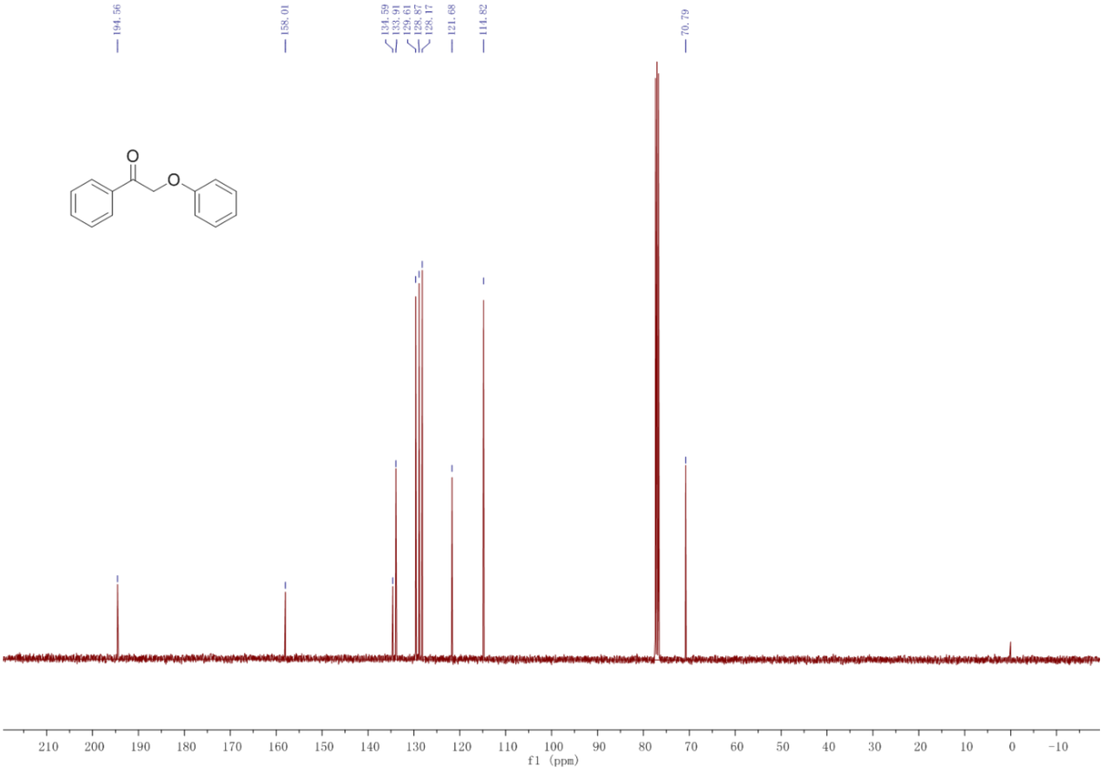
Fig. S14 2D HSQC NMR spectra (in DMSO-*d6*) of (A) birch lignin (B) oxidized birch lignin and (C) after the catalytic cleavage reaction. Equivalent internal of pyrazine was added to the solution, the conversion was calculated according to the relative cross peaks areas of A’ and A’’ to the internal.

NMR spectra of the compounds.

