Electronic Supplementary information for

Selective C–C bond cleavage of oxidized lignin in aqueous phase under mild conditions

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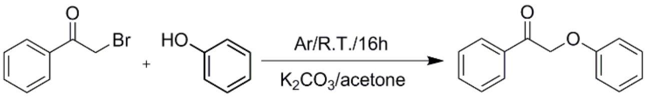
1. Chemicals and materials

CeO_2, Al_2O_3, MgO, ZnO, SiO_2, TiO_2, ZrO_2, CaO, HY, SBA-15, NaOH were all purchased from Meryer (Shanghai) Co., Ltd. Dichloromethane (99%), hydrochloric acid (37%), anhydrous Na_2SO_4 (99%), 1,2-Diphenylethanone (98%), Diphenylethanedione (98%), 2-Hydroxy-1-phenylethanone (98%), phenyl formate (>97%), phenol (99.5%), 2-bromoacetophenone (99%), and acetone (99%) were all purchased from Shanghai Macklin Biochemical Co., Ltd. D_2O (99.5%) and DMSO-d_6 (99.9%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All analytical reagent chemicals were used as received without further purification. Bamboo was obtained from the southern China. The CEL bmboom lignin was extracted according to a reported procedure. [1]

2. Synthesis and characterization of lignin models

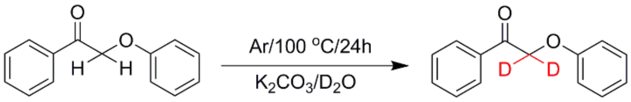
Preparation of 2-phenoxy-1-phenylethanone (1a)

2-Phenoxy-1-phenylethanone was prepared by reference.[2] To a solution of phenol (2.4 g, 25 mmol) and K_2CO_3 (3.5 g, 25 mmol) in acetone (50 mL) was added 2-bromoacetophenone (4.7g, 23 mmol) with Ar atmosphere protection and was stirred at RT for 16 h. After reaction, the suspension was filtered and concentrated in vacuum. The solid was dissolved in ethyl acetate and washed with NaOH aqueous and water successively. The organic phase was then dried by anhydrous Na_2SO_4. The crude product was recrystallized from ethanol to give 2-phenoxy-1-phenylethanone as a white solid in 78% yield. For the other methoxy substituted β-O-4 compounds, the procedures are the same as described above, except that different stating materials were used.

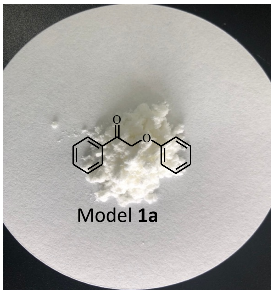


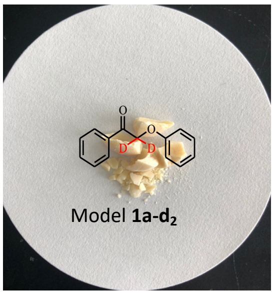
Procedure for the preparation of deuterium labelled 1a-d₂

The deuterated compound (Model 1a-d_2) was synthesized according to following procedure: 2-phenoxy-1-phenylethanone (1.1 g, 5.0 mmol) and anhydrous K_2CO_3 (0.1 g, 0.5 mmol) were added into D_2O (10 mL) in a 25 mL round bottom flask under argon atmosphere. The mixture was refluxed in an oil bath at 100 °C for 12 h. After cooling down to room temperature, the solvent was replaced by fresh D_2O under argon atmosphere, and further refluxed at 100 °C for another 12 h. Then the obtained solid was washed to remove K_2CO_3 residues. Finally, the solid was dried under vacuum to give a deuterated compound as a light yellow solid.



The structures of these compounds are confirmed by ^1H NMR and ^{13}C(Fig. S1-S5).


Model **1a**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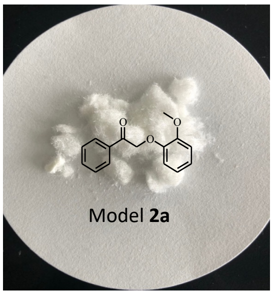
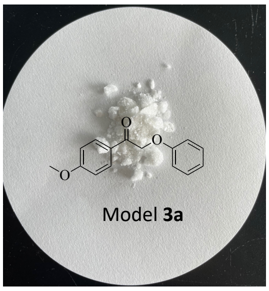

Model **2a**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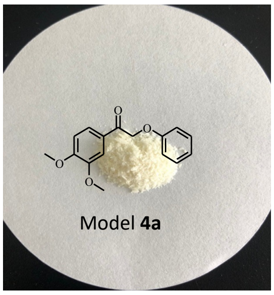
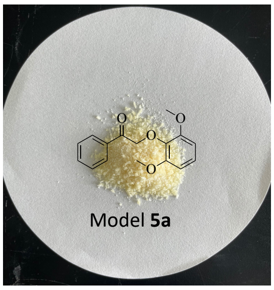
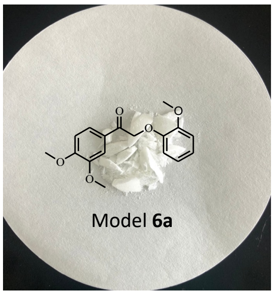
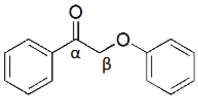

Model **4a**


Model **5a**


Model **6a**

^{1}H NMR and ^{13}C NMR:

Model **1a**:  2-phenoxy-1-phenylethanone.

White solid.^{1}H NMR (400 MHz, DMSO-d6) δ 8.03-8.05 (t, J = 7.3 Hz, 2H), 7.68-7.72 (t, J = 7.4 Hz, 1H), 7.56-7.60 (t, J = 7.7 Hz, 2H), 7.26-7.32 (m, 2H), 6.93-6.99 (m, 3H), 5.58 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ = 195.11, 158.39, 134.90, 134.25, 129.89, 129.31, 128.34, 121.34, 115.08, 70.50.

