

**Photo-Induced solvent-enabled catalyst-/additive-free
selective C(α)-C(β) bond cleavage of β -O-4 ketone lignin
model compounds at room temperature**

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Content of the supporting information

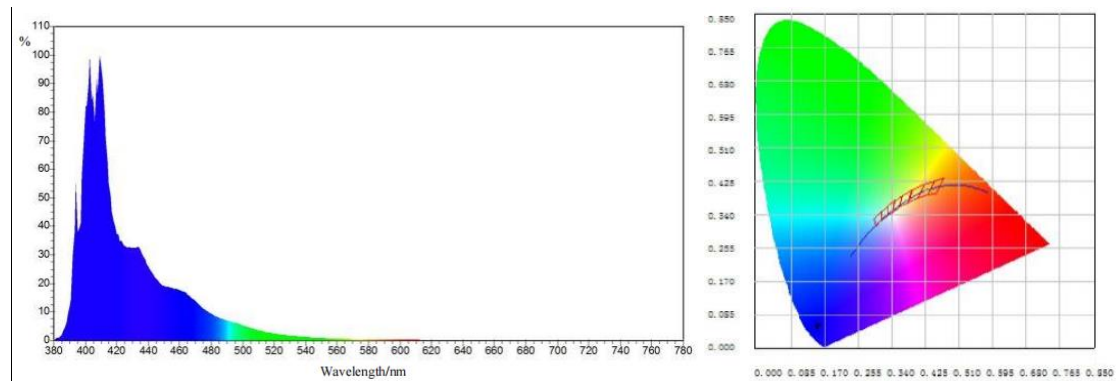
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1. General Information

¹H NMR spectra were recorded on 600 MHz or 400 MHz spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl₃. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ¹³C NMR spectra were obtained at 151 MHz or 100 MHz spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl₃). CDCl₃ was used as the NMR solvent. Shimadzu GCMS-QP2010SE was used to monitor the reaction process. Bruker EMXplus was used to measure the Electron Paramagnetic Resonance (EPR). The reaction was performed in a Quartz tube. Organic solutions were concentrated by rotary evaporation below 40 °C in vacuum with carefully control of the vacuum.

All the reagents (including the aromatic sulfonyl chlorides) and solvents were purchased as reagent grade and were used without further purification. The lignin model compounds **1aa**, **1ab**, **1ac**, **1ad**, **1ae**, **1af**, **1ag**, **1ah**, **1ba**, **1ca**, **1cd**, **1da**, **1dd**, **1ea**, **1ed**, **1fa**, **4aa**, **4ac**, **4da**, **4de**, **4ae** and **4ah** were synthesized based on the literature reports.⁷ Flash column chromatography was performed over silica gel 200-300 mesh and the eluent was a mixture of petroleum ether (PE)/ethyl acetate (EtOAc) as shown in detailed procedure.

2. Light source test report

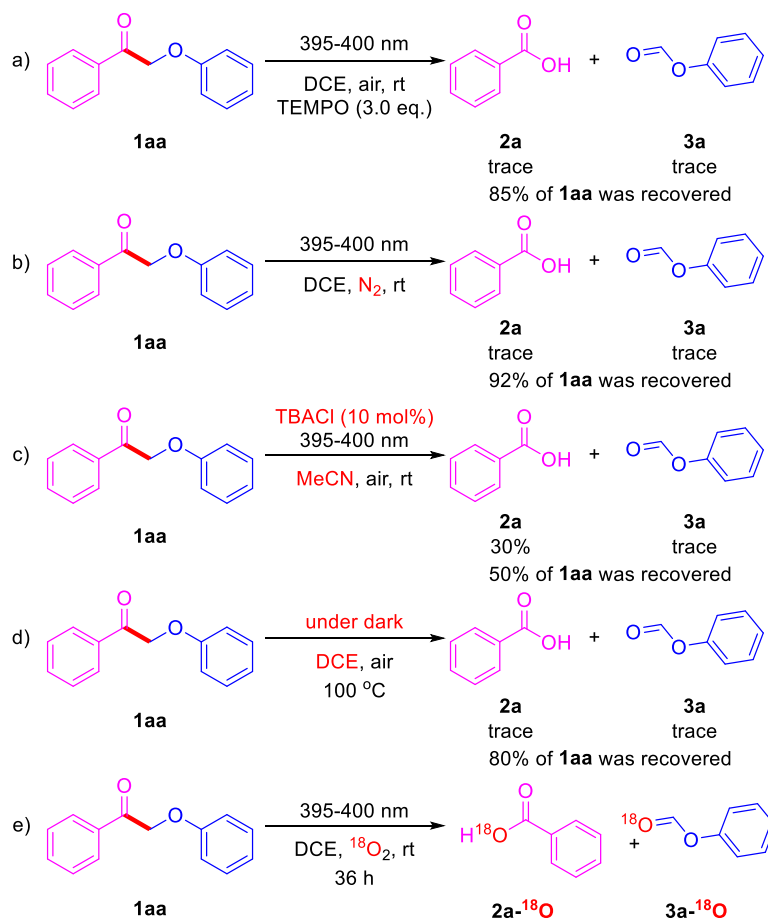


Chromaticity coordinates	X=0.1582	y=0.0607/u=01855	V=0.1067	Duv=-0.1085	
Correlated color temperature	Tc=100000 K	dominant wavelength	$\lambda_d=462.1$ nm	color purity	Purity-90.1%
color ratio	R=0.3% G=4.0% B=95.7%	peak wavelength	$\lambda_p=409.6$ nm	half width	$\Delta\lambda_d=18.6$ nm
Color rendering index: Ra=-2.5					
R1=9.2	R2 =37.9	R3 =-53.3	R4=-46.6	R5=20.5	
R6=10.4	R7 =13.7	R8=-11.4	R9 =-230.1	R10=-45.0	
R11=-75.5	R12=-69.4	R13=24.7	R14=15.2	R15=34.0	
Photometric parameters:					
Luminous flux	$\Phi=14.833$ Lm	light micro 5.606 Lm/W	5.606 Lm/W $\Phi_e = 508.82$ mW		
Electrical parameters					
Forward Voltage: VF=3.78 V	Forward current: IF=700.0 mA		Power P=2.646 W		

Figure S1. LED Spectral Test Report

3. Experimental Section

3.1 Control experiment to explore the mechanism.



Scheme S1. Control experiments to explore the possible mechanism. Conditions: The reaction was performed with standard condition open to air unless otherwise noted. Substrate **1aa** (21.2 mg, 0.1 mmol) in DCE (1 mL, 0.1 M) under 395-400 nm light irradiation. a) TEMPO (46.8 mg, 0.3 mmol) was added; b) the reaction was performed under N₂ atmosphere. c) TBACl in MeCN (0.1 M, 1 mL) irradiated at 395-400 nm at air atmosphere for 24 h. d) The reaction was performed in the dark. e) the reaction was performed in the ¹⁸O₂ atmosphere.

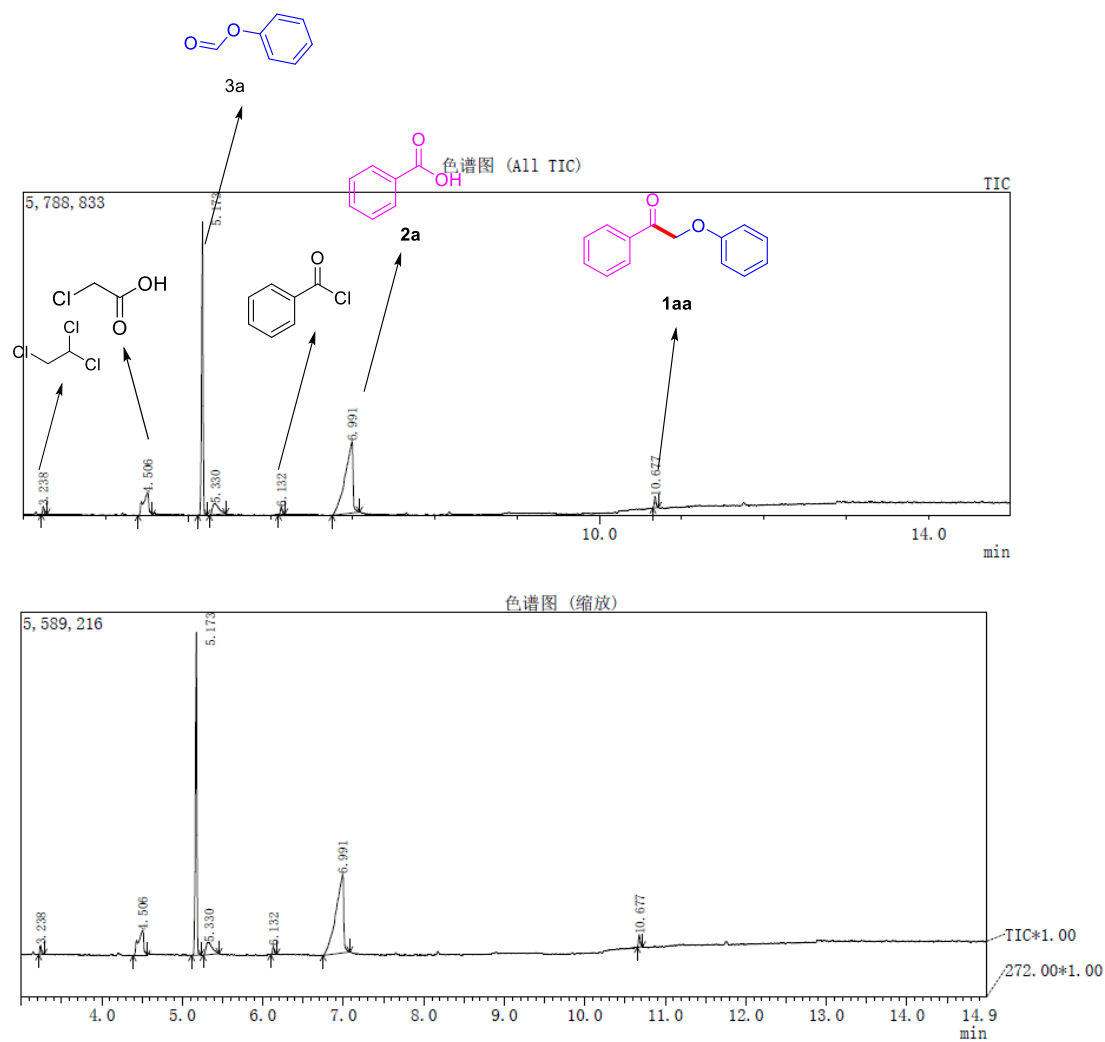


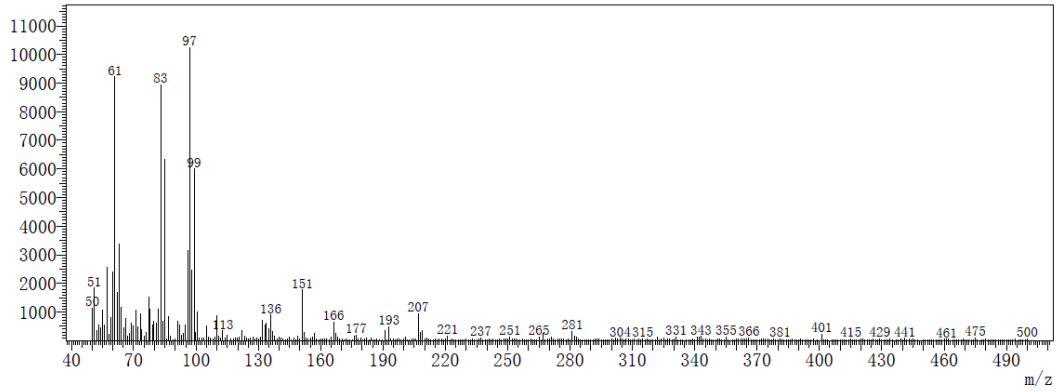
Figure S2. GC-MS trace of reaction in Scheme S1-a.