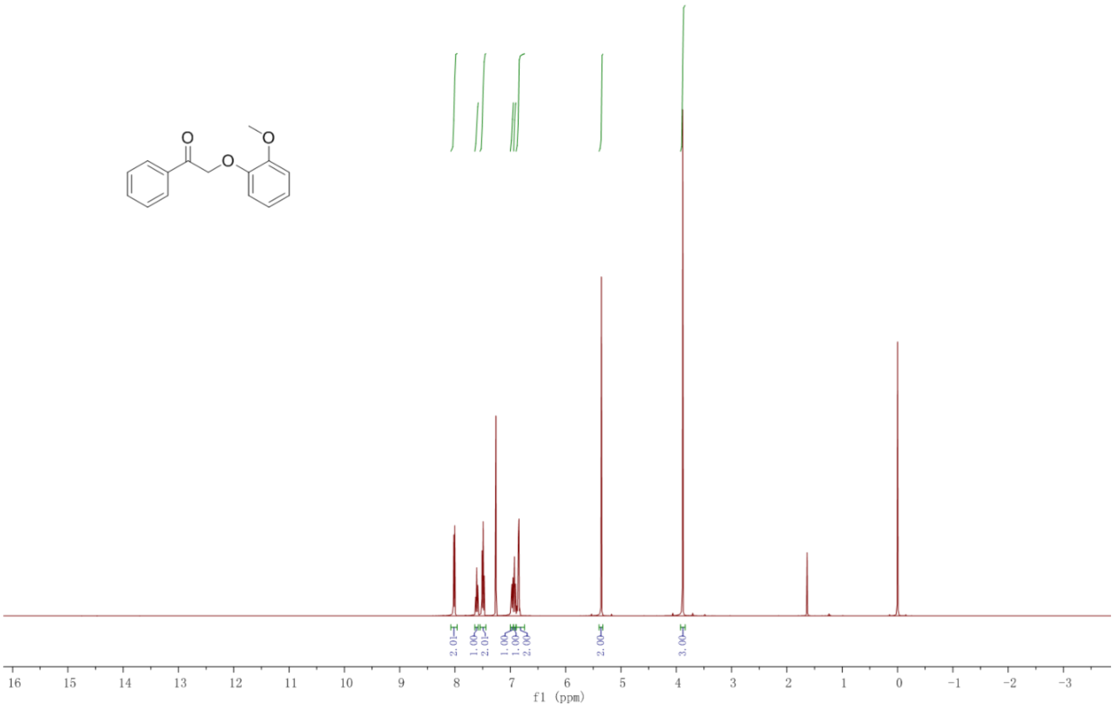
^{1}H NMR



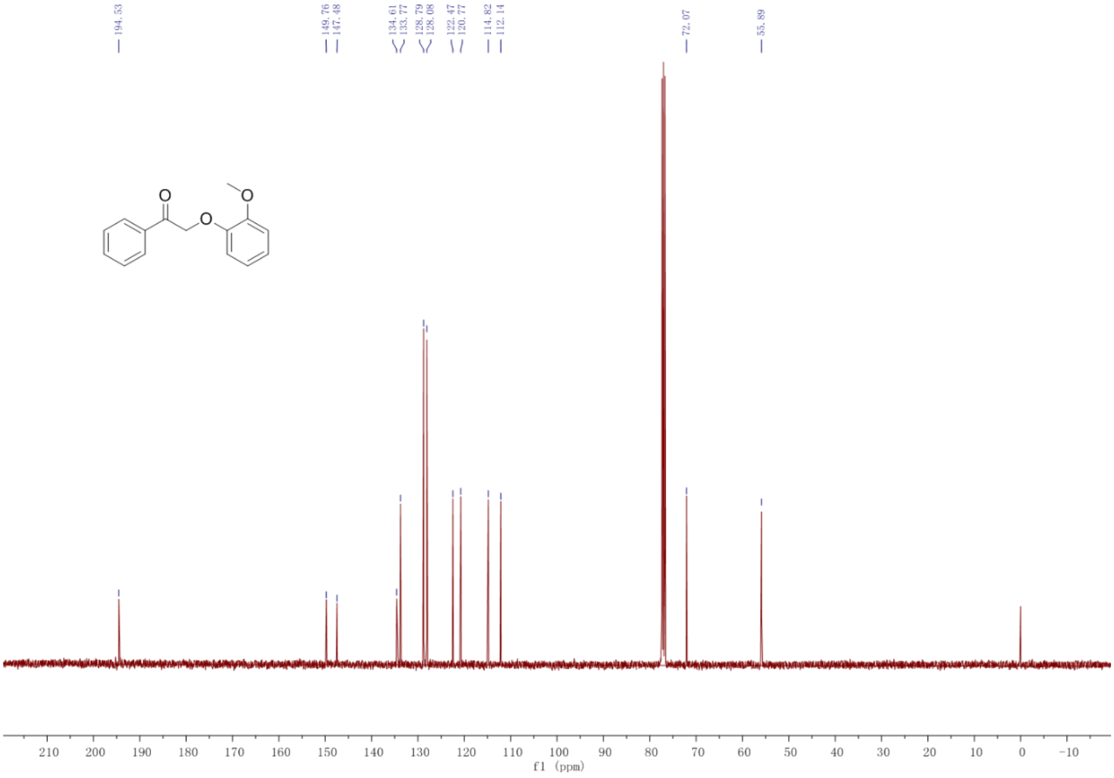
^{13}C NMR



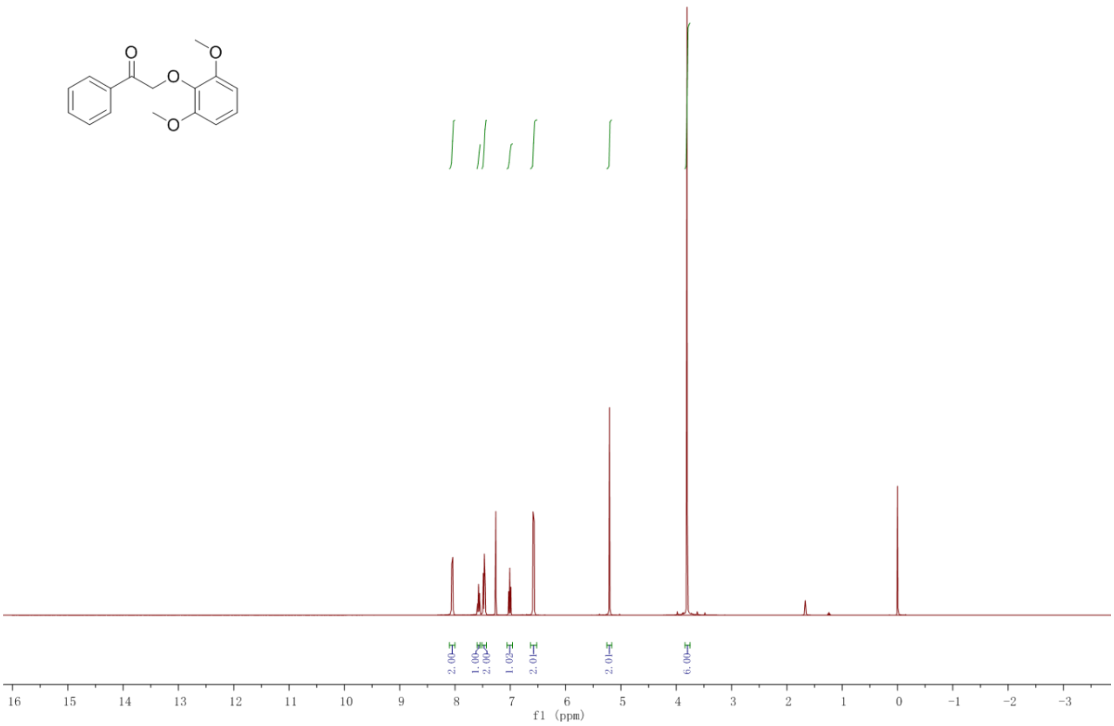
^{1}H NMR