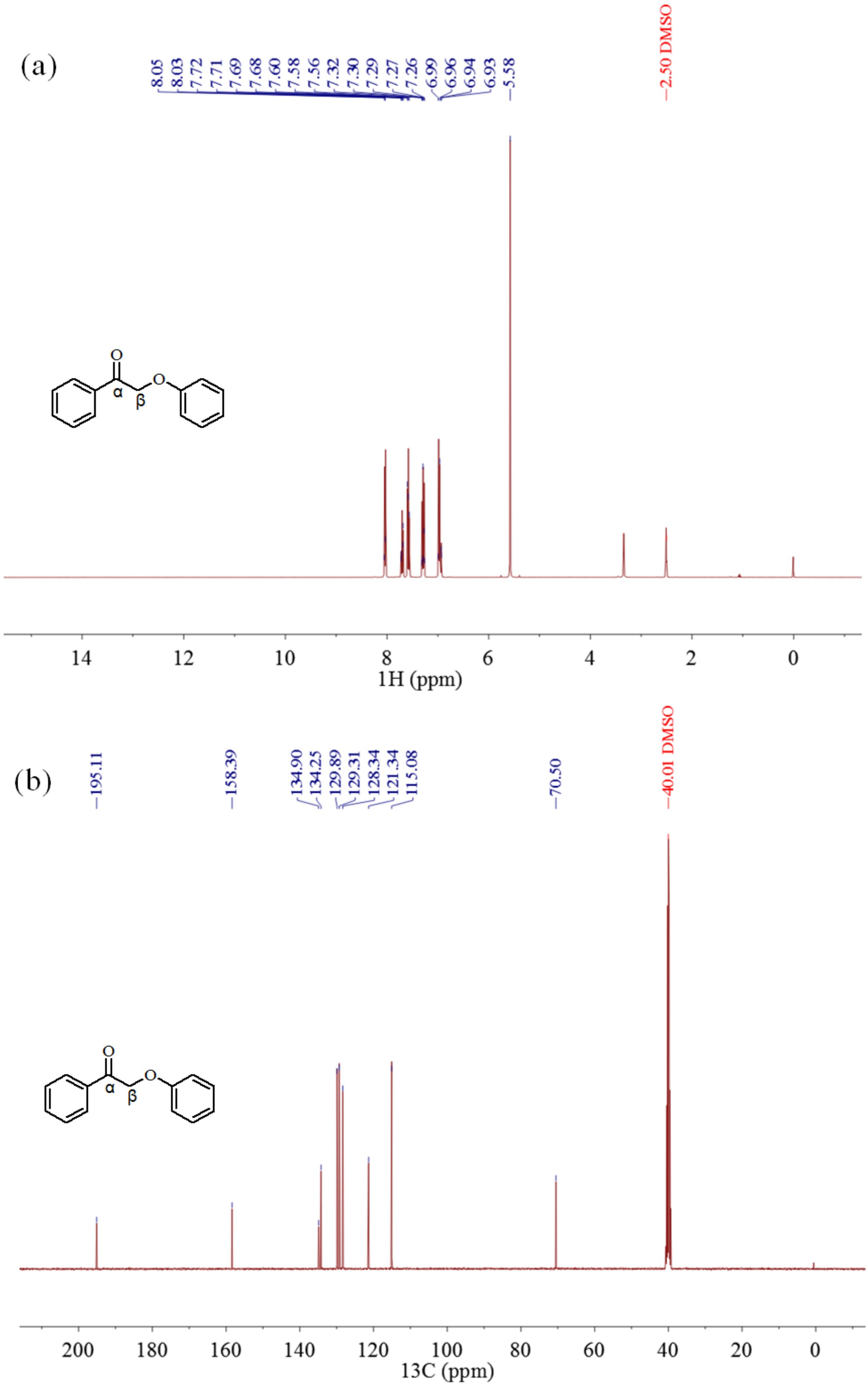
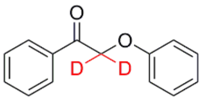
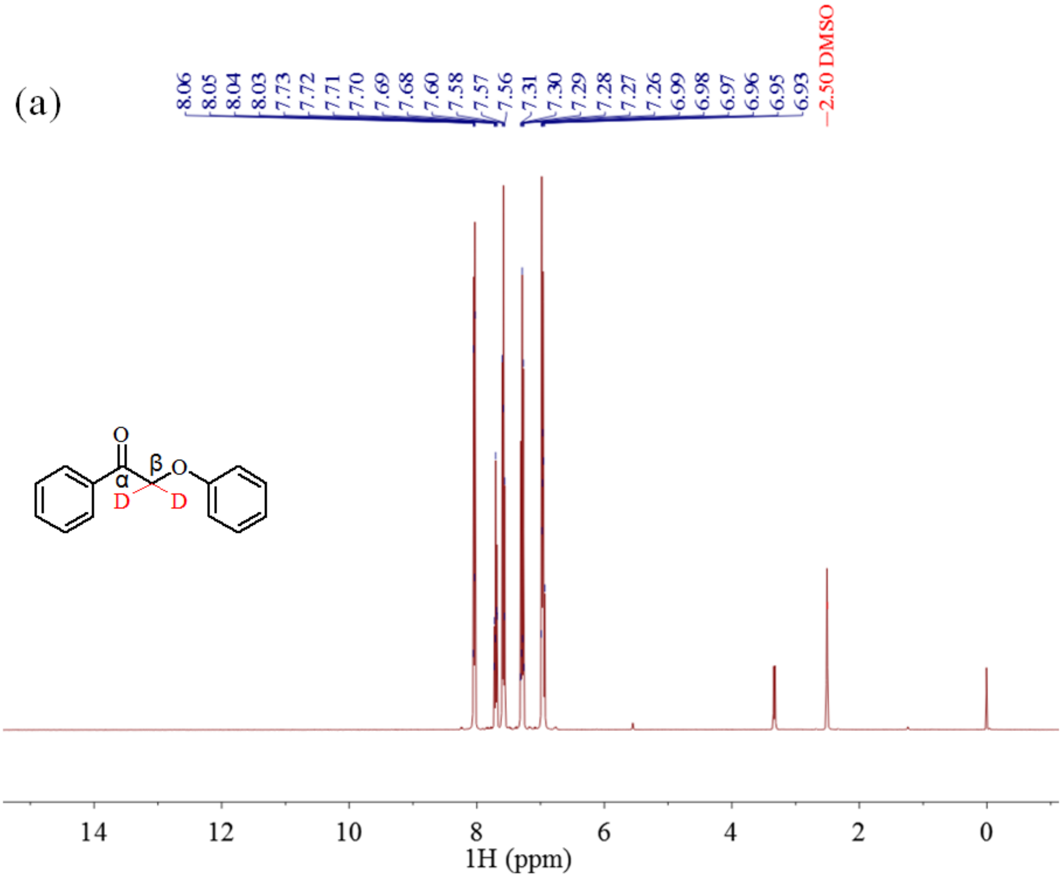


Fig. S1 ^{1}**H NMR and** ^{13}**C NMR spectra of model 1a**

Model 1a-d2:  2-phenoxy-1-phenylethanone.

Light yellow solid. 1H NMR (400 MHz, DMSO-d6) δ 8.03-8.06 (t, J = 7.3 Hz, 2H), 7.68-7.73 (t, J = 7.4 Hz, 1H), 7.56-7.60 (t, J = 7.7 Hz, 2H), 7.26-7.31 (m, 2H), 6.93-6.99 (m, 3H). 13C NMR (101 MHz, DMSO-d6) δ = 195.21, 158.39, 134.91, 134.26, 129.89, 129.31, 128.35, 121.32, 115.07.



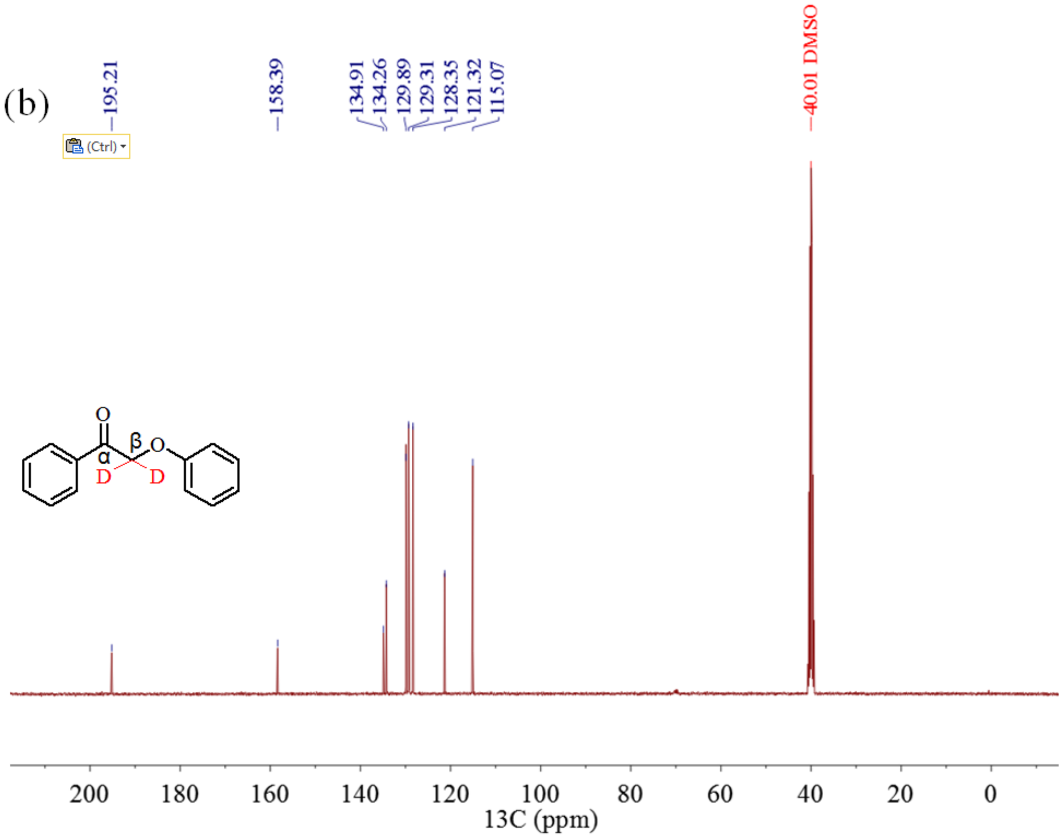
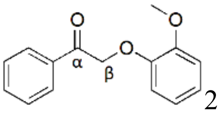


Fig. S2 ^{1}H NMR and ^{13}C NMR spectra of model 1a-d$_2$

Model 2a: 

2-(2-methoxyphenoxy)-1-phenyl-ethanone.