GC-MS method:

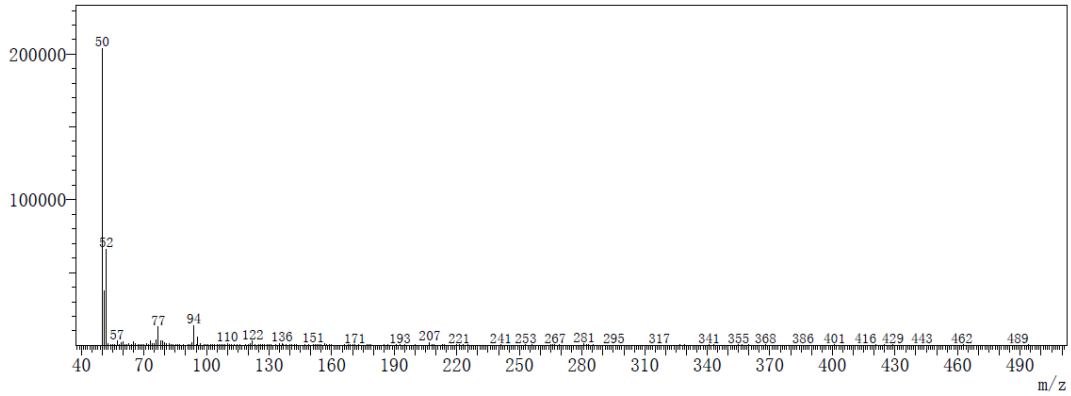
entry	Rate (°C/min)	Final Temperature (°C)	Keep time (min)
0	-	50	2
1	25.0	280	3.8
Total time			15

The column: Rtx-5MS, film thickness: 0.25 μm , length: 30 m, inside diameter: 0.25 mm

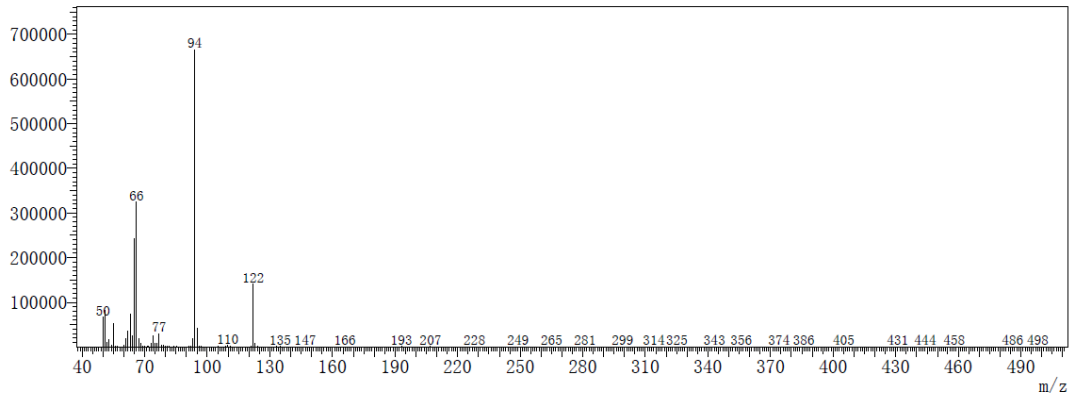
流路号:1 保留时间:3.250(扫描数:31)
质量峰:447
原始模式:单个 3.250(31) 基峰:96.90(10233)
背景模式:无 组 1 - 事件 1 Scan



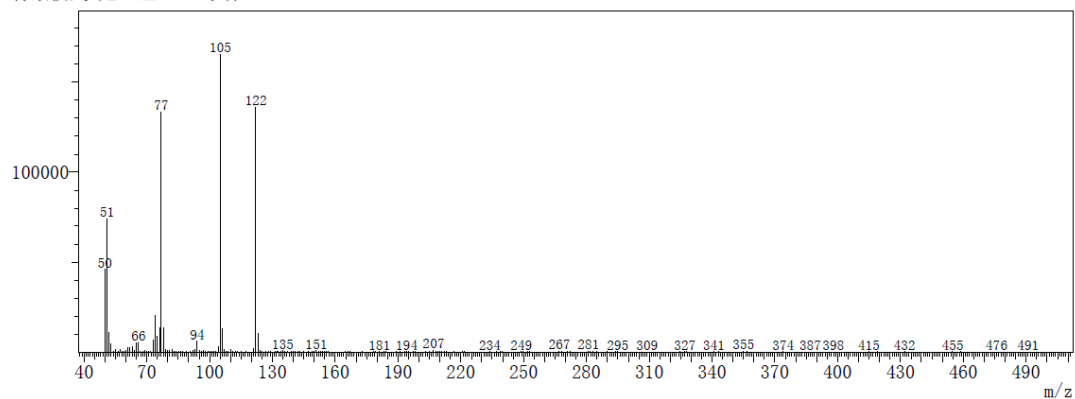
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质量峰:439
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背景模式:无 组 1 - 事件 1 Scan



流路号:1 保留时间:5.183(扫描数:263)
质量峰:442
原始模式:单个 5.183(263) 基峰:94.00(664788)
背景模式:无 组 1 - 事件 1 Scan



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质量峰:445
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背景模式:无 组 1 - 事件 1 Scan



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背景模式:无 组 1 - 事件 1 Scan

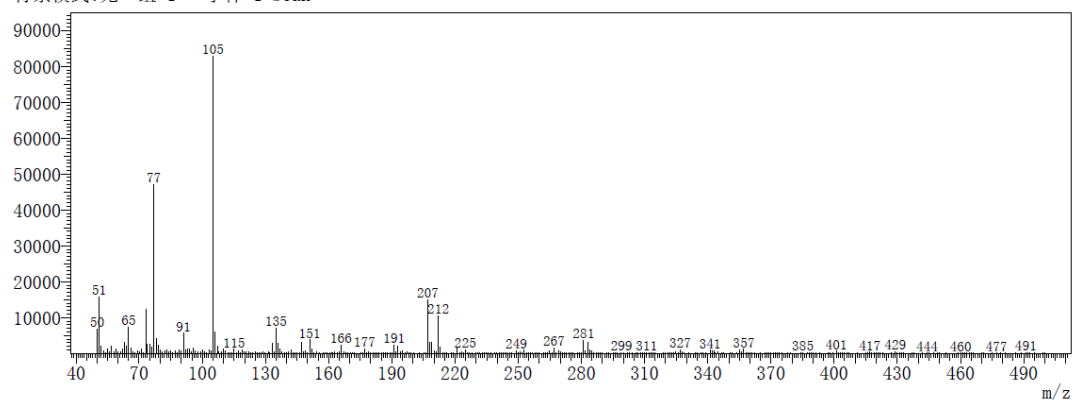
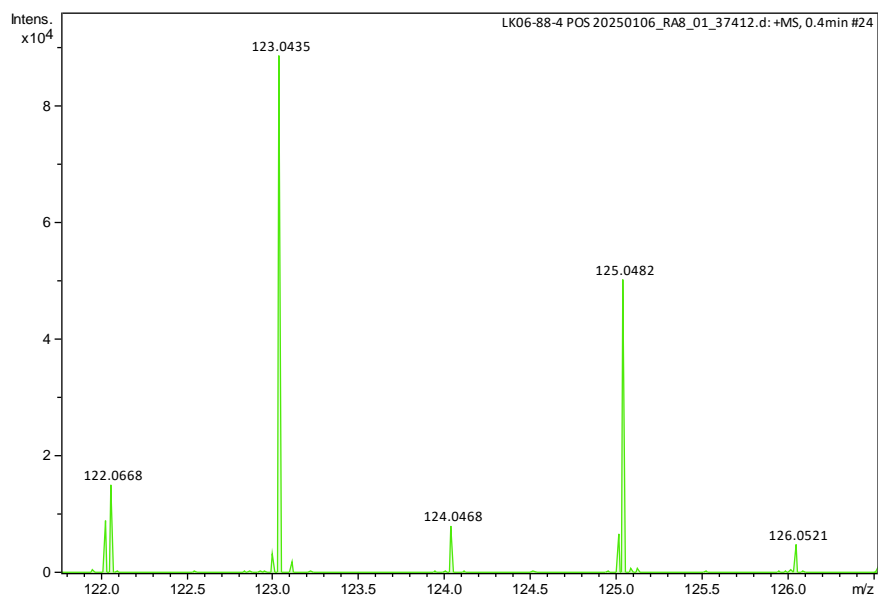


Figure S3. MS spectrum details of the trace of reaction in Scheme S1-a.