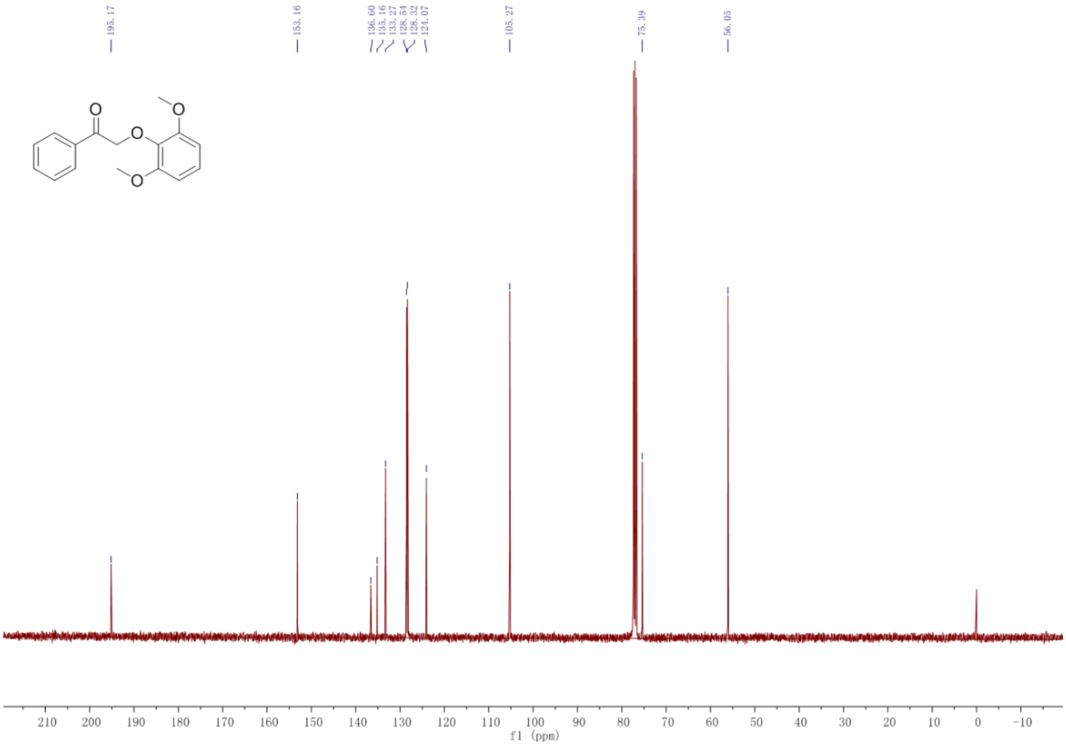
^{13}C NMR



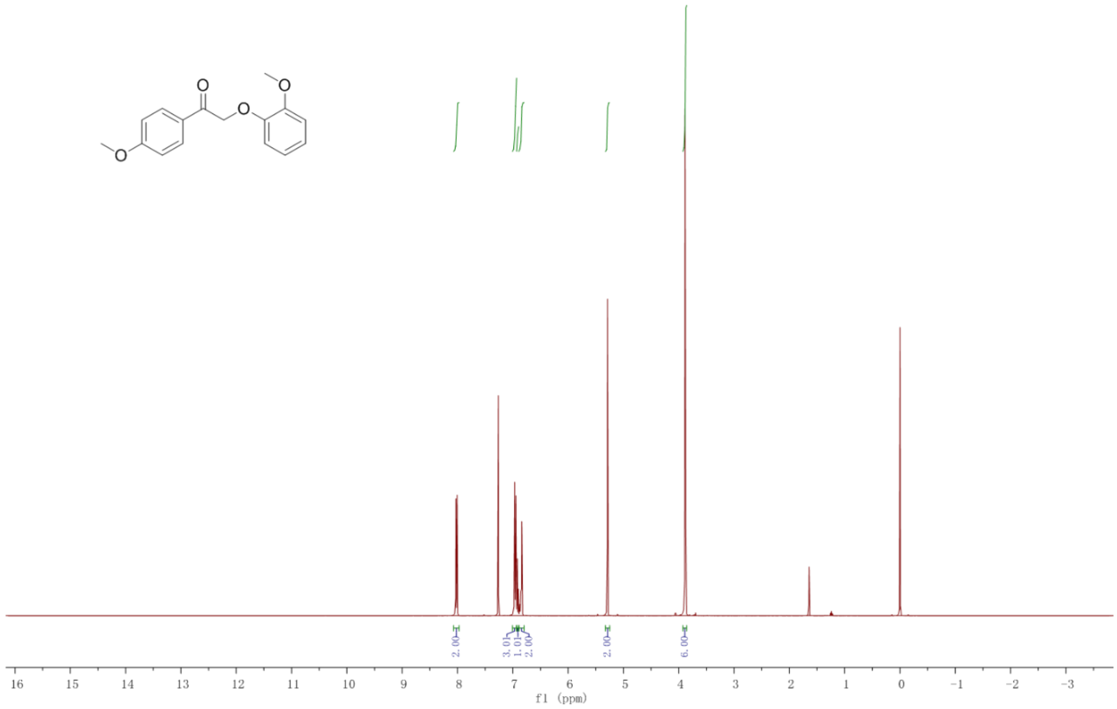
^{1}H NMR



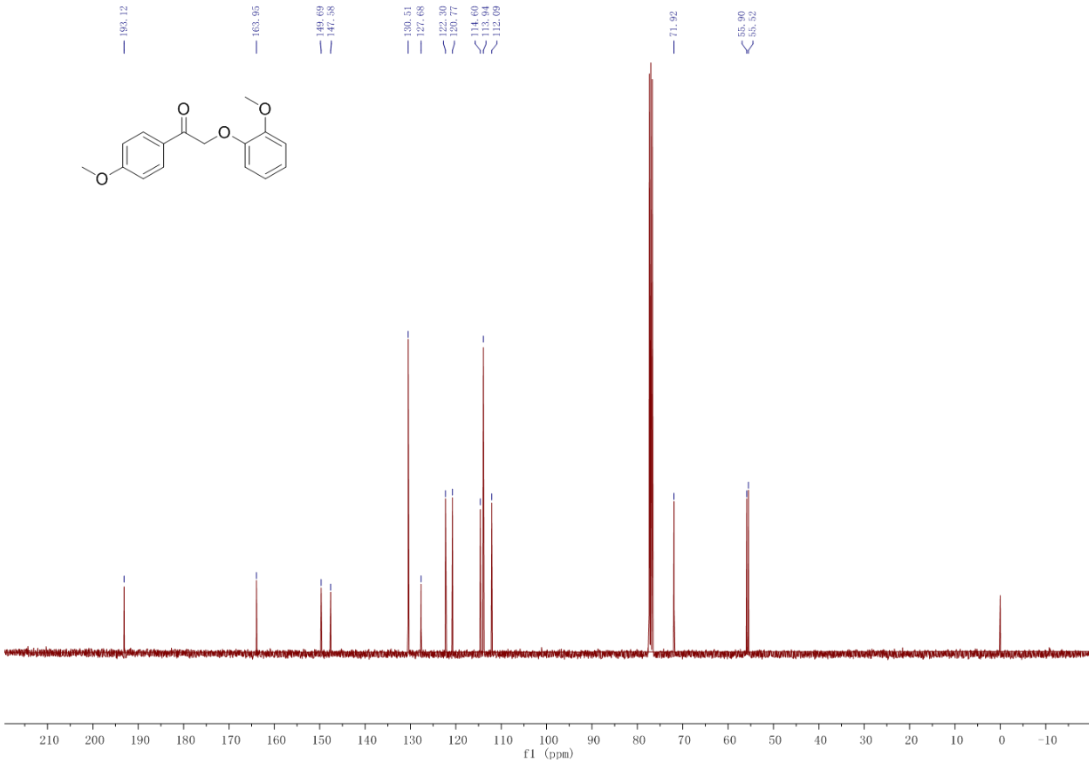
^{13}C NMR



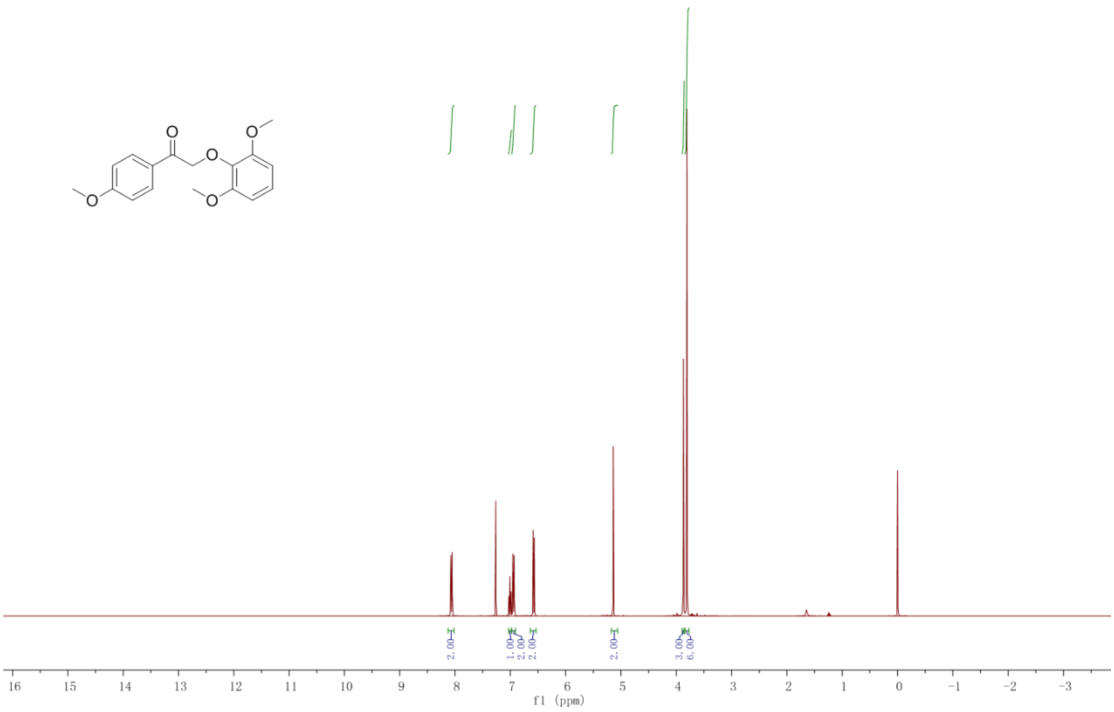