White solid.1H NMR (400 MHz, DMSO-d6) δ 8.03-8.04 (t, J = 7.4 Hz, 2H), 7.68-7.72 (t, J = 7.4 Hz, 1H), 7.55-7.59 (t, J = 7.8 Hz, 2H), 6.89-7.01 (m, 2H), 6.81-6.85 (m, 3H), 5.54 (s, 2H), 3.79(s, 3H). 13C NMR (101 MHz, DMSO-d6) δ = 195.20, 149.47, 147.91, 134.94, 134.21, 129.29, 128.36, 121.84, 121.02, 114.21, 112.96, 71.23, 56.03.

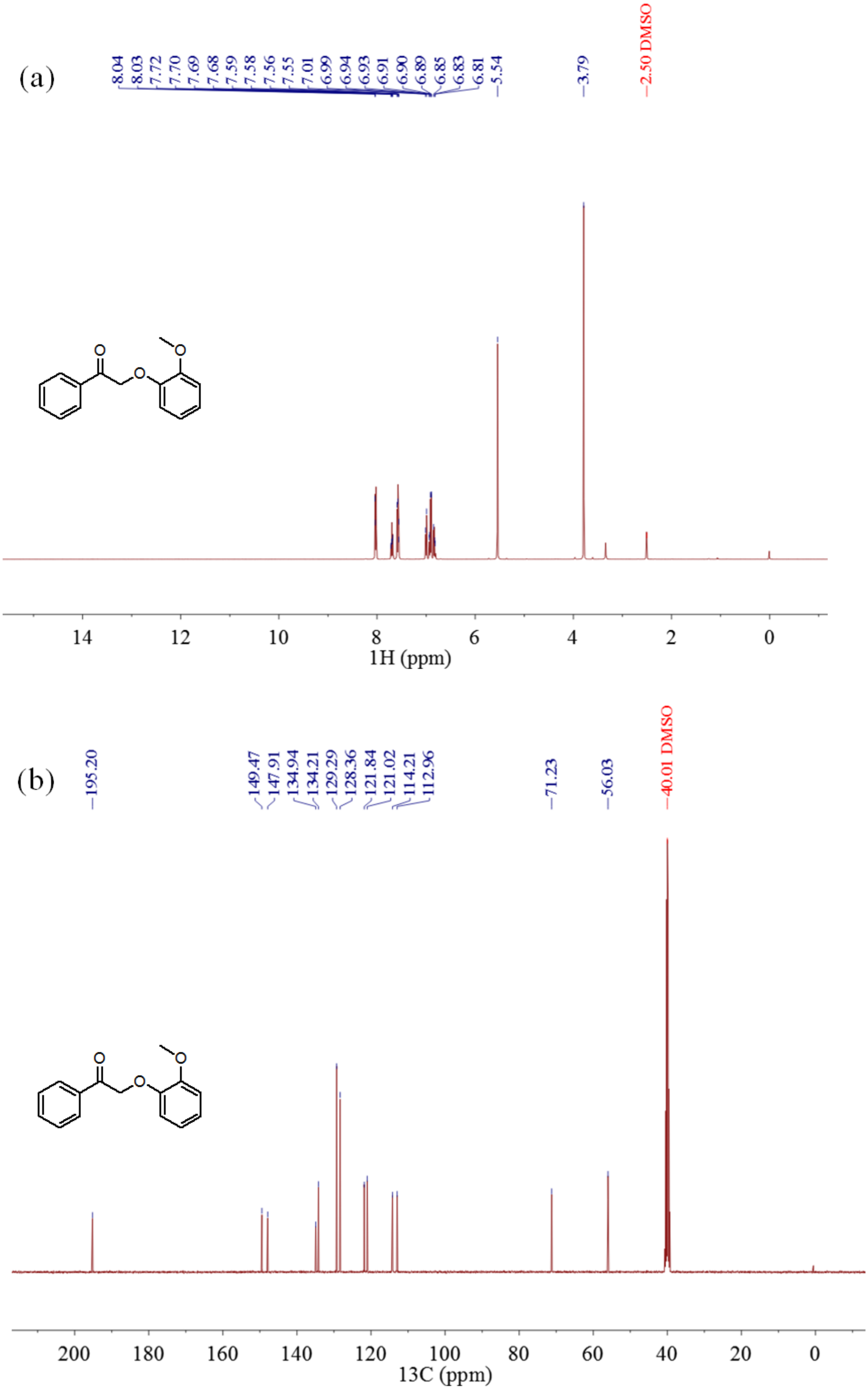
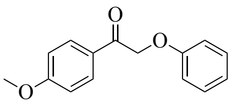
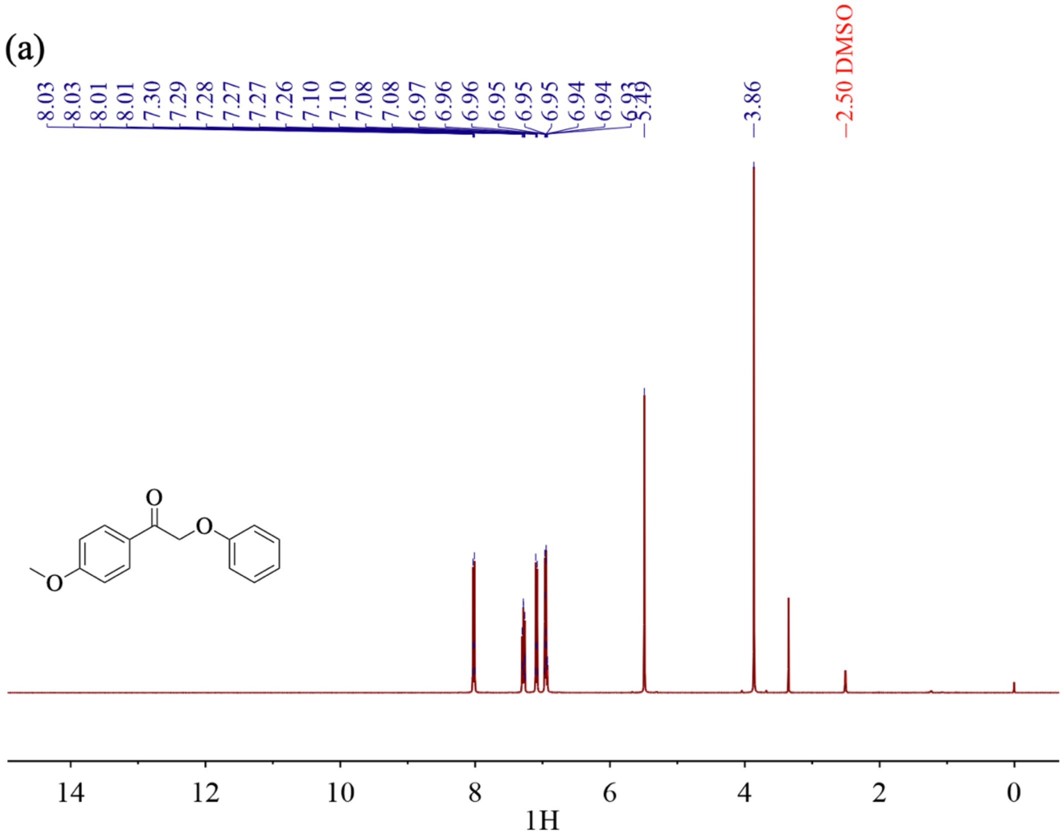


Fig. S3 ^{1}H NMR and ^{13}C NMR spectra of model 2a.

Model 3a: 

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 – 7.98 (m, 1H), 7.33 – 7.23 (m, 1H), 7.13 – 7.05 (m, 1H), 7.00 – 6.90 (m, 2H), 5.49 (s, 1H), 3.86 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.40 , 164.02 , 158.45 , 130.70 , 129.86 , 127.79 , 121.26 , 115.05 , 114.52 , 70.23 , 56.07 , 40.00 .