Phenyl formate **3a-¹⁸O**: C₇H₇O¹⁸O⁺ calc: 125.0483, exp. 125.0482



HRMS of the ¹⁸O₂-labeled reaction product

Benzoyl **2a-¹⁸O**: C₇H₅O¹⁸O⁻ calc: 123.0332, exp. 123.0340

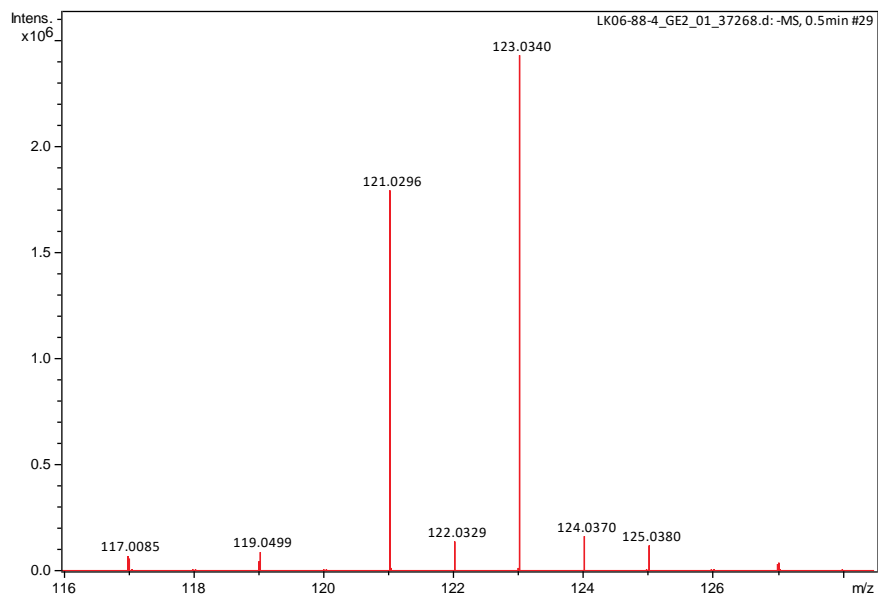


Figure S4. HRMS of the ¹⁸O₂-labeled reaction product.

3.2 Light on/off experiment

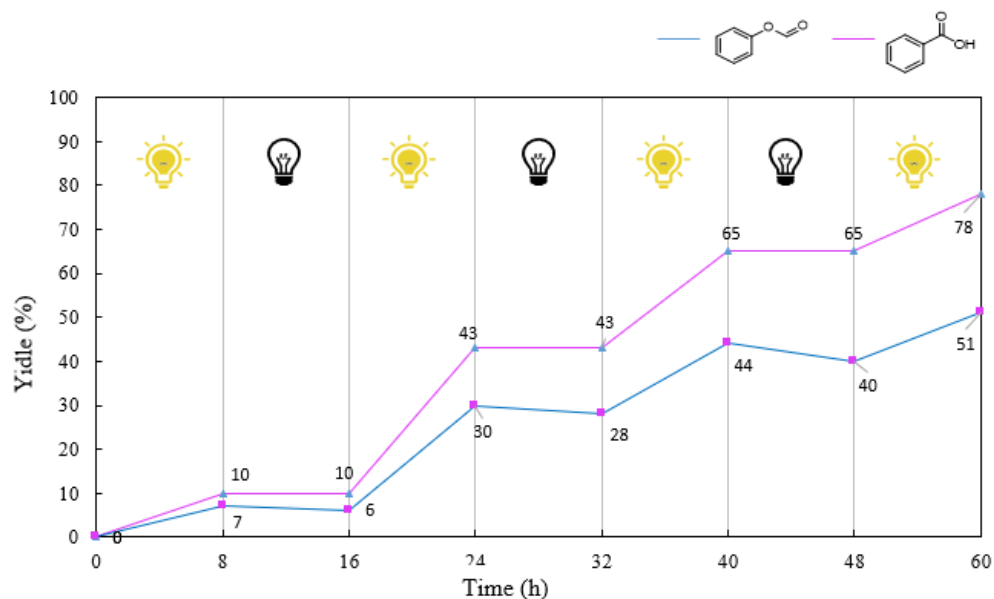


Figure S5. Light On-Off Experiments. The reaction was performed with **1aa** as substrate in DCE for light on/off per 8 h. The reaction process was monitored by GC-MS.

3.3 Electron paramagnetic resonance (EPR) spectra.

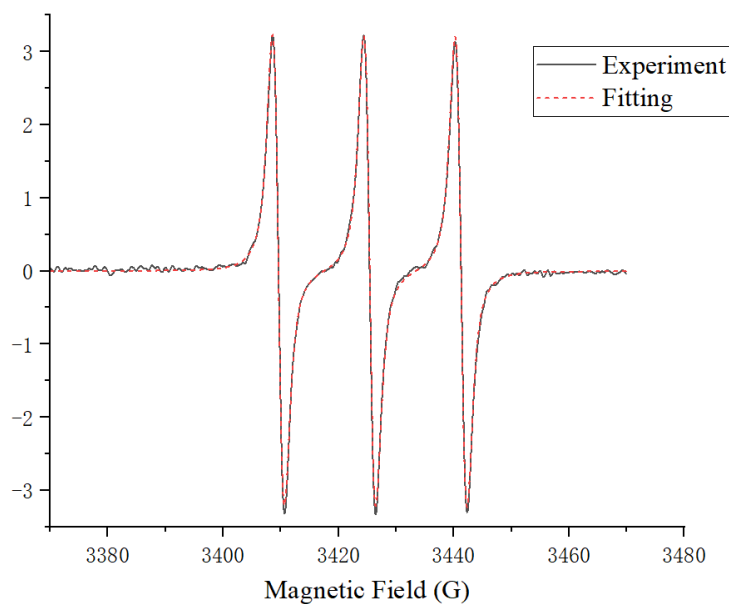
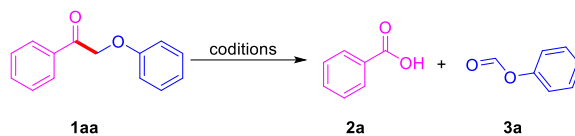


Figure S6. The electron paramagnetic resonance (EPR) Spectra UV-vis absorption spectra. After irradiated at 395-400 nm for 12 h, TEMP was added and the reaction was further stirred for 10 min and then the EPR reaction was conducted.

3.4 Detailed optimization of the reaction conditions^a



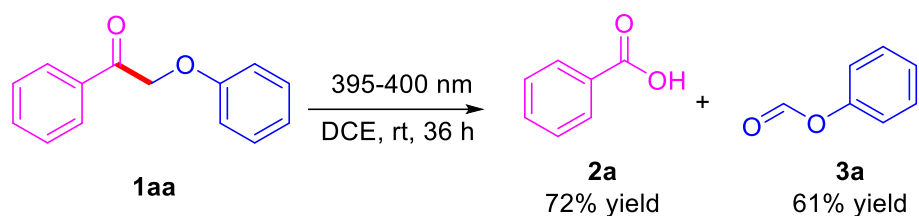
Entry	Light	Solvent	Conversion (%)	Yield (%) ^b
1	400-410 nm	Toluene	15	Trace
2	400-410 nm	MeCN	20	Trace
3	400-410 nm	PhCl	25	Trace
4	400-410 nm	DMSO	/	ND
5	400-410 nm	DMA	/	ND
6	400-410 nm	NMP	/	ND
7	400-410 nm	MeOH	/	ND
8	400-410 nm	EtOAc	/	ND
9	400-410 nm	Dioxane	/	ND
10	400-410 nm	DCE	85	2a: 70%; 3a: 59%
11	395-400 nm	DCE	99	2a: 72%; 3a: 61%
12	390-395 nm	DCE	95	2a: 71%; 3a: 60%
13	380-385 nm	DCE	90	2a: 65%; 3a: 51%
14	5 W blue LED	DCE	/	2a: 25%; 3a: 15%
15	365 nm	DCE	50	ND
16	yellow LED	DCE	/	ND
17	green LED	DCE	/	ND
18	white LED	DCE	/	ND
19 ^c	/	DCE	/	ND
20 ^d	/	DCE	/	ND
21 ^e	395-400 nm	DCE	Trace	Trace
22 ^f	100 °C	DCE	/	ND
23	395-400 nm	DCM	/	ND
24	395-400 nm	CHCl ₃	78%	2a: 56%; 3a: 27%
25	395-400 nm	CCl ₄	/	ND

^[a] Unless otherwise noted, the reaction was carried out with **1aa** (0.05 mmol) in solvent (0.50 mL, 0.1 M) under the irradiation of indicated light. ^[b] Yields refer to the isolated products. ^[c] under dark, rt. ^[d] under dark, 100 °C. ^[e] N₂ atmosphere. ^[f] N₂ atmosphere, under dark, 100 °C.

3.5 General procedure for the photo-induced C(α)-C(β) cleavage of the lignin model compounds

The substrate β -O-4 ketone lignin model compound **1** (0.10 mmol) was dissolved in DCE (1.0 mL, 0.1 M) in a quartz tube. The reaction mixture was then stirred at room temperature with the irradiation under 395-400 nm light (3W, 2 cm distance). The process of the reaction was monitored by TLC and GC-MS (about 36 h). Upon completion, the solution was transferred to a random flask. Then the solvent was removed under vacuum and the residue was purified by silica gel chromatography with petroleum ether (PE)/ethyl acetate (EtOAc) as mobile phase to afford the corresponding products **2** and **3**.

3.6 Data and references.

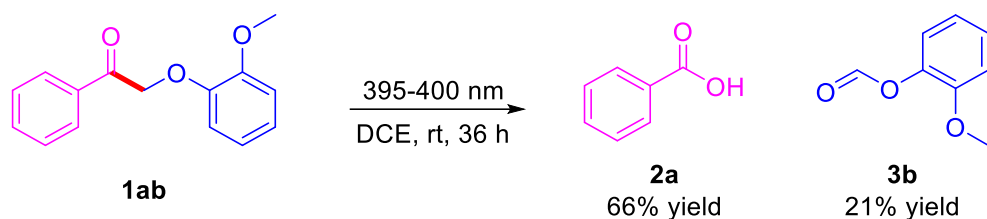


Lignin model compound **1aa**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.32 (dd, $J = 8.7, 7.3$ Hz, 2H), 7.04 - 6.96 (m, 3H), 5.30 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.5, 158.0, 134.6, 133.8, 129.5, 128.8, 128.1, 121.6, 114.8, 70.7.

Lignin model compound **1aa** (21.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (8.8 mg, 72% yield), phenyl formate **3a** (7.4 mg, 61% yield).

Benzoic acid **2a**^[1]: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Phenyl formate **3a**^[2]: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.18 (s, 1H), 7.29 (dd, $J = 8.5, 7.4$ Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 159.2, 149.8, 129.6, 126.3, 121.0.