^{1}H NMR



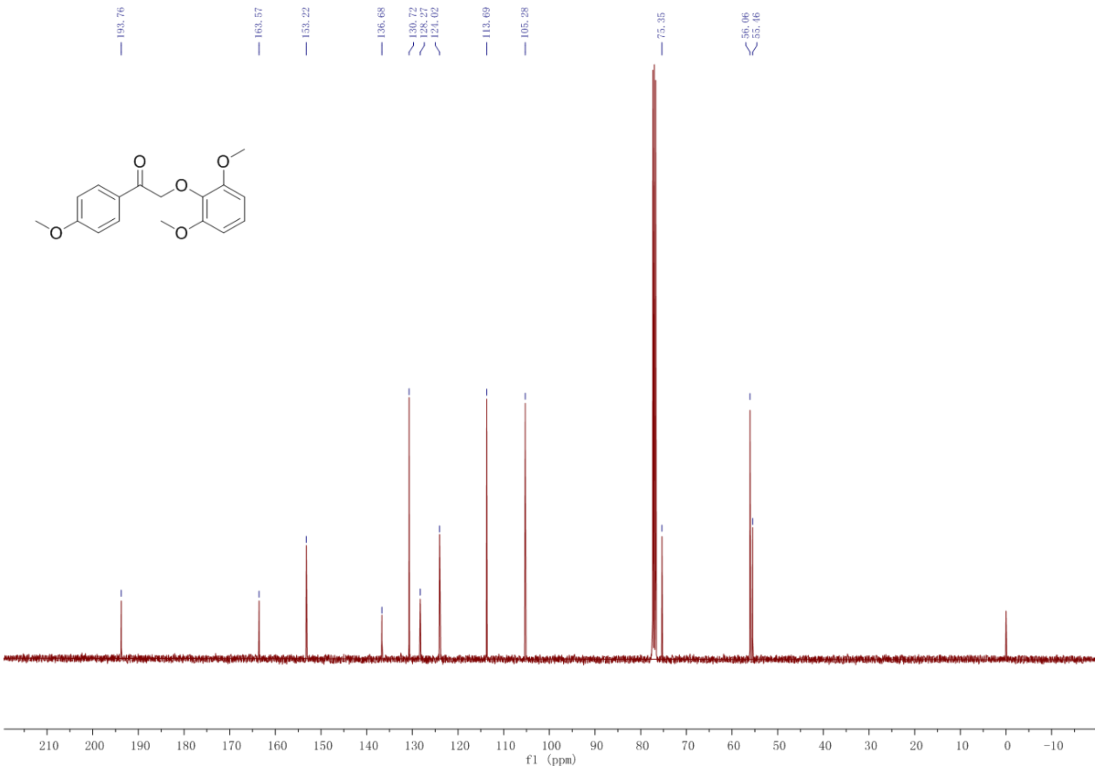
^{13}C NMR



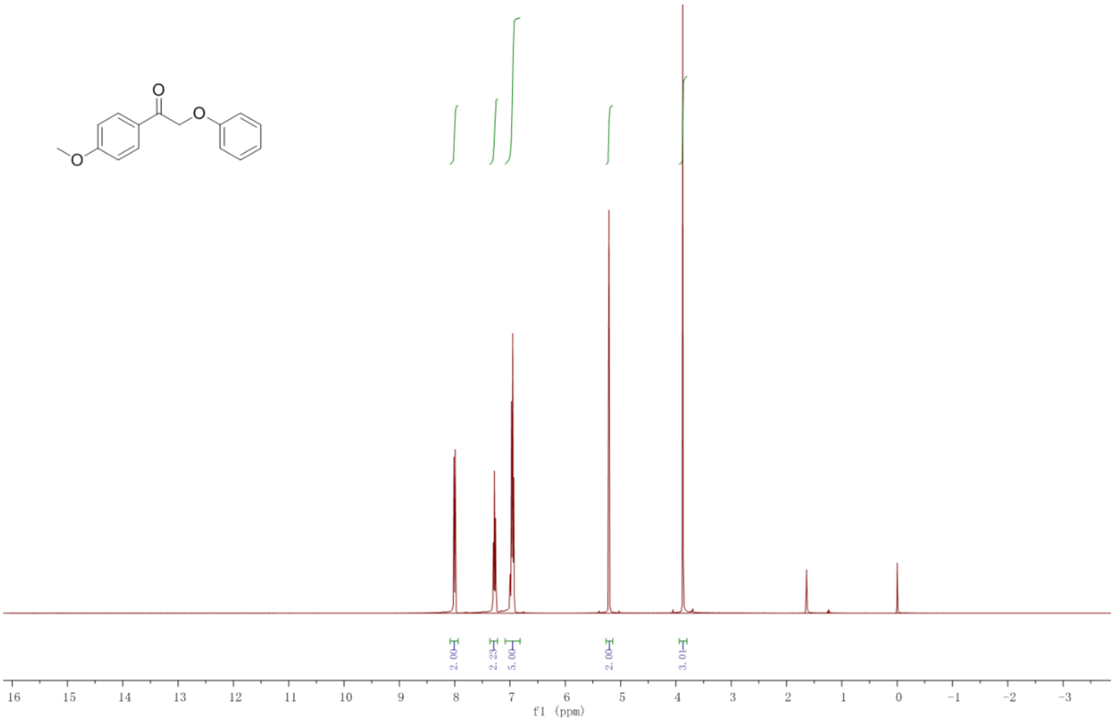
^{1}H NMR



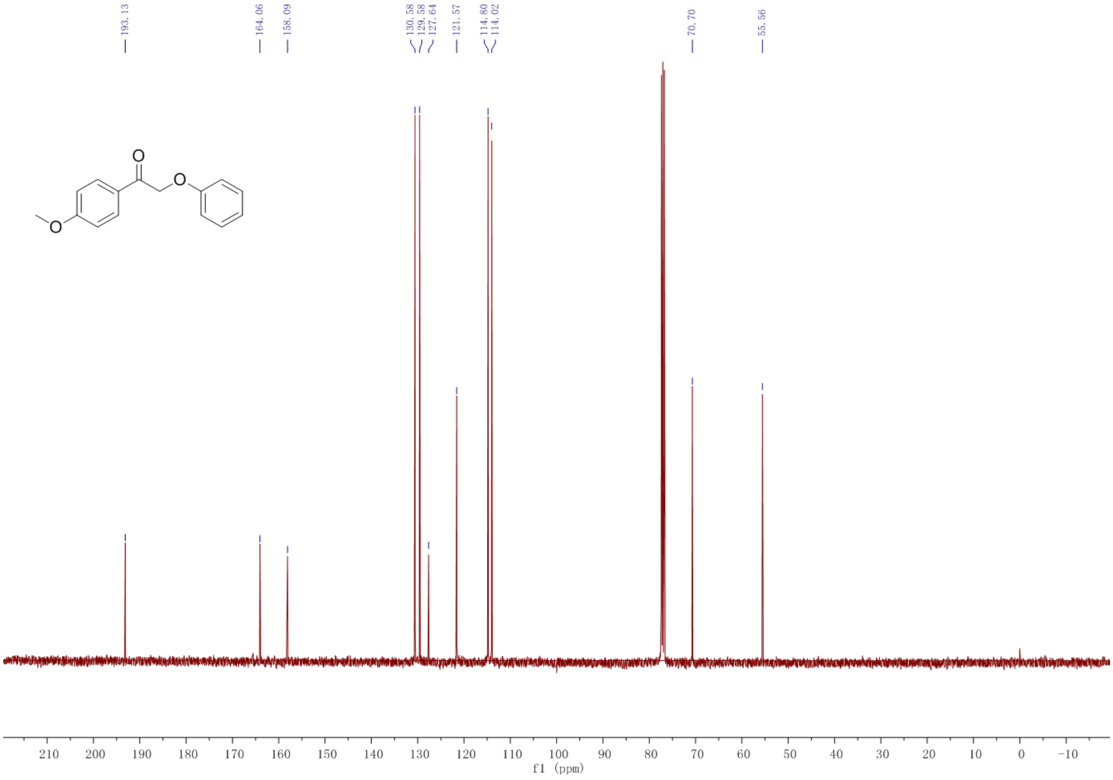
^{13}C NMR