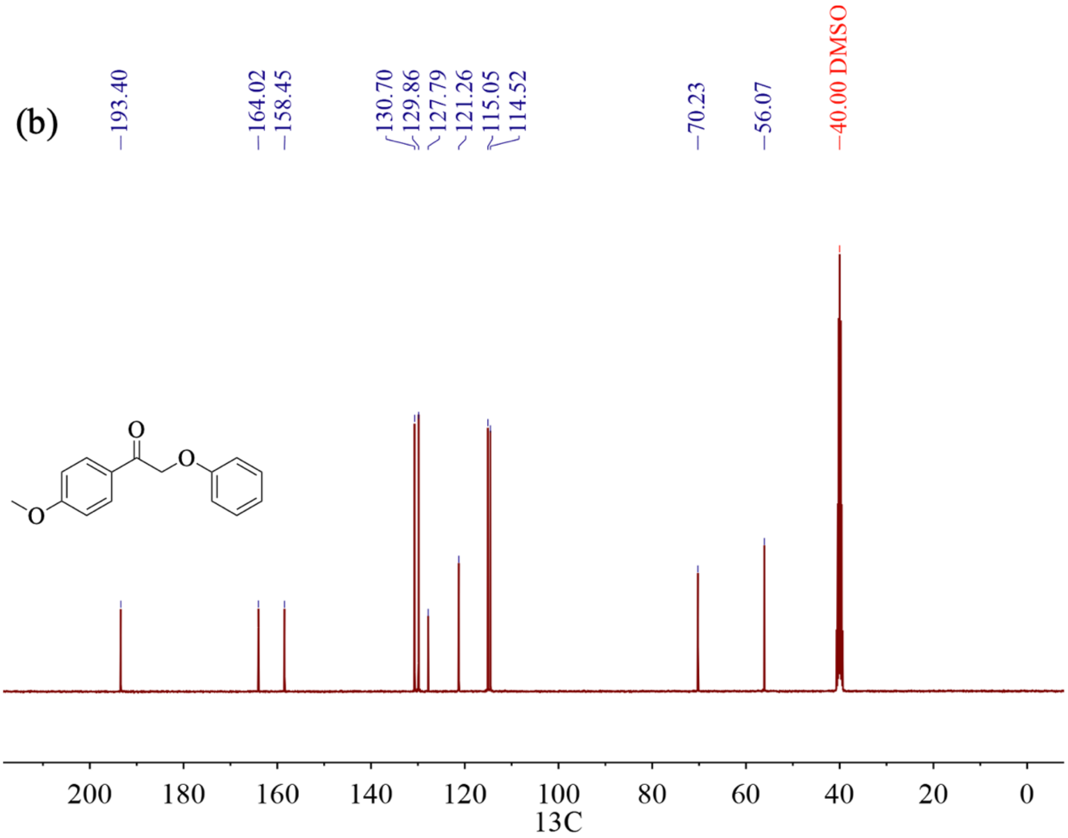
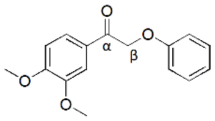


Fig. S4 ^{1}H NMR and ^{13}C NMR spectra of model 3a.



Model 4a: 1-(3,4-dimethoxyphenyl)-2-phenoxyethanone.

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d6) δ = 7.72-7.74 (dd, J = 8.4 Hz, 1.9, 1H),7.50 (d, J = 1.9 Hz, 1H), 7.26-7.31 (m, 2H), 6.93 –7.12(m, 4H), 5.51 (s, 2H), 3.84-3.87(d, J = 8.5 Hz, 6H). 13C NMR (101 MHz, DMSO-d6) δ = 193.47, 158.48, 154.02, 149.19, 129.87, 127.72, 123.07, 121.27, 115.09, 111.50, 110.63, 70.24, 56.30, 56.06.

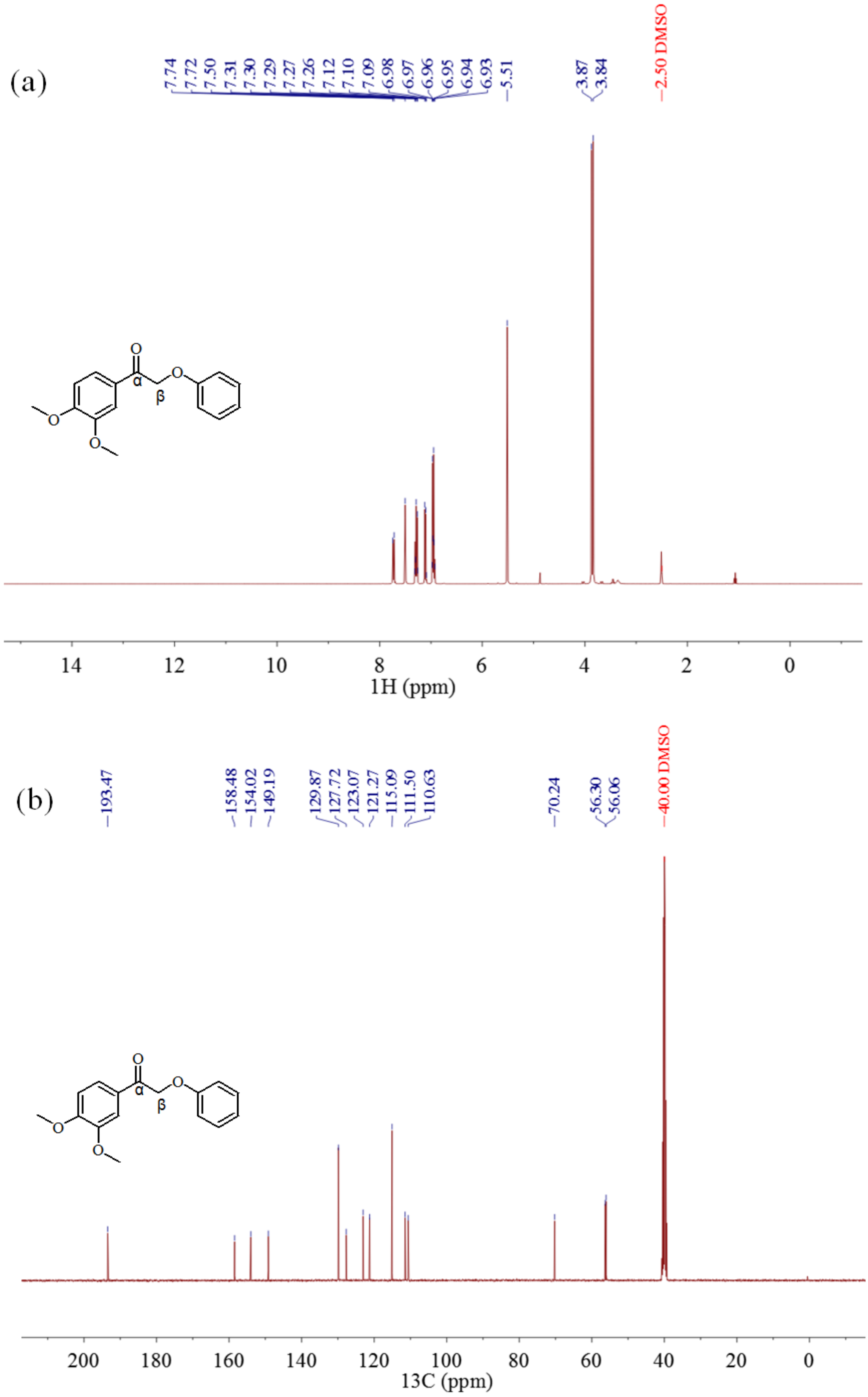
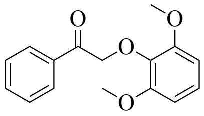
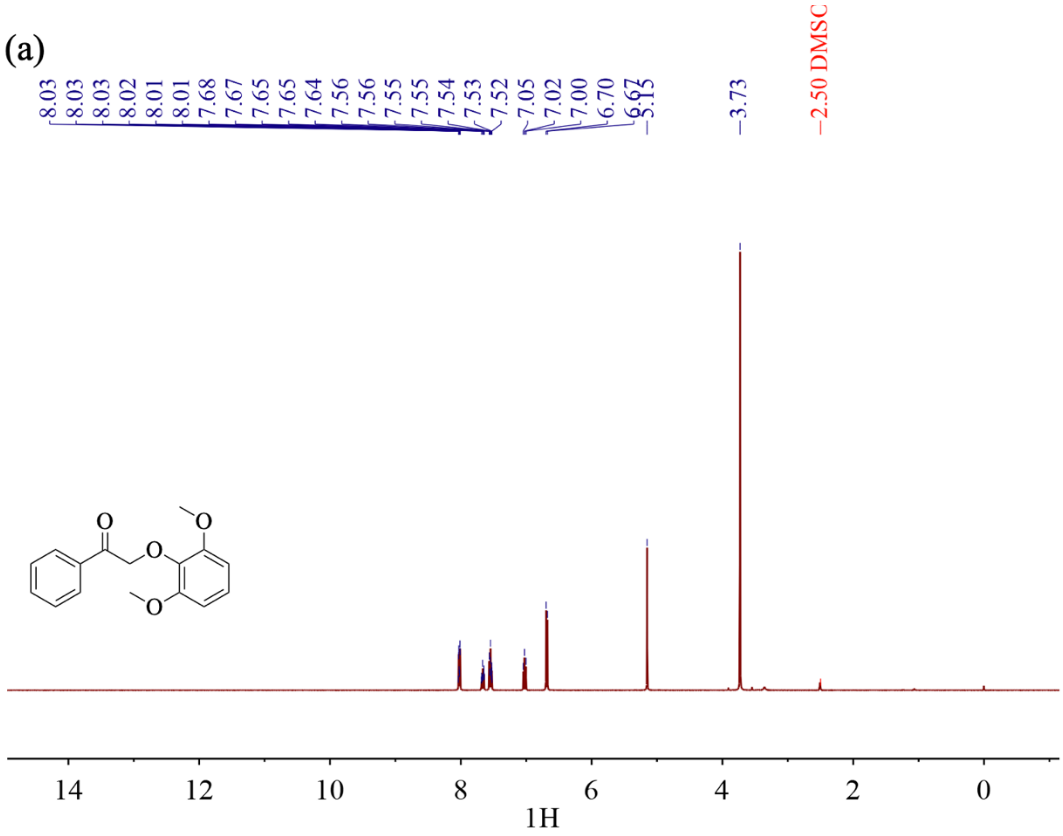