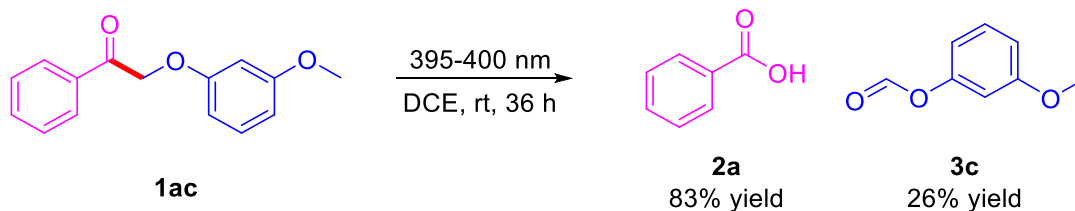


Lignin model compound **1ab**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 - 7.99 (m, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.7$ Hz, 2H), 7.00 (dt, $J = 8.5, 4.4$ Hz, 1H), 6.94 (d, $J = 7.9$ Hz, 1H), 6.88 (d, $J = 3.6$ Hz, 2H), 5.37 (s, 2H), 3.90 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.5, 149.8, 147.5, 134.6, 133.7, 128.7, 128.1, 122.5, 120.8, 114.9, 112.2, 72.1, 55.9.

Lignin model compound **1ab** (24.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (8.1 mg, 66% yield), *ortho*-methoxyl phenyl formate **3b** (3.2 mg, 21% yield).

Benzoic acid **2a**^[1]: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Phenyl formate **3b**^[3]: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.28 (s, 1H), 7.25 (ddd, $J = 9.1, 7.6, 1.7$ Hz, 1H), 7.12 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.03 - 6.97 (m, 2H), 3.84 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 159.1, 150.7, 138.7, 127.2, 122.4, 120.7, 112.4, 55.6.

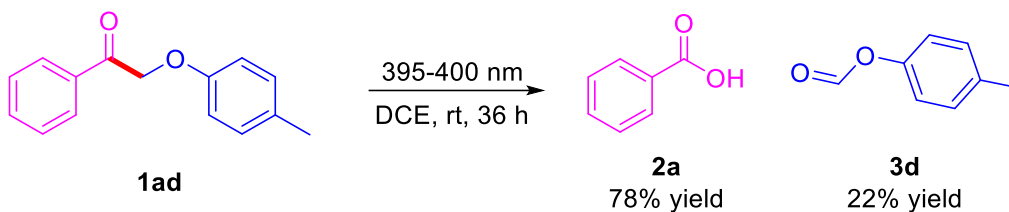


Lignin model compound **1ac**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 - 8.03 (m, 2H), 7.66 - 7.58 (m, 1H), 7.50 (dd, $J = 8.4, 7.1$ Hz, 2H), 7.15 (t, $J = 8.2$ Hz, 1H), 6.55 - 6.48 (m, 2H), 5.59 (dd, $J = 6.0, 4.0$ Hz, 1H), 4.21 - 4.10 (m, 2H), 3.75 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 196.6, 160.9, 158.4, 134.7, 134.0, 130.0, 128.8, 128.7, 107.6, 107.0, 102.0, 81.0, 63.1, 55.2.

Lignin model compound **1ac** (24.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (10.1 mg, 83% yield), phenyl formate **3c** (4.0 mg, 26% yield).

Lignin model compound **2a**^[1]: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Lignin model compound **3c**^[4]: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.29 (s, 1H), 7.30 (t, $J = 8.2$ Hz, 1H), 6.83 (ddd, $J = 8.4, 2.5, 0.9$ Hz, 1H), 6.76 - 6.73 (m, 1H), 6.71 (t, $J = 2.4$ Hz, 1H), 3.79 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 160.5, 159.2, 150.7, 129.9, 113.0, 111.9, 107.0, 55.2.

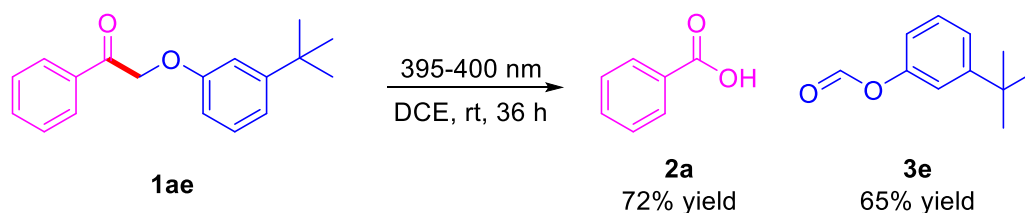


Lignin model compound **1ad**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 - 7.99 (m, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.52 (dd, $J = 8.5, 7.0$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 5.27 (s, 2H), 2.31 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.7, 155.9, 134.6, 133.8, 130.9, 130.0, 128.8, 128.1, 114.6, 71.0, 20.4.

Lignin model compound **1ad** (22.6 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (9.5 mg, 78% yield), phenyl formate **3d** (3.0 mg, 22% yield).

Product **2a**^[1]: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3d**^[4]: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.31 (s, 1H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 8.5$ Hz, 2H), 2.39 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 159.4, 147.6, 135.9, 130.0, 120.6, 20.6.

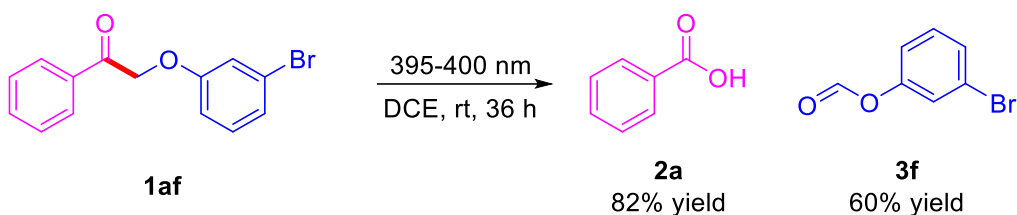


Lignin model compound **1ae**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (d, $J = 7.1$ Hz, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 2H), 7.14 - 7.07 (m, 2H), 6.99 (d, $J = 6.8$ Hz, 1H), 6.78 (dd, $J = 8.1, 2.6$ Hz, 1H), 5.33 (s, 2H), 1.35 (d, $J = 5.9$ Hz, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.9, 157.7, 153.1, 134.5, 133.8, 128.9, 128.7, 128.0, 118.8, 117.3, 113.2, 112.6, 112.3, 110.5, 70.7, 34.6, 31.2.

Lignin model compound **1ae** (26.8 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (8.8 mg, 72% yield), phenyl formate **3e** (11.6 mg, 65% yield).

Product **2a**^[1]: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

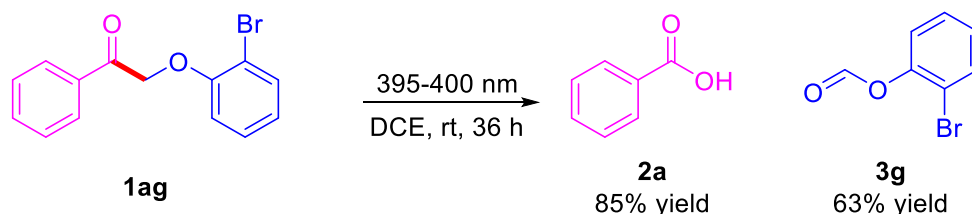
Product **3e**: $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.19 (s, 1H), 7.32 (d, $J = 8.7$ Hz, 2H), 6.96 (d, $J = 8.7$ Hz, 2H), 1.23 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 159.5, 149.2, 147.5, 126.5, 120.4, 34.4, 31.3.



Lignin model compound **1af** (29.0 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (10.0 mg, 82% yield), phenyl formate **3f** (12.0 mg, 60% yield).

Product **2a**¹¹: ¹H NMR (400 MHz, CDCl₃) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3f**: ¹H NMR (600 MHz, CDCl₃) δ 8.15 (s, 1H), 7.30 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.23 (t, *J* = 2.0 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.02 - 6.98 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 158.5, 150.1, 130.6, 129.5, 124.5, 122.5, 119.9.

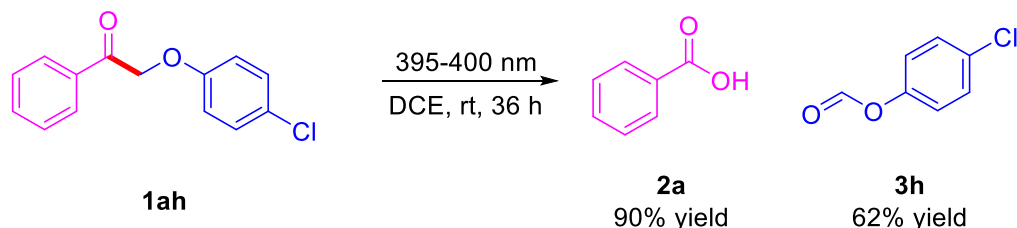


Lignin model compound **1ag**: ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.60 - 7.48 (m, 3H), 7.26 - 7.20 (m, 1H), 6.92 - 6.81 (m, 2H), 5.36 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.0, 154.5, 134.3, 133.9, 133.6, 128.8, 128.4, 128.2, 122.8, 113.8, 112.3, 71.8.

Lignin model compound **1ag** (29.0 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (10.4 mg, 85% yield), phenyl formate **3g** (12.6 mg, 63% yield).

Product **2a**¹¹: ¹H NMR (400 MHz, CDCl₃) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3g**: ¹H NMR (600 MHz, CDCl₃) δ 8.34 (d, *J* = 0.9 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.39 - 7.35 (m, 1H), 7.22 - 7.15 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 158.0, 158.0, 147.2, 133.5, 128.6, 128.6, 127.8, 123.4, 115.6.



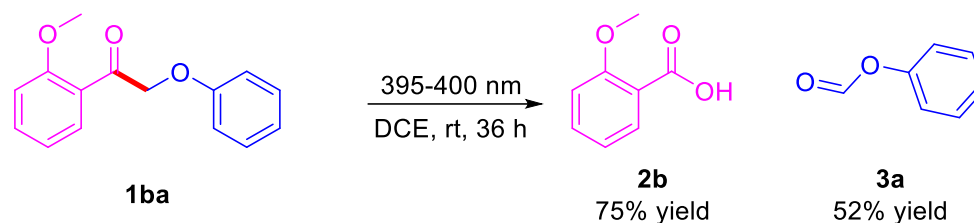
Lignin model compound **1ah**: ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.89 (d,

$J = 8.4$ Hz, 2H), 5.29 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.0, 156.6, 134.3, 134.0, 129.4, 128.9, 128.0, 126.5, 116.1, 116.1, 70.9.

Lignin model compound **1ah** (24.8 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (11.0 mg, 90% yield), phenyl formate **3h** (9.7 mg, 62% yield).

Product **2a**^[1]: ^1H NMR (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3h**^[4]: ^1H NMR (600 MHz, CDCl_3) δ 8.28 (s, 1H), 7.41 - 7.36 (m, 2H), 7.13 - 7.08 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.7, 148.2, 131.7, 129.6, 122.5.