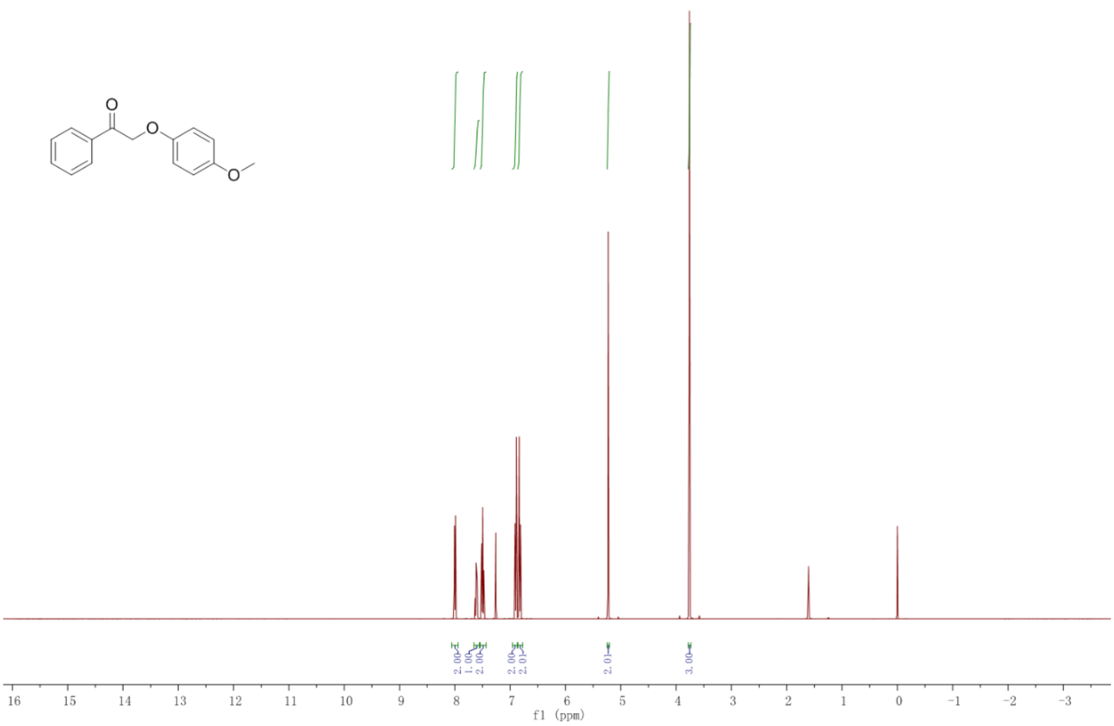
^1H NMR



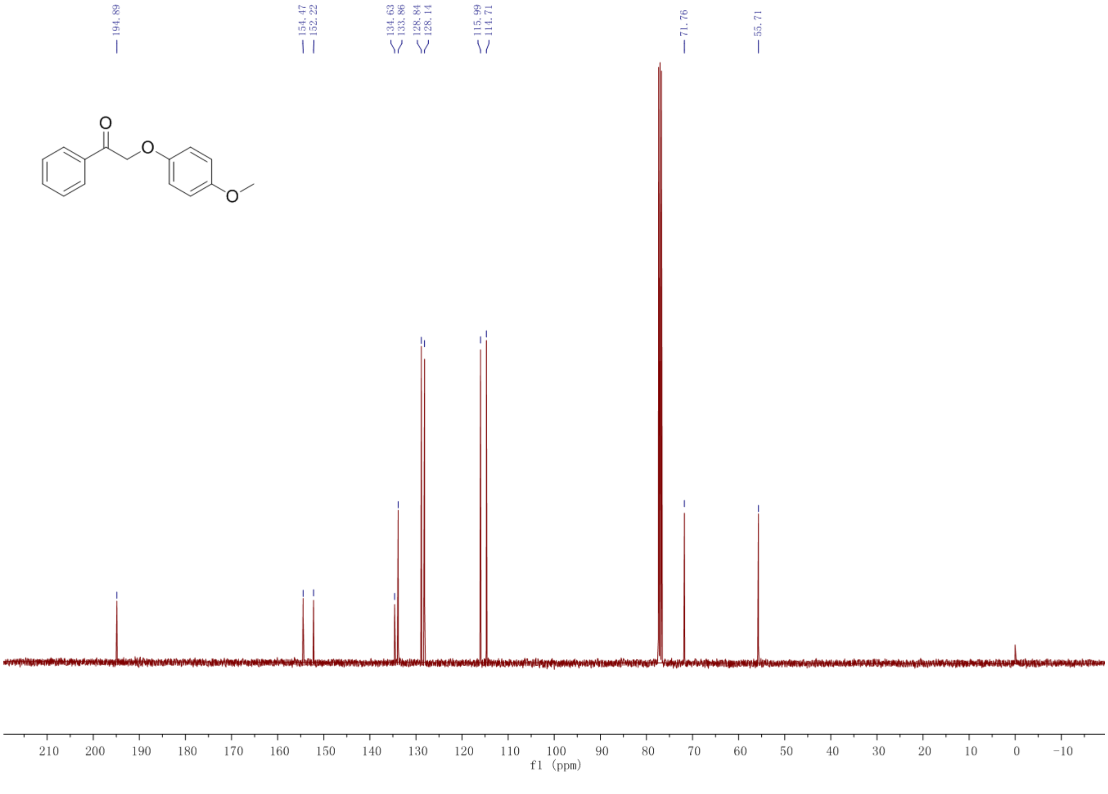
^{13}C NMR



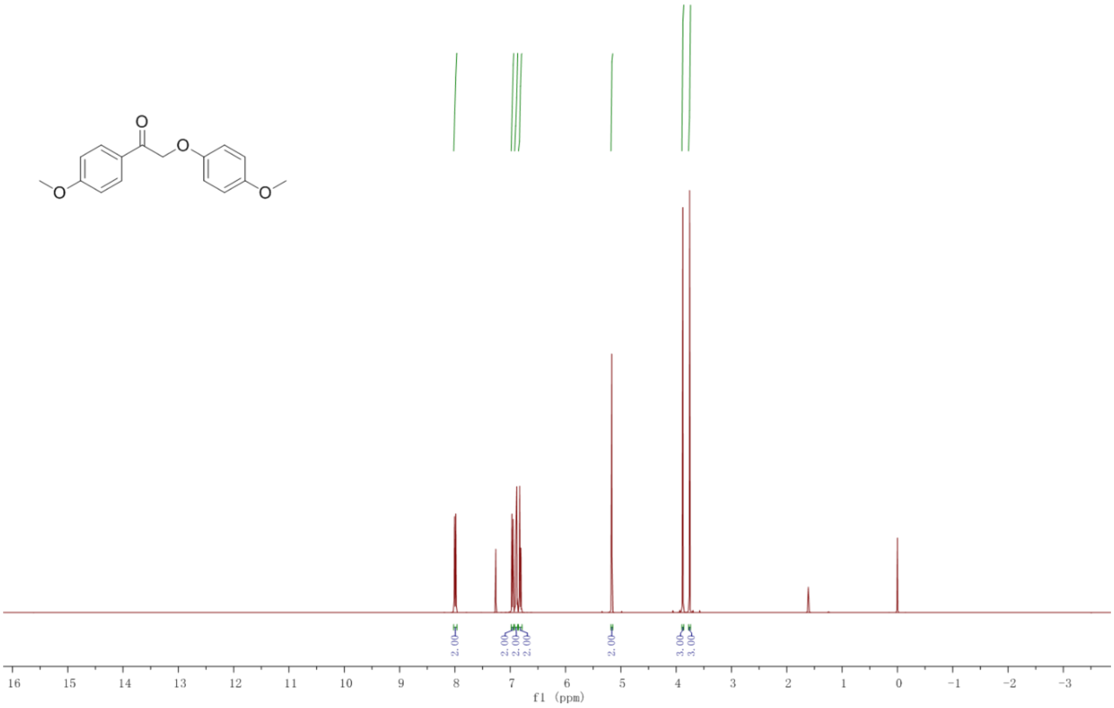
^{1}H NMR