Fig. S5 ^{1}H NMR and ^{13}C NMR spectra of model 3a

Model 5a: 

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.06 – 7.98 (m, 2H), 7.71 – 7.62 (m, 1H), 7.59 – 7.50 (m, 2H), 7.02 (t, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 195.41 , 153.19 , 133.92 , 129.16 , 128.58 , 124.40 , 106.09 , 75.21 , 56.32 , 40.20 .



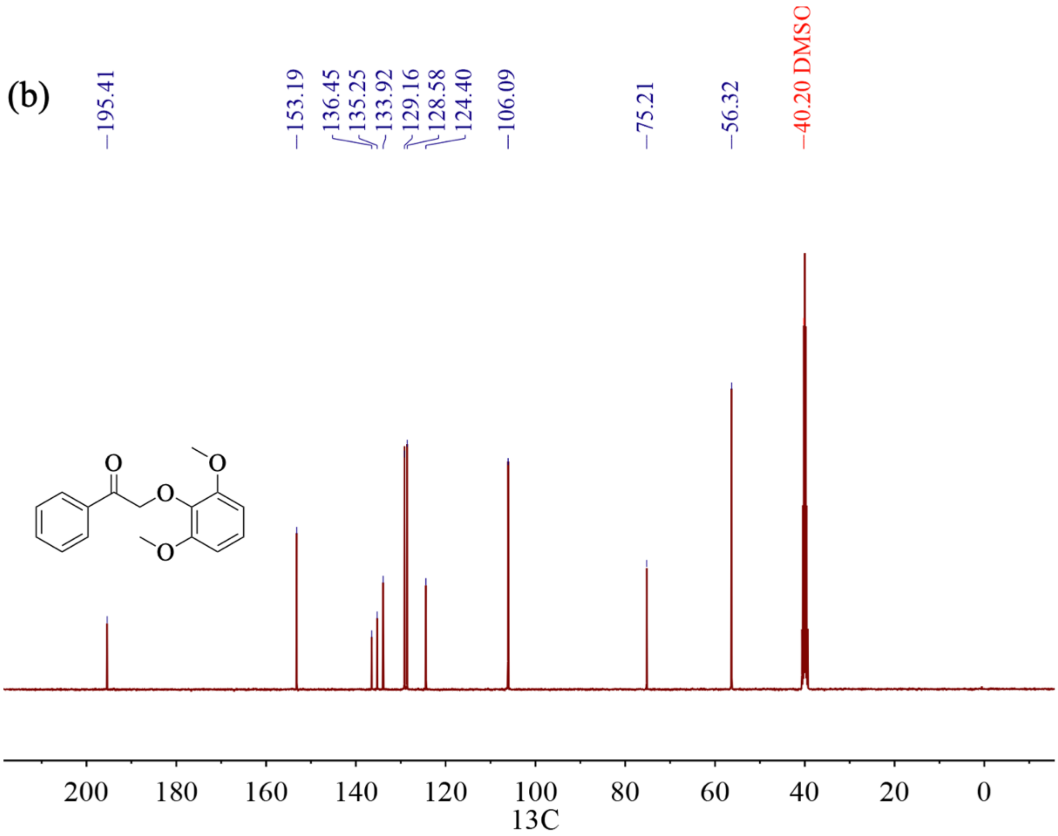
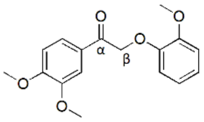


Fig. S6 ^{1}H NMR and ^{13}C NMR spectra of model 5a.

Model 6a: 

1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone. White solid. 1H NMR (400 MHz, DMSO-d6) δ 7.72 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 6.99 (dd, J = 8.0, 1.5 Hz, 2H), 6.96 – 6.78 (m, 2H), 5.47 (s, 2H), 3.85 (d, J = 12.6 Hz, 9H). 13C NMR (101 MHz, DMSO-d6) δ = 193.58, 153.99, 149.46, 149.16, 147.99, 127.76, 123.08, 121.78, 121.00, 114.15, 112.95, 111.48, 110.70, 71.01, 56.29, 56.03.