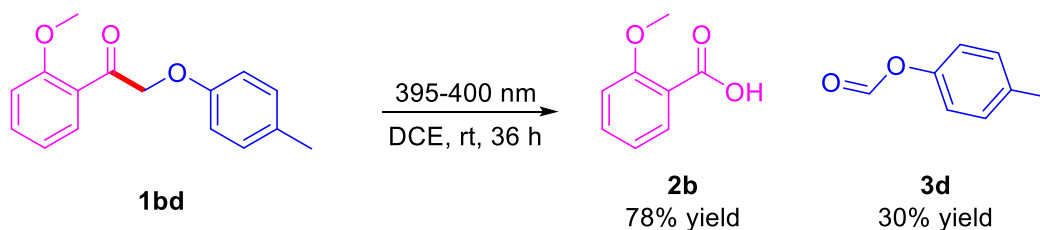


Lignin model compound **1ba**: ^1H NMR (400 MHz, CDCl_3) δ 7.83 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.46 - 7.39 (m, 1H), 7.20 - 7.15 (m, 2H), 6.97 - 6.85 (m, 3H), 6.82 (d, $J = 8.1$ Hz, 2H), 5.14 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.3, 159.2, 158.2, 134.7, 130.8, 129.3, 124.8, 121.1, 121.0, 114.7, 111.5, 74.1, 55.5.

Lignin model compound **1ba** (24.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2b** (11.4 mg, 75% yield), phenyl formate **3a** (6.3 mg, 52% yield).

Product **2b**^[5]: ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dt, $J = 7.6$, 1.3 Hz, 1H), 7.66 (dd, $J = 2.7$, 1.5 Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.19 (ddd, $J = 8.2$, 2.7, 1.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 159.6, 130.5, 129.5, 122.7, 120.5, 114.4, 55.4.

Product **3a**^[2]: ^1H NMR (600 MHz, CDCl_3) δ 8.18 (s, 1H), 7.29 (dd, $J = 8.5$, 7.4 Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.2, 149.8, 129.6, 126.3, 121.0.



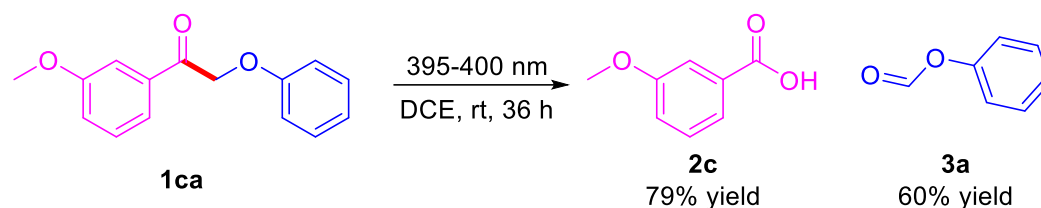
Lignin model compound **1bd**: ^1H NMR (400 MHz, CDCl_3) δ 7.85 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.50 - 7.41 (m, 1H), 7.01 - 6.91 (m, 4H), 6.76 - 6.71 (m, 2H), 5.13 (s, 2H), 3.87 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.6, 159.2, 156.2, 134.6, 131.0, 130.4, 129.8, 125.0, 121.1, 114.6, 111.5, 74.4, 55.6, 20.4.

Lignin model compound **1bd** (25.6 mg, 0.10 mmol) was used under standard

condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2b** (11.9 mg, 78% yield), phenyl formate **3d** (4.1 mg, 30% yield).

Product **2b**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.66 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 159.6, 130.5, 129.5, 122.7, 120.5, 114.4, 55.4.

Product **3d**^[4]: ¹H NMR (600 MHz, CDCl₃) δ 8.31 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.4, 147.6, 135.9, 130.0, 120.6, 20.6.

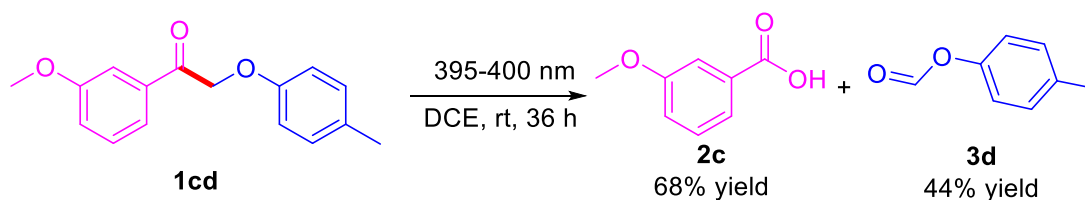


Lignin model compound **1ca**: ¹H NMR (400 MHz, CDCl₃) δ 7.52 - 7.44 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.24 - 7.18 (m, 2H), 7.08 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.93 - 6.84 (m, 3H), 5.18 (s, 2H), 3.78 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.3, 159.9, 158.0, 135.8, 129.8, 129.5, 121.6, 120.5, 120.4, 114.8, 112.4, 70.8, 55.5.

Lignin model compound **1ca** (24.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2c** (12.0 mg, 79% yield), phenyl formate **3a** (7.3 mg, 60% yield).

Product **2c**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.66 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 159.6, 130.5, 129.5, 122.7, 120.5, 114.4, 55.4.

Product **3a**^[2]: ¹H NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 7.29 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 159.2, 149.8, 129.6, 126.3, 121.0.



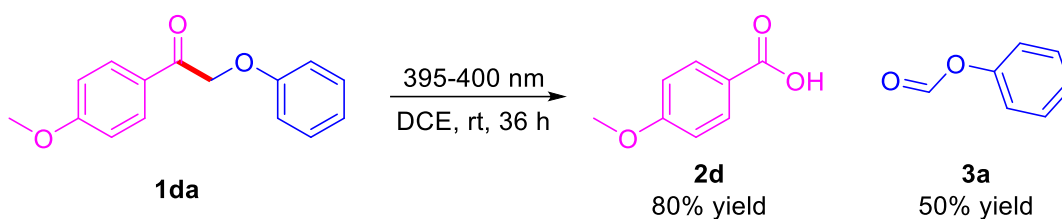
Lignin model compound **1cd**: ¹H NMR (400 MHz, CDCl₃) δ 7.62 - 7.53 (m, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.25 (s, 2H), 3.88 (s, 3H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.5, 159.9, 155.9, 135.9, 130.9, 130.0, 129.8, 120.5, 120.3, 114.6, 112.3, 71.0, 55.4, 20.4.

Lignin model compound **1cd** (25.6 mg, 0.10 mmol) was used under standard

condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2c** (10.3 mg, 68% yield), phenyl formate **3d** (6.0 mg, 44% yield).

Product **2c**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.66 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 159.6, 130.5, 129.5, 122.7, 120.5, 114.4, 55.4.

Product **3d**^[4]: ¹H NMR (600 MHz, CDCl₃) δ 8.31 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.4, 147.6, 135.9, 130.0, 120.6, 20.6.

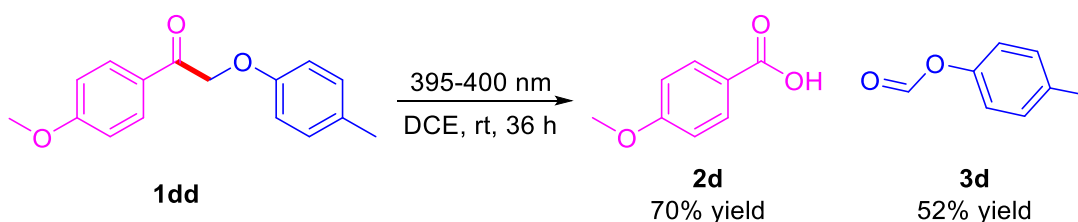


Lignin model compound **1da**: ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.9 Hz, 2H), 7.31 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.99 (td, *J* = 8.7, 7.8, 6.5 Hz, 5H), 5.23 (s, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.1, 164.0, 158.0, 130.5, 129.5, 127.6, 121.5, 114.7, 114.0, 70.6, 55.5.

Lignin model compound **1da** (24.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2d** (12.2 mg, 80% yield), phenyl formate **3a** (6.1 mg, 50% yield).

Product **2d**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.5, 164.1, 132.4, 121.6, 113.8, 55.5.

Product **3a**^[2]: ¹H NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 7.29 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 159.2, 149.8, 129.6, 126.3, 121.0.



Lignin model compound **1dd** (25.6 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2d** (10.6 mg, 70% yield), phenyl formate **3d** (7.1 mg, 52% yield).

Product **2d**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.5, 164.1, 132.4, 121.6, 113.8, 55.5.

Product **3d**^[4]: ¹H NMR (600 MHz, CDCl₃) δ 8.31 (s, 1H), 7.23 (d, *J* = 8.5 Hz,

2H), 7.06 (d, $J = 8.5$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.4, 147.6, 135.9, 130.0, 120.6, 20.6.

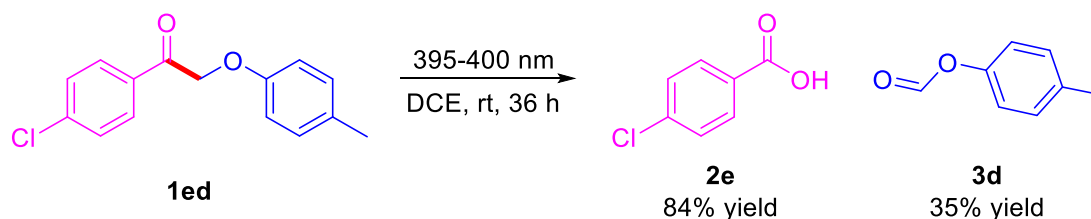


Lignin model compound **1ea**: ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.38 - 7.26 (m, 2H), 7.02 (t, $J = 7.3$ Hz, 1H), 6.96 (d, $J = 8.2$ Hz, 2H), 5.23 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.7, 157.8, 140.3, 132.8, 129.7, 129.6, 129.1, 121.8, 114.7, 70.8.

Lignin model compound **1ea** (24.7 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2e** (9.4 mg, 60% yield), phenyl formate **3a** (5.5 mg, 45% yield).

Product **2e**^[5]: ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.97 (d, $J = 8.1$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 166.5 (d, $J = 3.2$ Hz), 137.9 (d, $J = 3.3$ Hz), 131.2 (d, $J = 3.3$ Hz), 129.7 (d, $J = 3.1$ Hz), 128.8 (d, $J = 3.0$ Hz).

Product **3a**^[2]: ^1H NMR (600 MHz, CDCl_3) δ 8.18 (s, 1H), 7.29 (dd, $J = 8.5, 7.4$ Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.2, 149.8, 129.6, 126.3, 121.0.