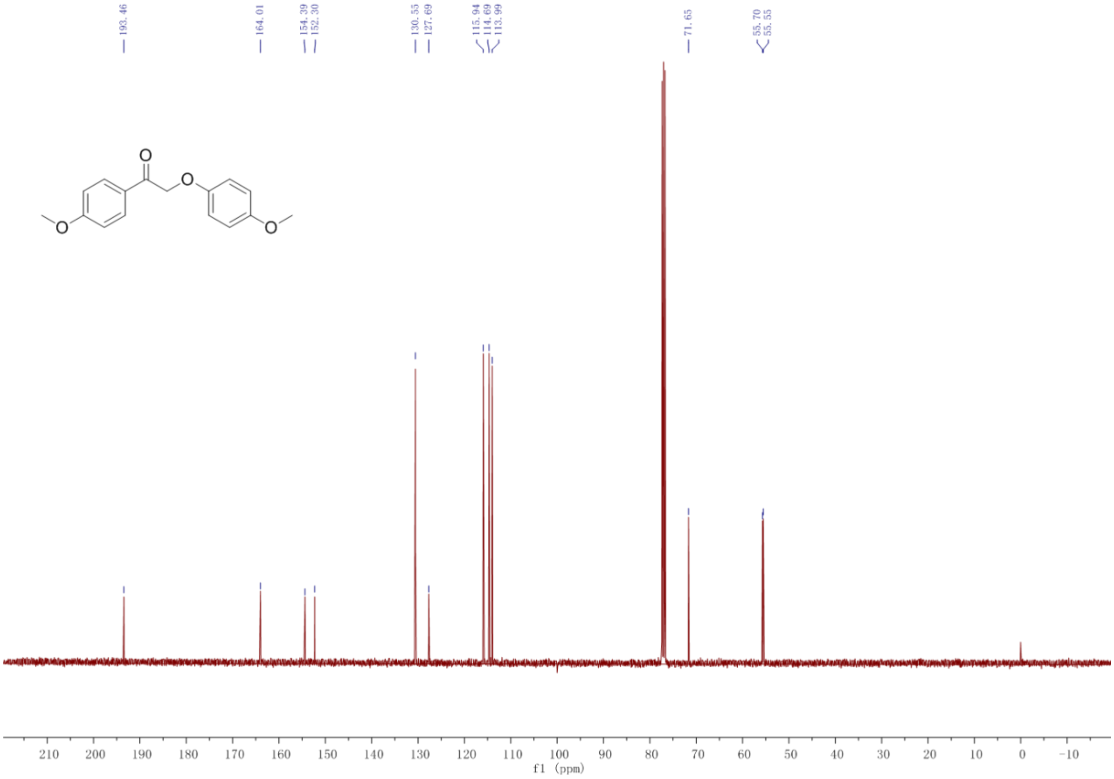
^{13}C NMR



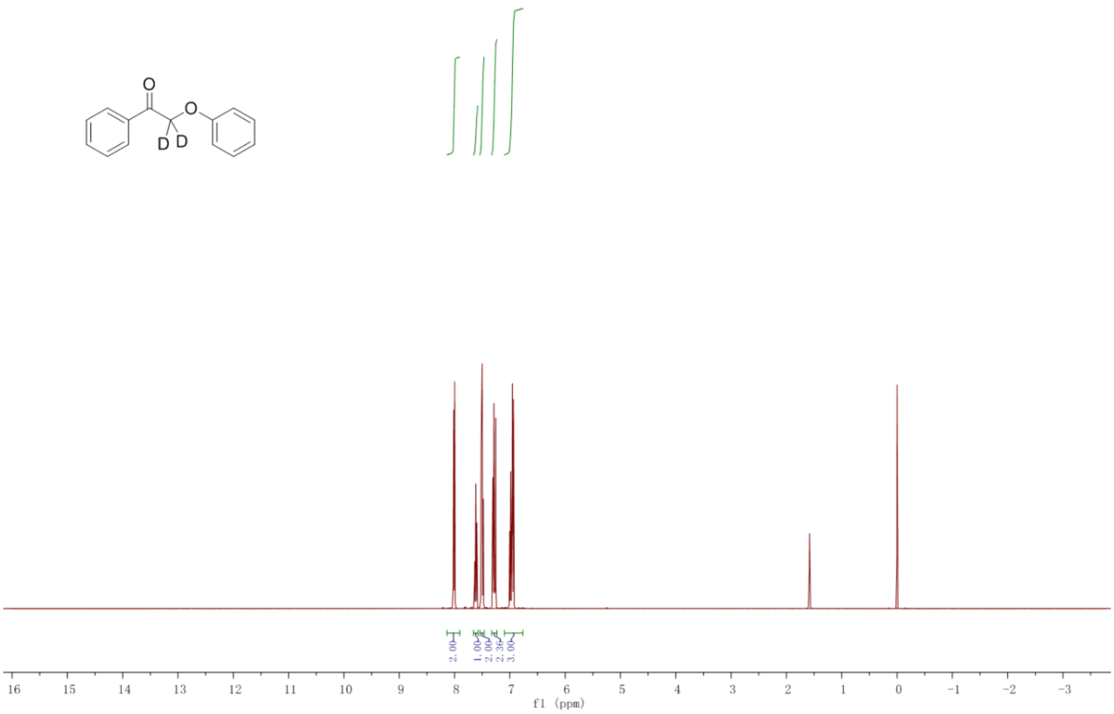
^{1}H NMR



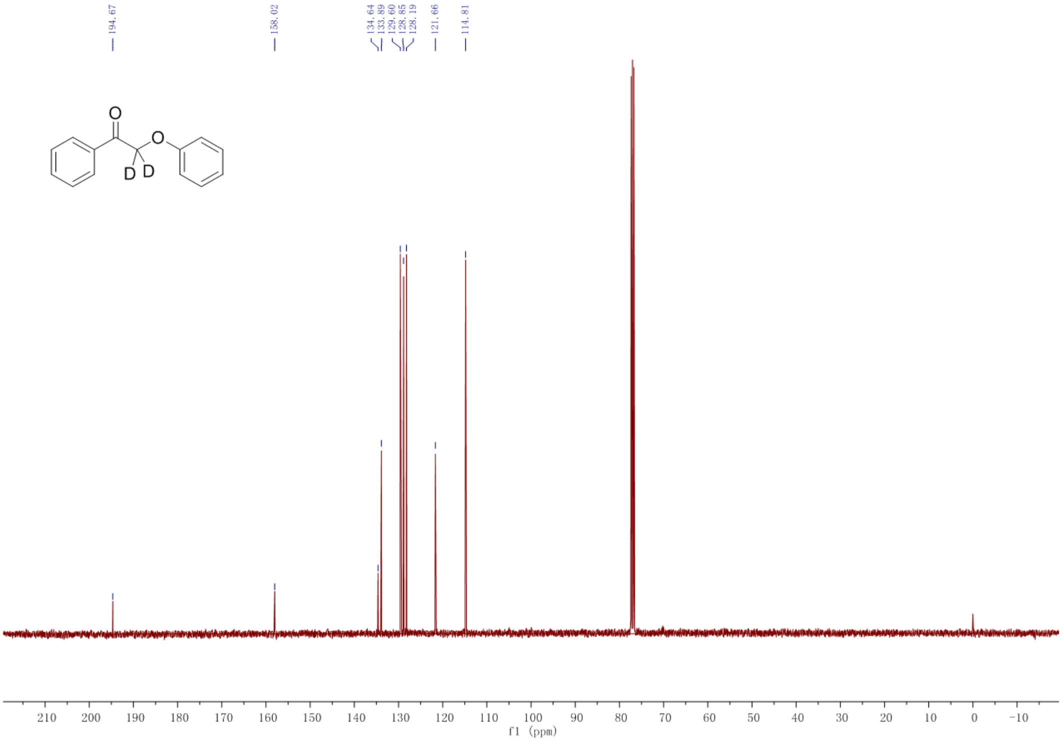
^{13}C NMR



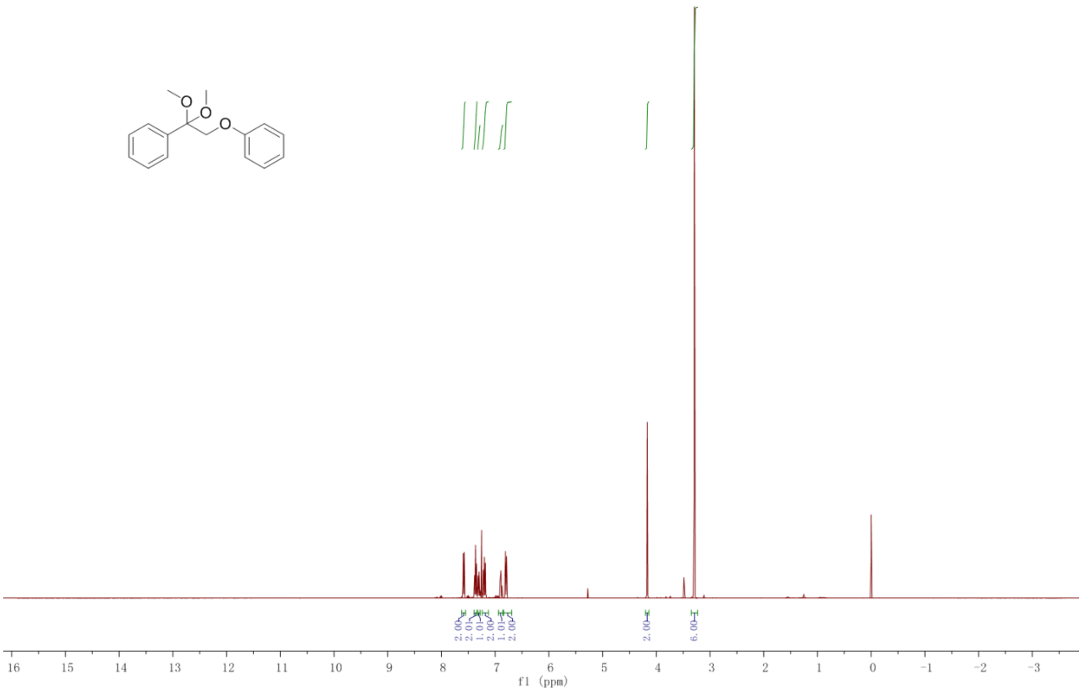