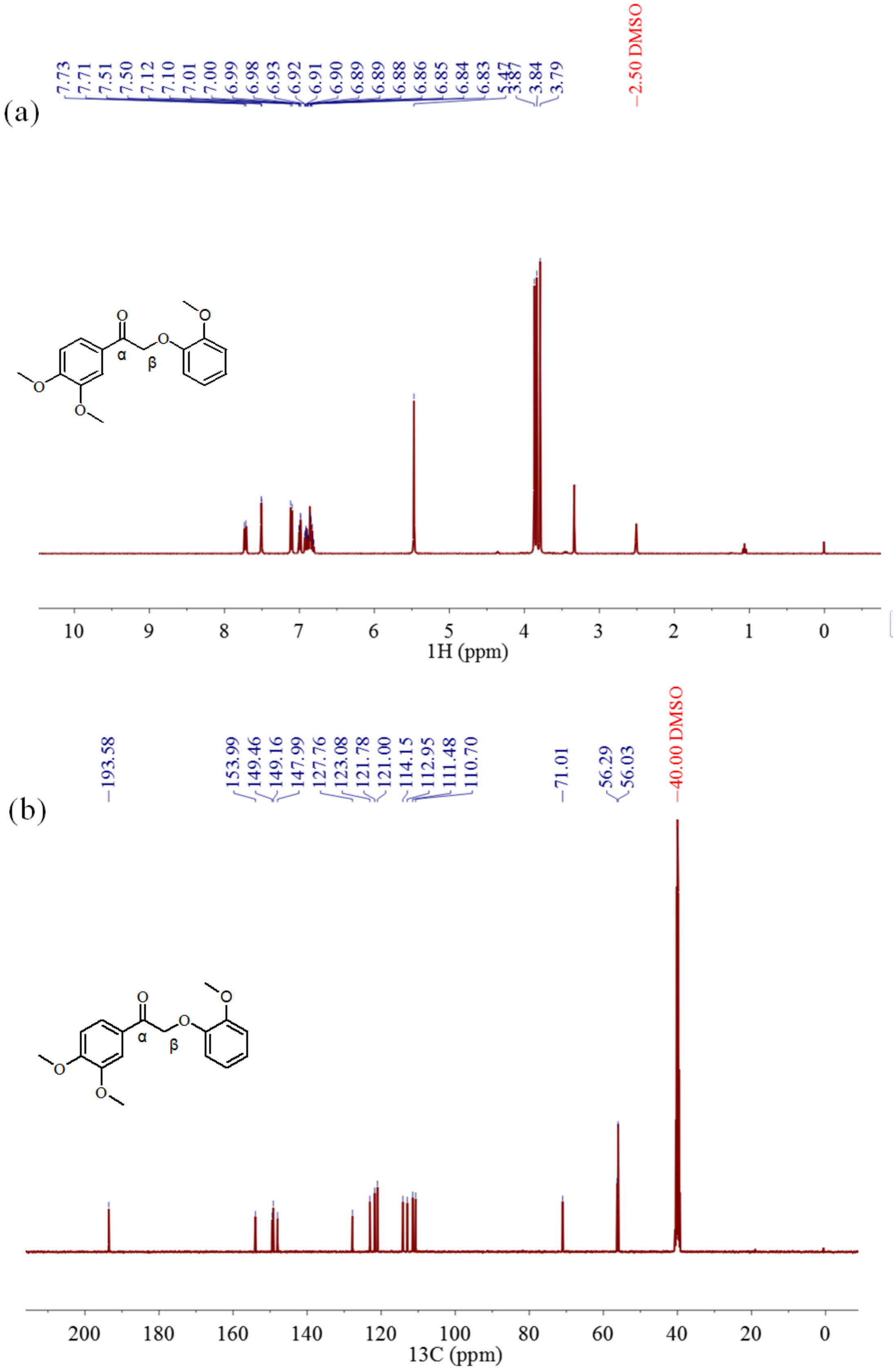


Fig. S7 ^{1}H NMR and ^{13}C NMR spectra of model 6a.

3. Bond dissociation energies of lignin model and possible intermediates calculated by DFT

BDEs were obtained as the difference of the sum of the energies of the dissociated product fragments and the energy of the molecule.

$$BDE= (E_{Frag1} + E_{Frag2})- E_{Mol} \qquad (1)$$

where E_{Mol} is the total energy of the molecule, E_{Frag1} and E_{Frag2} are energies of the dissociated products through the selected C-C linkages. All dissociated fragments were fully optimized.

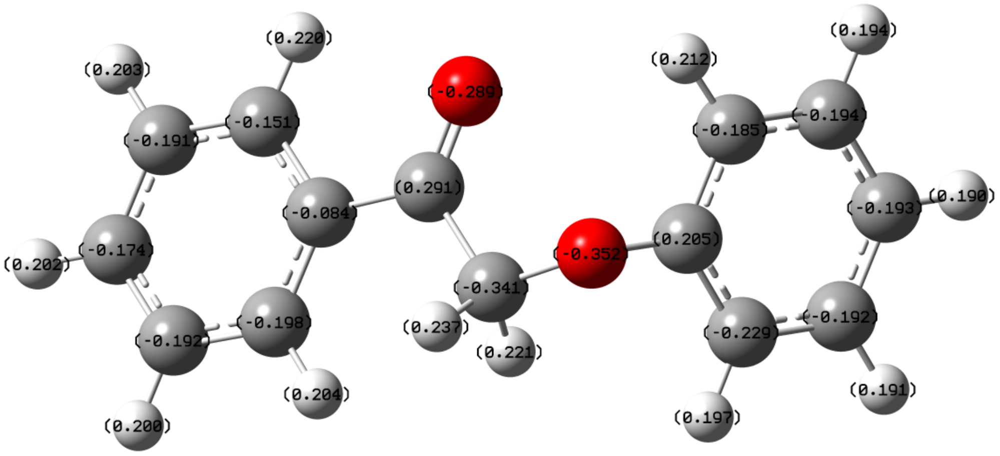


Fig. S8 Optimized structure and Charge distribution of model 1a.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.995225	-1.304849	-0.431142
2	6	0	-2.694516	-1.147097	0.037367
3	6	0	-2.131487	0.130777	0.143863
4	6	0	-2.893480	1.245296	-0.227425
5	6	0	-4.190174	1.087167	-0.696105
6	6	0	-4.743869	-0.189369	-0.798308
7	1	0	-4.424240	-2.297917	-0.509687
8	1	0	-2.129135	-2.027688	0.318975
9	1	0	-2.442505	2.226170	-0.137543
10	1	0	-4.772605	1.956359	-0.982137
11	1	0	-5.757707	-0.314063	-1.163838
12	6	0	-0.743423	0.366637	0.648995

13	6	0	0.087472	-0.860950	1.040627
14	1	0	0.149696	-1.545209	0.185133
15	1	0	-0.419880	-1.393863	1.849793
16	6	0	2.332679	-0.270388	0.561823
17	6	0	2.822213	1.024399	0.418554
18	6	0	2.851812	-1.313132	-0.203822
19	6	0	3.842239	1.272452	-0.495466
20	1	0	2.380896	1.812928	1.013349
21	6	0	3.864823	-1.053829	-1.123923
22	1	0	2.479303	-2.321905	-0.058861
23	6	0	4.362831	0.238555	-1.272176
24	1	0	4.224982	2.281479	-0.607930
25	1	0	4.272141	-1.866384	-1.716566
26	1	0	5.155183	0.438230	-1.985533
27	8	0	1.367312	-0.521321	1.521675
28	8	0	-0.285749	1.483552	0.750533

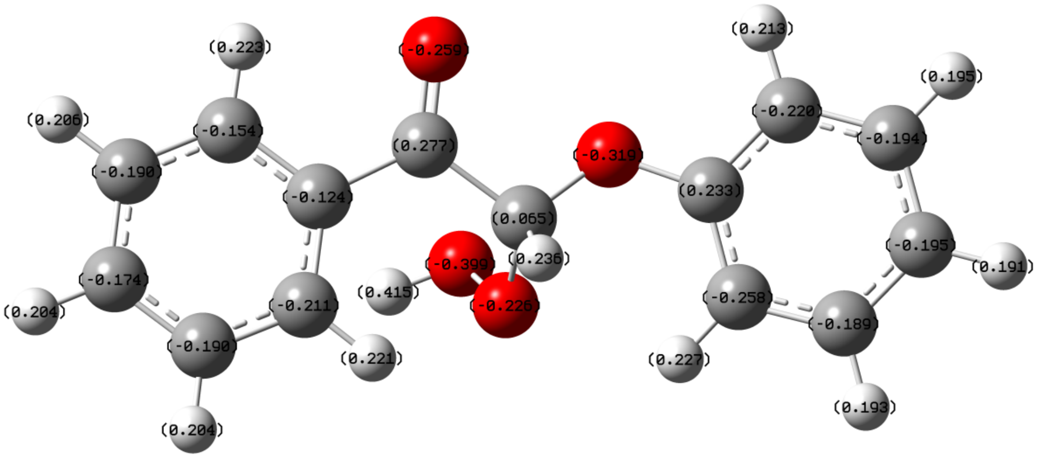


Fig. S9 Optimized structure and Charge distribution of hydroperoxide intermediate f.

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	3.901793	-1.516573	-0.685262
2	6	0	2.604361	-1.039977	-0.518476
3	6	0	2.383080	0.312745	-0.222639
4	6	0	3.483203	1.173540	-0.105721
5	6	0	4.775314	0.693113	-0.263004
6	6	0	4.987496	-0.654800	-0.554076

7	1	0	4.063249	-2.563214	-0.919399
8	1	0	1.773791	-1.726416	-0.612924
9	1	0	3.295254	2.218543	0.108360
10	1	0	5.618958	1.367254	-0.162612
11	1	0	5.997064	-1.031186	-0.680666
12	6	0	1.024887	0.923182	-0.062619
13	6	0	-0.200131	-0.025444	0.013782
14	6	0	-2.558728	0.264143	0.042143
15	6	0	-2.867293	-1.087528	-0.109598
16	6	0	-3.548550	1.236454	-0.102022
17	6	0	-4.174605	-1.452944	-0.431706
18	1	0	-2.115902	-1.846662	0.060996
19	6	0	-4.847737	0.856350	-0.411852
20	1	0	-3.271847	2.276318	0.025294
21	6	0	-5.166813	-0.490905	-0.585266
22	1	0	-4.414418	-2.504766	-0.547438
23	1	0	-5.613445	1.616478	-0.525499
24	1	0	-6.181374	-0.785691	-0.829610
25	8	0	-1.302850	0.739981	0.350018
26	8	0	0.867169	2.117882	-0.022615
27	8	0	0.028092	-1.114232	0.888332
28	8	0	0.529899	-0.584598	2.145529
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30	1	0	-0.351063	-0.530321	-0.950711