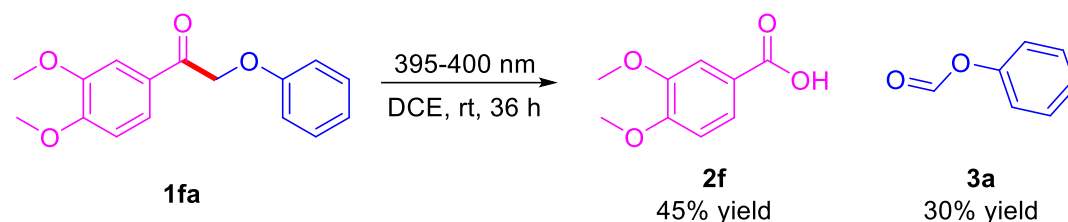
Lignin model compound **1ed**: ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.6$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 5.20 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.9, 155.7, 140.2, 132.9, 131.1, 130.0, 129.7, 129.1, 114.6, 71.1, 20.4.

Lignin model compound **1ed** (26.0 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2e** (13.1 mg, 84% yield), phenyl formate **3d** (4.8 mg, 35% yield).

Product **2e**^[5]: ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.01 - 7.91 (m, 1H), 7.57 (dd, $J = 12.3, 8.1$ Hz, 1H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 166.5 (d, $J = 3.2$ Hz), 137.9 (d, $J = 3.3$ Hz), 131.2 (d, $J = 3.3$ Hz), 129.7 (d, $J = 3.1$ Hz), 128.8 (d, $J = 3.0$ Hz).

Product **3d**^[4]: ^1H NMR (600 MHz, CDCl_3) δ 8.31 (s, 1H), 7.23 (d, $J = 8.5$ Hz,

2H), 7.06 (d, $J = 8.5$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.4, 147.6, 135.8, 130.0, 120.6, 20.6.

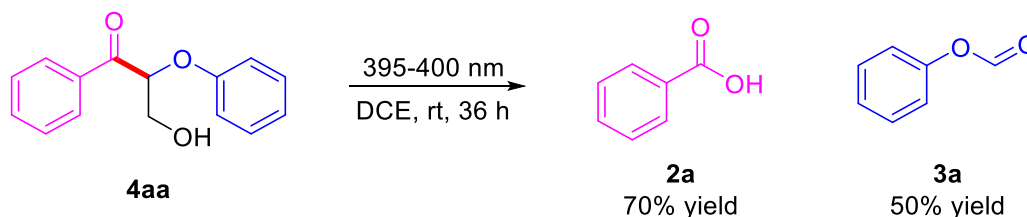


Lignin model compound **1fa**: ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 8.5$, 1.0 Hz, 1H), 7.49 (d, $J = 1.9$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 2H), 6.86 (td, $J = 16.0$, 7.8 Hz, 4H), 5.14 (s, 2H), 3.86 (d, $J = 8.7$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.1, 158.0, 153.8, 149.2, 129.5, 127.7, 122.8, 121.5, 114.7, 110.3, 110.1, 70.6, 56.0, 55.9.

Lignin model compound **1fa** (27.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2f** (8.2 mg, 45% yield), phenyl formate **3a** (3.7 mg, 30% yield).

Product **2f**^{6f}: ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.62 (d, $J = 1.9$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 3.97 (d, $J = 2.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.1, 153.7, 148.6, 124.6, 121.7, 112.2, 110.3, 56.0, 55.9.

Product **3a**^{2l}: ^1H NMR (600 MHz, CDCl_3) δ 8.18 (s, 1H), 7.29 (dd, $J = 8.5$, 7.4 Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.2, 149.8, 129.6, 126.3, 121.0.

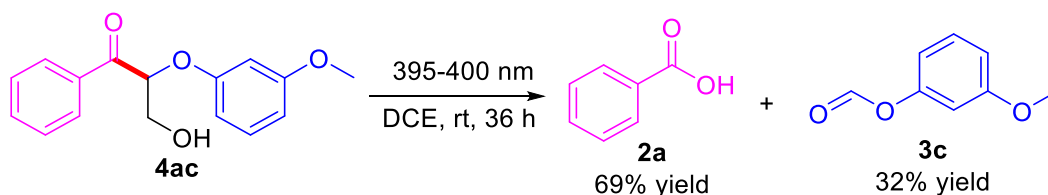


Lignin model compound **4aa**: ^1H NMR (400 MHz, CDCl_3) δ 8.10 - 8.00 (m, 2H), 7.65 - 7.56 (m, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.27 - 7.21 (m, 2H), 6.97 (t, $J = 7.4$ Hz, 1H), 6.90 (d, $J = 8.1$ Hz, 2H), 5.58 (dd, $J = 6.1$, 4.0 Hz, 1H), 4.21 - 4.06 (m, 2H), 2.49 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.7, 157.2, 134.7, 134.0, 129.7, 128.8, 128.7, 121.9, 115.3, 81.1, 63.2.

Lignin model compound **4aa** (24.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (8.5 mg, 70% yield), phenyl formate **3a** (6.1 mg, 50% yield).

Product **2a**^{1l}: ^1H NMR (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3a**^[2]: ¹H NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 7.29 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 159.2, 149.8, 129.6, 126.3, 121.0.

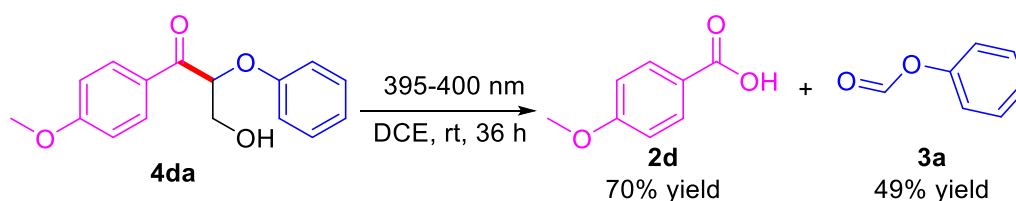


Lignin model compound **4ac**: ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.66 - 7.57 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 8.2 Hz, 1H), 6.59 - 6.45 (m, 3H), 5.59 (dd, *J* = 6.0, 4.0 Hz, 1H), 4.23 - 4.08 (m, 2H), 3.75 (s, 3H), 2.49 (d, *J* = 9.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.6, 160.8, 158.4, 134.6, 134.0, 130.1, 128.8, 128.6, 107.6, 107.0, 101.9, 80.9, 63.1, 55.2.

Lignin model compound **4ac** (27.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (8.4 mg, 69% yield), phenyl formate **3c** (4.9 mg, 32% yield).

Product **2a**^[1]: ¹H NMR (400 MHz, CDCl₃) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3c**^[4]: ¹H NMR (600 MHz, CDCl₃) δ 8.29 (s, 1H), 7.30 (t, *J* = 8.2 Hz, 1H), 6.83 (ddd, *J* = 8.4, 2.5, 0.9 Hz, 1H), 6.76 - 6.73 (m, 1H), 6.71 (t, *J* = 2.4 Hz, 1H), 3.79 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 160.5, 159.2, 150.7, 129.9, 113.0, 111.9, 107.0, 55.2.

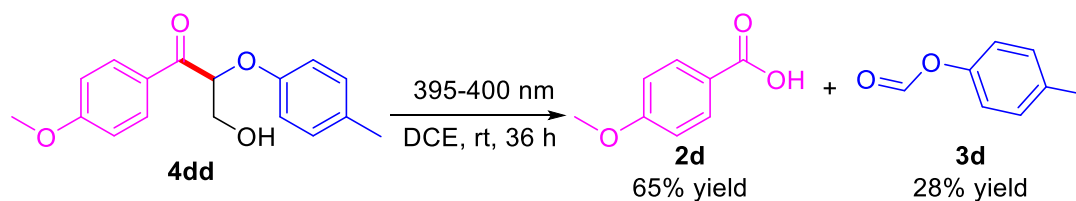


Lignin model compound **4da**: ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.66 - 7.57 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 8.2 Hz, 1H), 6.59 - 6.45 (m, 3H), 5.59 (dd, *J* = 6.0, 4.0 Hz, 1H), 4.23 - 4.08 (m, 2H), 3.75 (s, 3H), 2.49 (d, *J* = 9.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.6, 160.8, 158.4, 134.6, 134.0, 130.1, 128.8, 128.6, 107.6, 107.0, 101.9, 80.9, 63.1, 55.2.

Lignin model compound **4da** (27.2 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2d** (10.6 mg, 70% yield), phenyl formate **3a** (6.0 mg, 49% yield).

Product **2d**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.5, 164.1, 132.4, 121.6, 113.8, 55.5.

Product **3a**^[2]: ¹H NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 7.29 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.17 - 7.13 (m, 1H), 7.05 - 7.00 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 159.2, 149.8, 129.6, 126.3, 121.0.

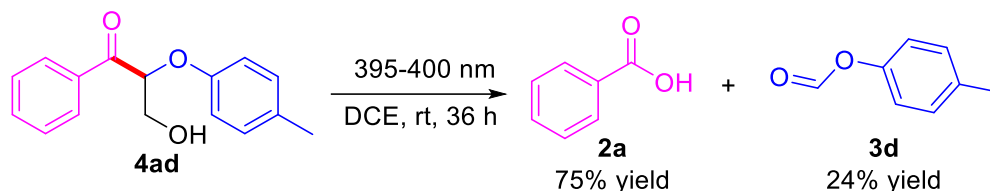


Lignin model compound **4dd**: ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.9 Hz, 2H), 7.31 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.99 (td, *J* = 8.7, 7.8, 6.5 Hz, 5H), 5.23 (s, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.1, 164.0, 158.0, 130.5, 129.5, 127.6, 121.5, 114.7, 114.0, 70.6, 55.5.

Lignin model compound **4dd** (28.6 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2d** (9.9 mg, 65% yield), phenyl formate **3d** (3.8 mg, 28% yield).

Product **2d**^[5]: ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.5, 164.1, 132.4, 121.6, 113.8, 55.5.

Product **3d**^[4]: ¹H NMR (600 MHz, CDCl₃) δ 8.31 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.4, 147.6, 135.9, 130.0, 120.6, 20.6.