^{1}H NMR



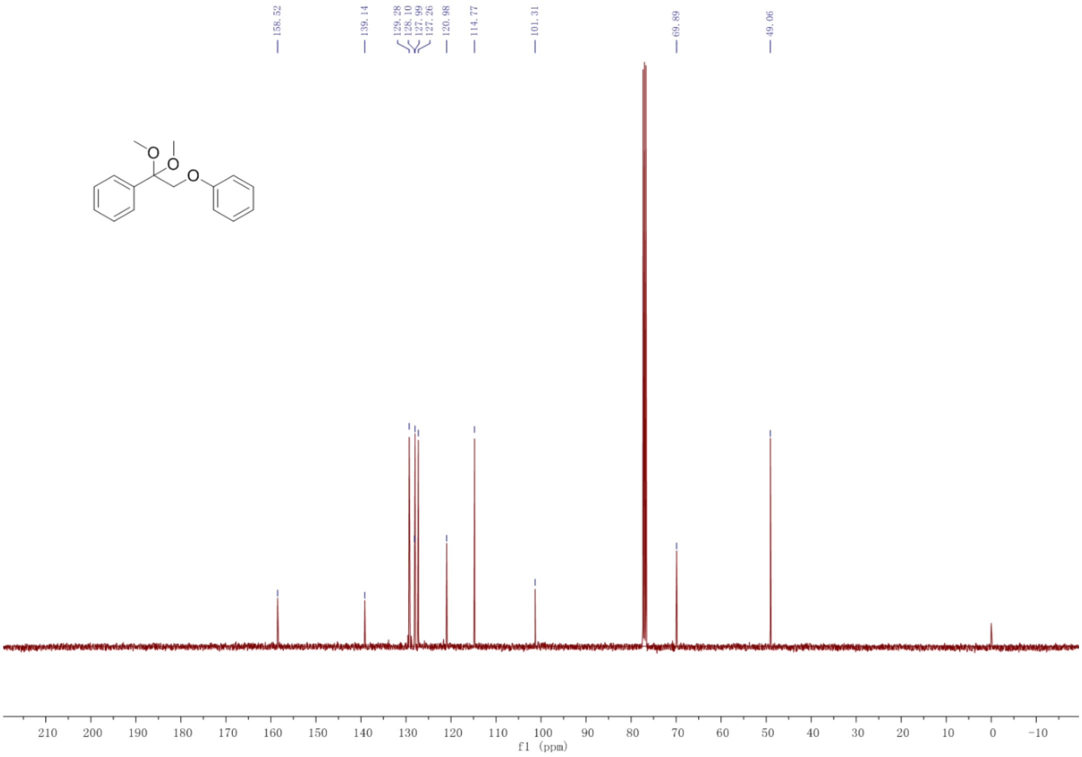
^{13}C NMR

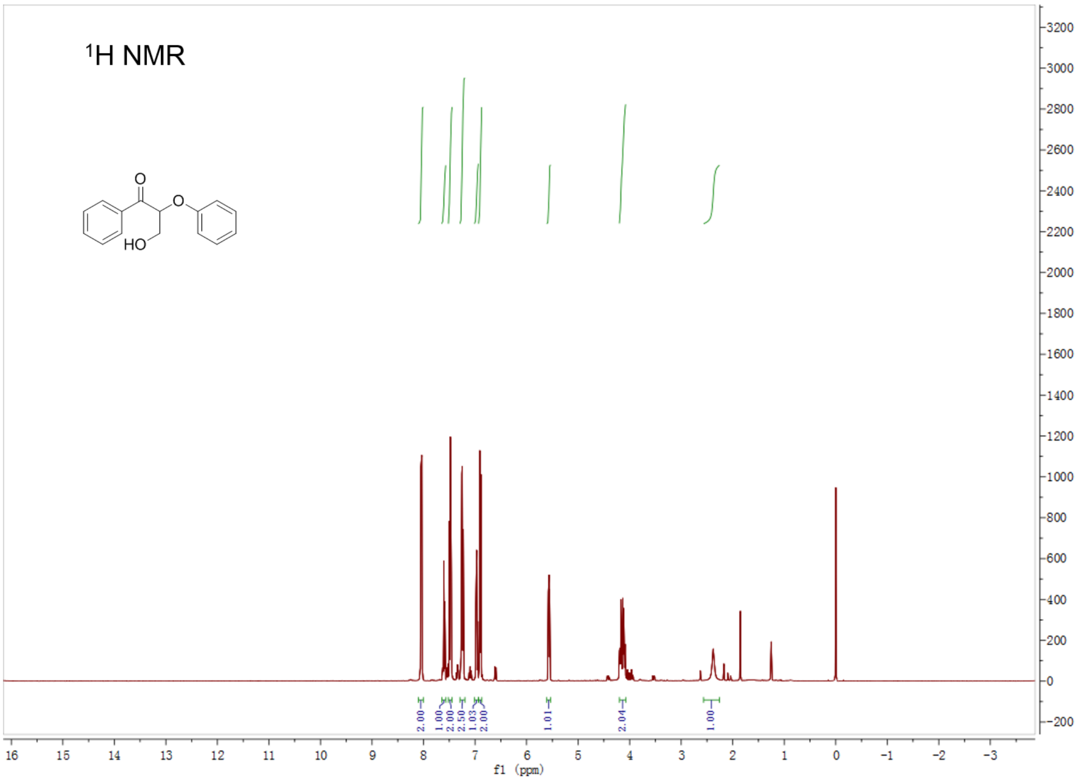


^{1}H NMR

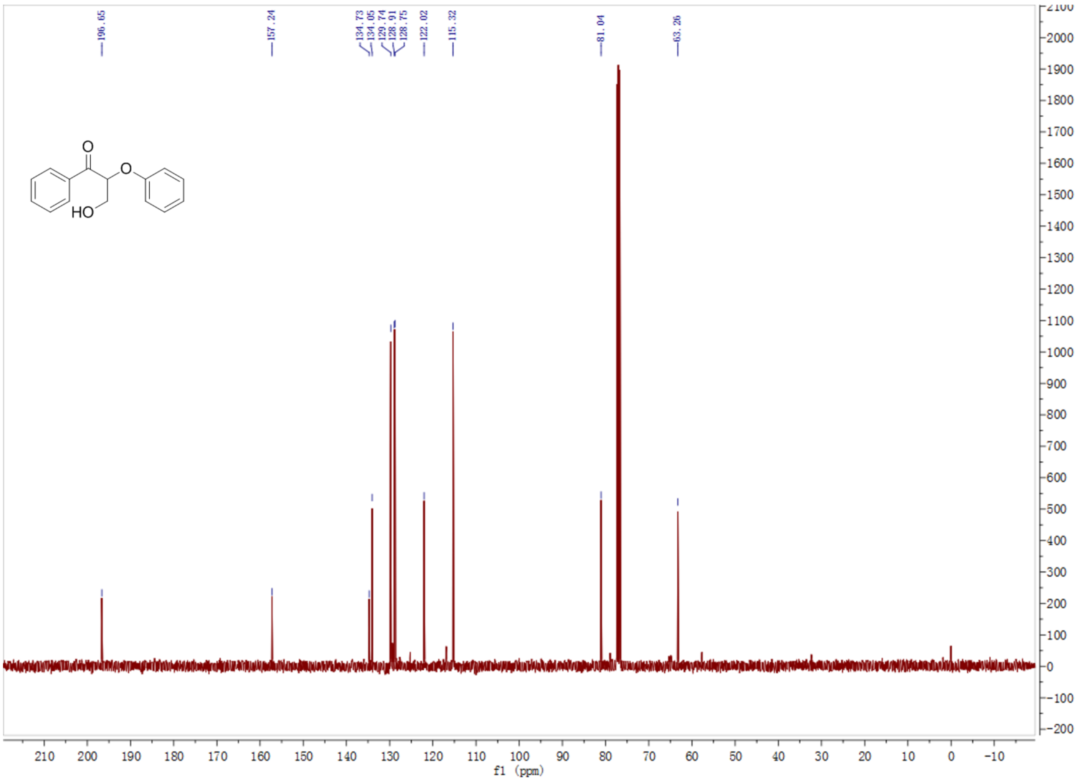


^{13}C NMR




^{1}H NMR
O
O
HO
2.00
1.00
2.00
2.50
1.03
2.00
1.01
2.04
1.00
f1 (ppm)

^{13}C NMR


196.65
157.24
134.73
134.05
129.74
128.91
128.75
122.02
115.32
81.04
63.26
O
O
HO
f1 (ppm)