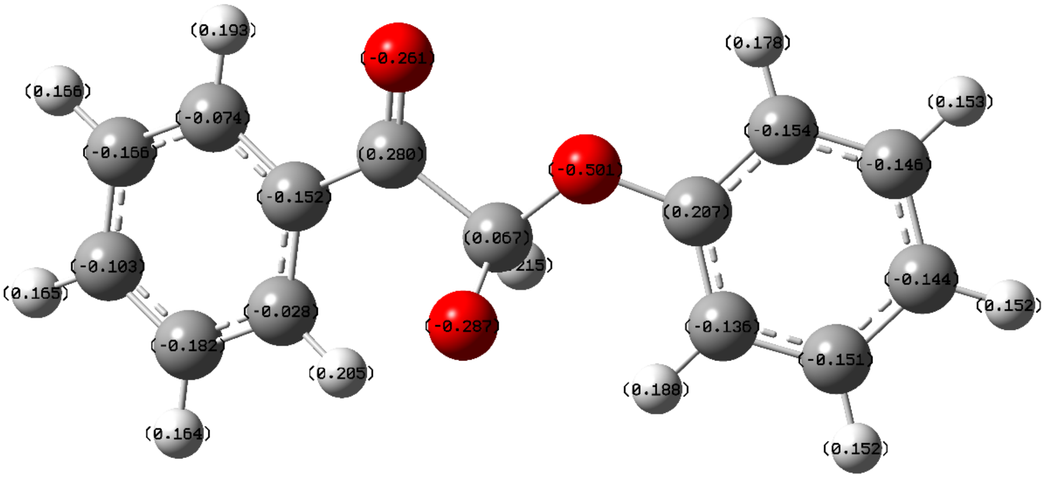

Fig. S10 Optimized structure and Charge distribution of radical intermediate g.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.779884	0.590962	0.571325
2	6	0	3.531647	1.114614	0.253985
3	6	0	2.456303	0.254023	-0.038340
4	6	0	2.654176	-1.137059	-0.015841
5	6	0	3.909742	-1.653889	0.299779
6	6	0	4.970601	-0.795028	0.597230
7	1	0	5.601383	1.256073	0.796897
8	1	0	3.364973	2.181409	0.227498
9	1	0	1.847887	-1.800414	-0.285092
10	1	0	4.060710	-2.723979	0.307200
11	1	0	5.941743	-1.201802	0.843392
12	6	0	1.155626	0.875317	-0.345302
13	6	0	-0.139739	-0.081739	-0.367737
14	1	0	-0.126810	-0.601525	0.604773
15	6	0	-2.531273	0.263471	-0.094817
16	6	0	-2.845816	-1.094762	-0.176883
17	6	0	-3.483334	1.197441	0.318716
18	6	0	-4.132325	-1.515383	0.176999
19	1	0	-2.121831	-1.807961	-0.541114
20	6	0	-4.763244	0.765790	0.659149
21	1	0	-3.199423	2.238096	0.361923
22	6	0	-5.092138	-0.593542	0.595866
23	1	0	-4.380485	-2.565938	0.111820
24	1	0	-5.502408	1.488069	0.977481
25	1	0	-6.085166	-0.925861	0.863855
26	8	0	0.993055	2.074775	-0.528536
27	8	0	-1.273302	0.791883	-0.432282
28	8	0	0.002592	-0.951342	-1.398358

4. Supplementary experimental results

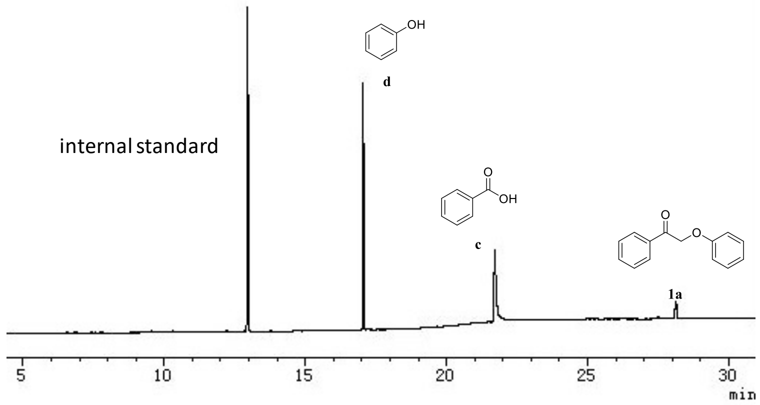

Fig. S11 Gas chromatogram of the conversion of **1a** over the Pd/CeO$_2$ catalyst at 50 °C for 3h. The external standard (ES) is acetophenone.

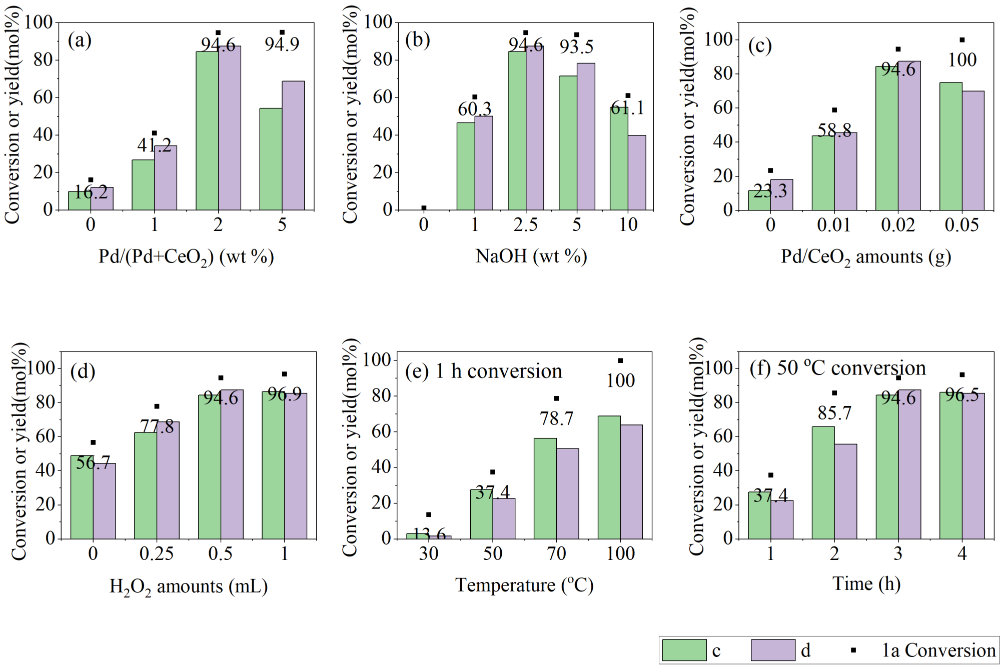

Fig. S12 Effect of (a) Pd loadings and (b) base concentration on catalytic performances of Pd/CeO$_2$ for the oxidation of **1a**. Optimization of reaction conditions by adjusting the amounts of (c) Pd/CeO$_2$ and (d) H$_2$O$_2$. Optimization of reaction conditions by changing (e) temperatures and (f) reaction time. Typical conditions: **1a** (0.1 mmol), catalyst (0.02 g), H_2O_2(30%, 0.5mL), NaOH aqueous solution (2.5 wt %, 2.5 mL), 50 °C, 3h.