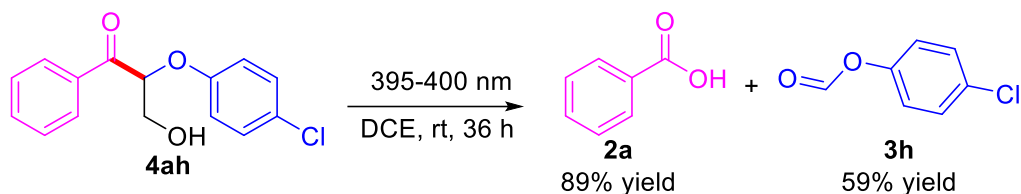
Lignin model compound **4ad**: ¹H NMR (400 MHz, CDCl₃) δ 8.01 - 7.89 (m, 2H), 7.57 - 7.46 (m, 1H), 7.38 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 5.43 (dd, *J* = 6.1, 4.1 Hz, 1H), 4.12 - 3.96 (m, 2H), 2.35 (s, 1H), 2.16 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.9, 155.1, 134.8, 133.9, 131.3, 130.1, 128.8, 128.7, 115.2, 81.3, 63.2, 20.4.

Lignin model compound **4ad** (25.6 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (9.2 mg, 75% yield), phenyl formate **3d** (3.3 mg, 24% yield).

Product **2a**^[1]: ¹H NMR (400 MHz, CDCl₃) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3d**^[4]: ¹H NMR (600 MHz, CDCl₃) δ 8.31 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H),

7.06 (d, $J = 8.5$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.4, 147.6, 135.9, 130.0, 120.6, 20.6.



Lignin model compound **4ah**: ^1H NMR (400 MHz, CDCl_3) δ 8.09 - 8.00 (m, 2H), 7.68 - 7.61 (m, 1H), 7.51 (t, $J = 7.7$ Hz, 2H), 7.22 (d, $J = 8.9$ Hz, 2H), 6.84 (d, $J = 8.9$ Hz, 2H), 5.56 (dd, $J = 6.1, 3.9$ Hz, 1H), 4.20 (dd, $J = 12.1, 3.9$ Hz, 1H), 4.13 (dd, $J = 12.1, 6.1$ Hz, 1H), 2.18 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.1, 155.8, 134.5, 134.2, 129.6, 129.0, 128.6, 126.9, 116.6, 81.4, 63.2.

Lignin model compound **4ah** (27.7 mg, 0.10 mmol) was used under standard condition irradiated for 36 h at 395-400 nm. After worked up and purification, the corresponding cleaved products were afforded, benzoic acid **2a** (10.9 mg, 89% yield), phenyl formate **3h** (9.2 mg, 59% yield).

Product **2a**^[1]: ^1H NMR (400 MHz, CDCl_3) δ 8.34 - 8.12 (m, 2H), 7.76 - 7.62 (m, 1H), 7.62 - 7.48 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 133.8, 130.2, 129.3, 128.5.

Product **3h**^[4]: ^1H NMR (600 MHz, CDCl_3) δ 8.28 (s, 1H), 7.41 - 7.36 (m, 2H), 7.13 - 7.08 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.7, 148.2, 131.7, 129.6, 122.5.

3.7 Gram-Scale reaction and solvent-recycling reaction

The substrate β -O-4 ketone lignin model compound **1aa** (2.12 g, 10 mmol) was dissolved in DCE (100 mL) in a random bottom flask. The reaction mixture was then stirred at room temperature with the irradiation under 395-400 nm light (20W, 2 cm distance). The process of the reaction was monitored by TLC and GC-MS (about 36 h). Upon completion, the solution was distilled directly and 82.5 mL DCE was recovered. Then the residue was purified by silica gel chromatography with petroleum ether (PE)/ethyl acetate (EtOAc) as mobile phase to afford the benzoic acid 0.732 g (60% yield).



Figure S7. Gram-Scale reaction of **1aa**.

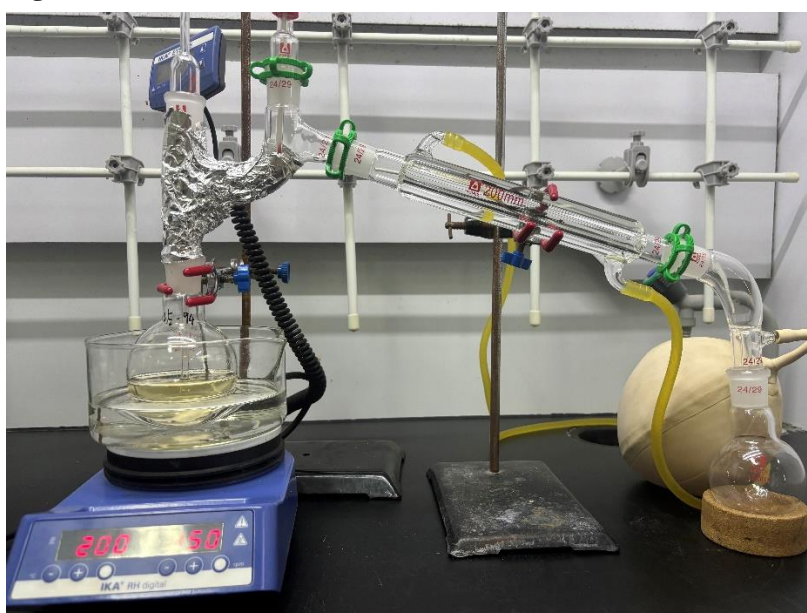
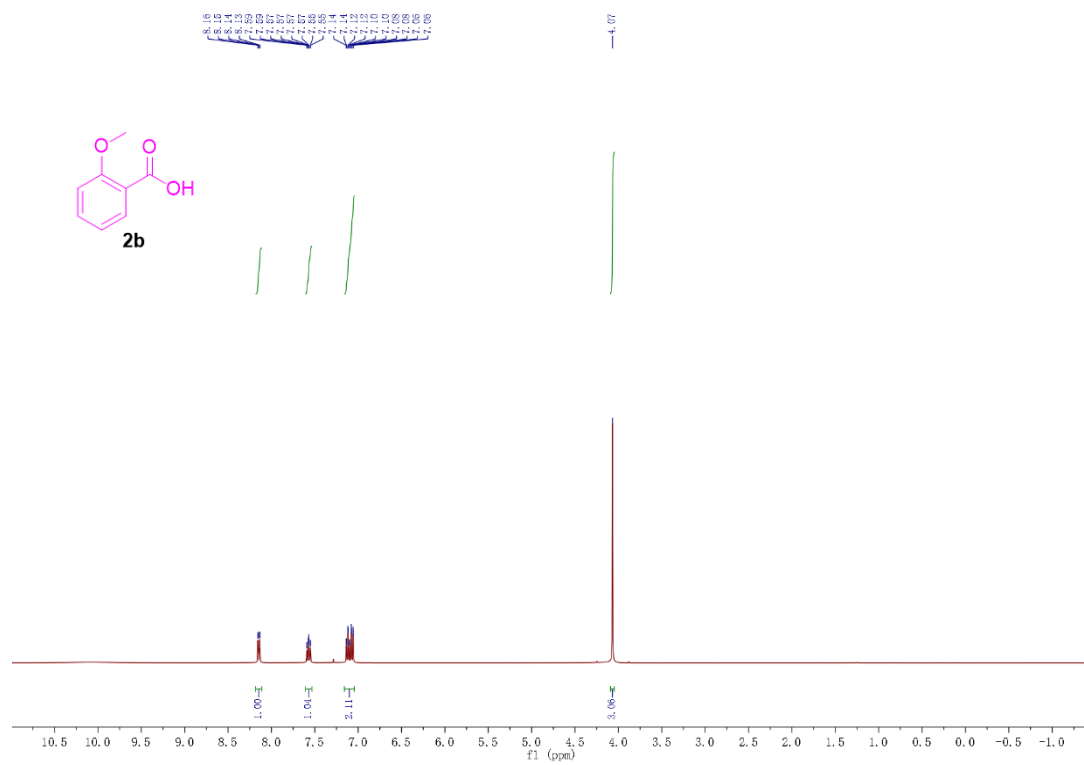


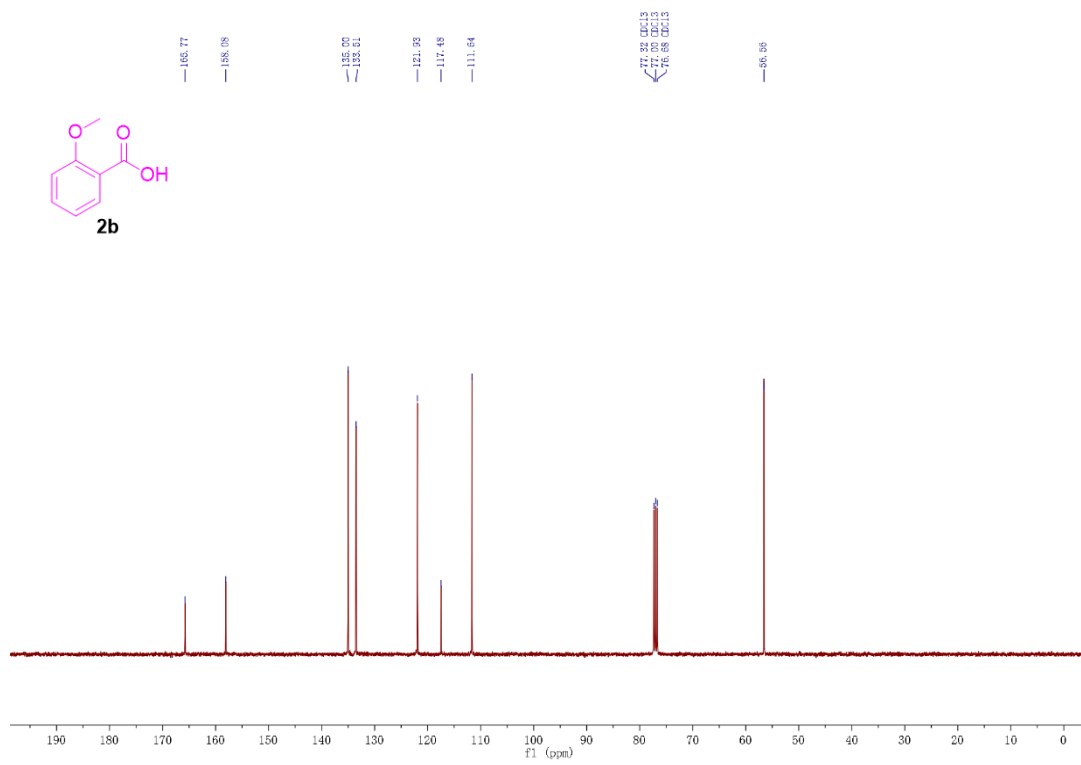
Figure S8. DCE-recycling reaction.