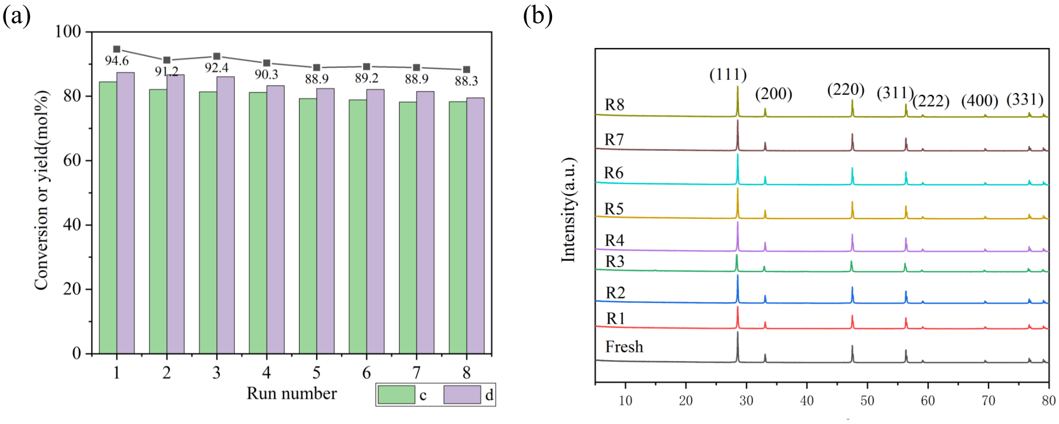

Fig. S13 (a) Performance on oxidative cleavage of 1a over recycled Pd/CeO_2 catalysts. (b) XRD spectra of fresh and recycled Pd/CeO_2 catalysts. Conditions: 1a (0.1 mmol), catalyst (0.02g), H_2O_2 (30%, 0.5mL), NaOH aqueous solution (2.5 wt.%, 2.5 mL), 50 °C, 3h.

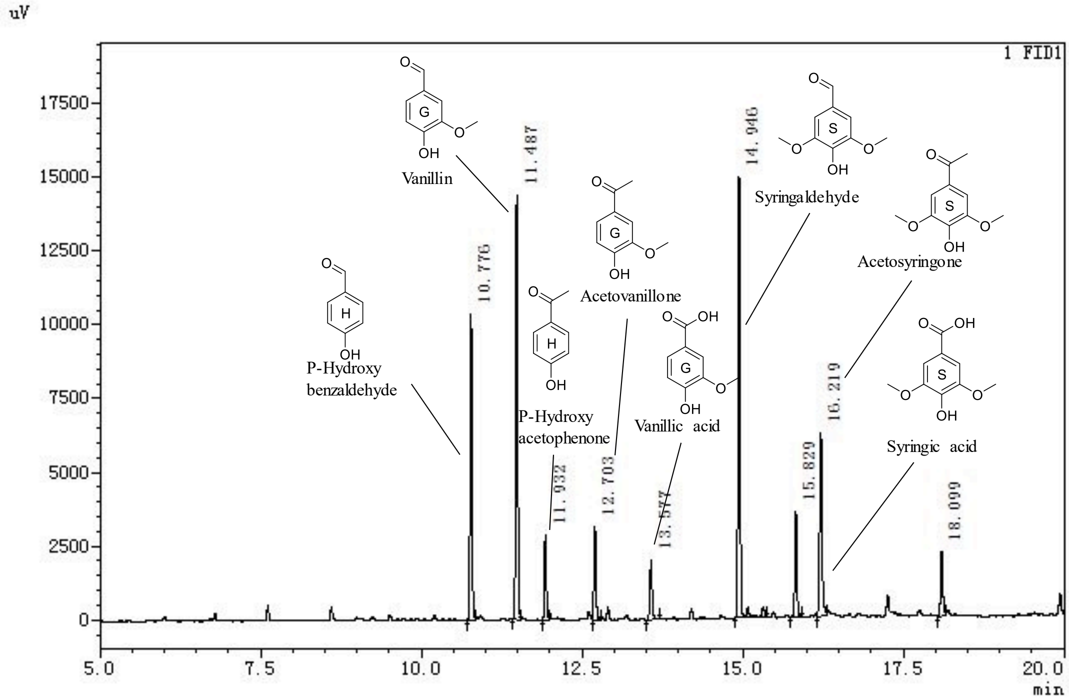

Fig. S14 Gas chromatogram of the monomers obtained from the depolymerisation of oxidized bamboo lignin.

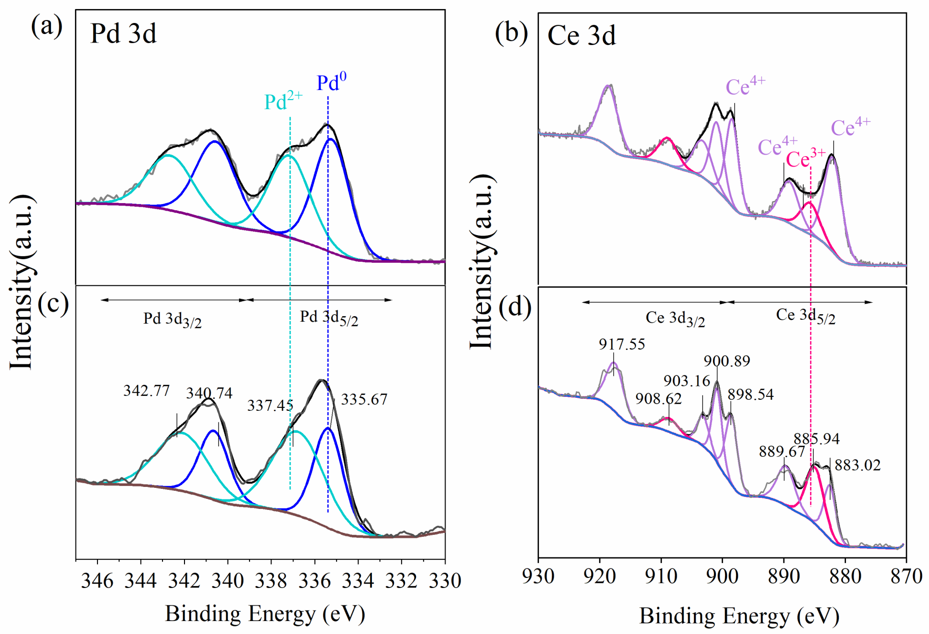

Fig. S15 Ex-situ XPS spectra of Pd 3d (a) before and (c) after treatment at reaction conditions without reactant. Ex-situ XPS spectra of Ce 3d (b) before and (d) after treatment at reaction conditions without reactant.

Table S1 The actual palladium content of the prepared catalysts determined by ICP.

Entry	Sample	Pd content (wt.%)
1	1 wt.% Pd/CeO_2	0.95
2	2 wt.% Pd/CeO_2	1.90
3	5 wt.% Pd/CeO_2	4.56
4	Pd/Al_2O_3	1.82
5	Pd/ZrO_2	1.94
6	Pd/MgO	1.82
7	Pd/ZnO	1.88
8	Pd/TiO_2	1.95
9	Pd/CaO	1.89
10	Pd/SiO_2	1.99

11	Pd/HY	1.83
12	Pd/SBA-15	1.92

Table S2 The Pd^0/Pd^{2+} value of different Pd catalysts determined by XPS.

Entry	Sample	Pd^0/Pd^{2+}
1	Pd	1.15
3	Pd/CeO_2	1.16
5	Pd/SiO_2	0.96
6	Pd/Al_2O_3	0.90

Table S3 Radical inhibition experiments using TEMPO as a radical quenching agent.

Substrate	TEMPO (equiv.)	Conversion (%)	Yields (C mol%)	
			acid	**phenol**
1a	-	94.6	84.5	87.4
	1	33.7	16.9	19.3
	0.5	57.2	40.5	35.7
2a	-	100.0	81.3	94.9
	1	41.2	23.9	27.8
	0.5	62.9	50.2	49.8
3a	-	95.5	82.4	89.5
	1	22.3	12.2	10.8
	0.5	49.7	33.5	38.9
4a	-	93.7	76.8	88.3
	1	30.9	15.9	17.7
	0.5	59.8	42.8	45.5
5a	-	92.0	80.2	79.9
	1	35.5	23.6	22.1
	0.5	58.7	46.3	42.2

6a	-	100.0	78.3	92.2
	1	34.3	18.9	17.7
	0.5	60.4	49.4	45.8

Conditions: lignin model (0.1 mmol), 2 wt% Pd/CeO_2 (0.02g), H_2O_2 (30%, 0.5mL), NaOH aqueous solution (2.5 wt %, 2.5 mL), 50 °C and 3 h.

Reference

[1] H.M. Chang, E.B. Cowling, W. Brown, E. Adler, G. Miksche, COMPARATIVE STUDIES ON CELLULOLYTIC ENZYME LIGNIN AND MILLED WOOD LIGNIN OF SWEETGUM AND SPRUCE, Holzforschung, 29 (1975) 153-159.