4. References

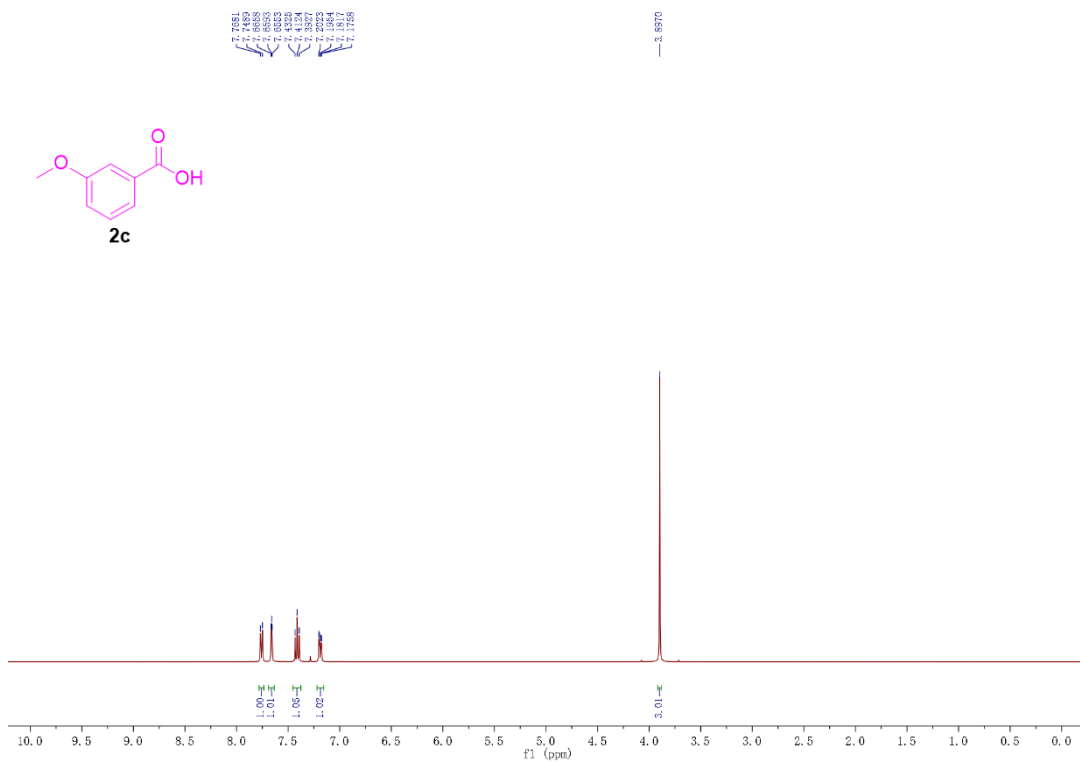
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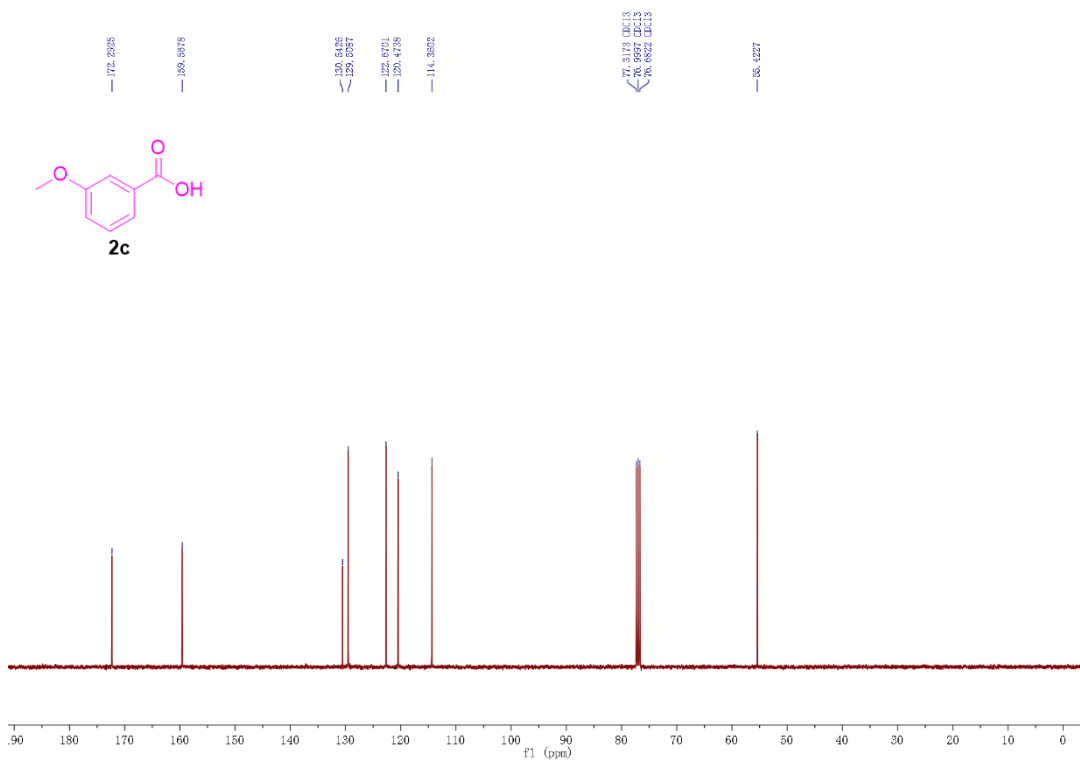
¹H NMR of 2b



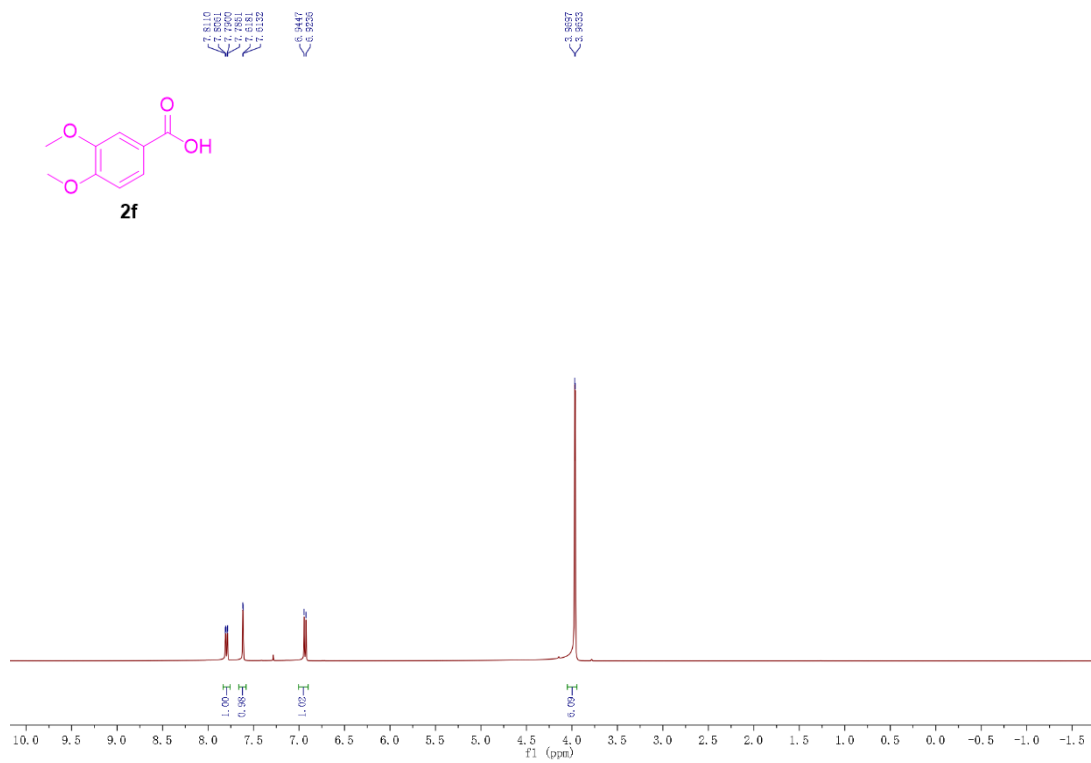
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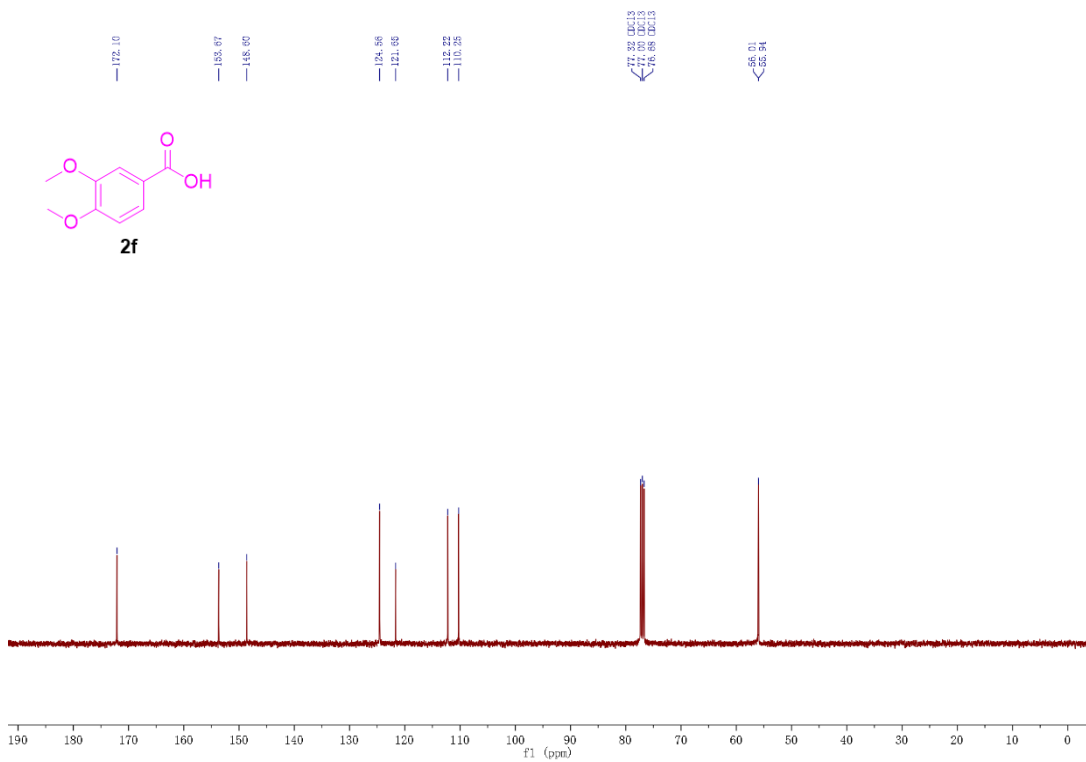
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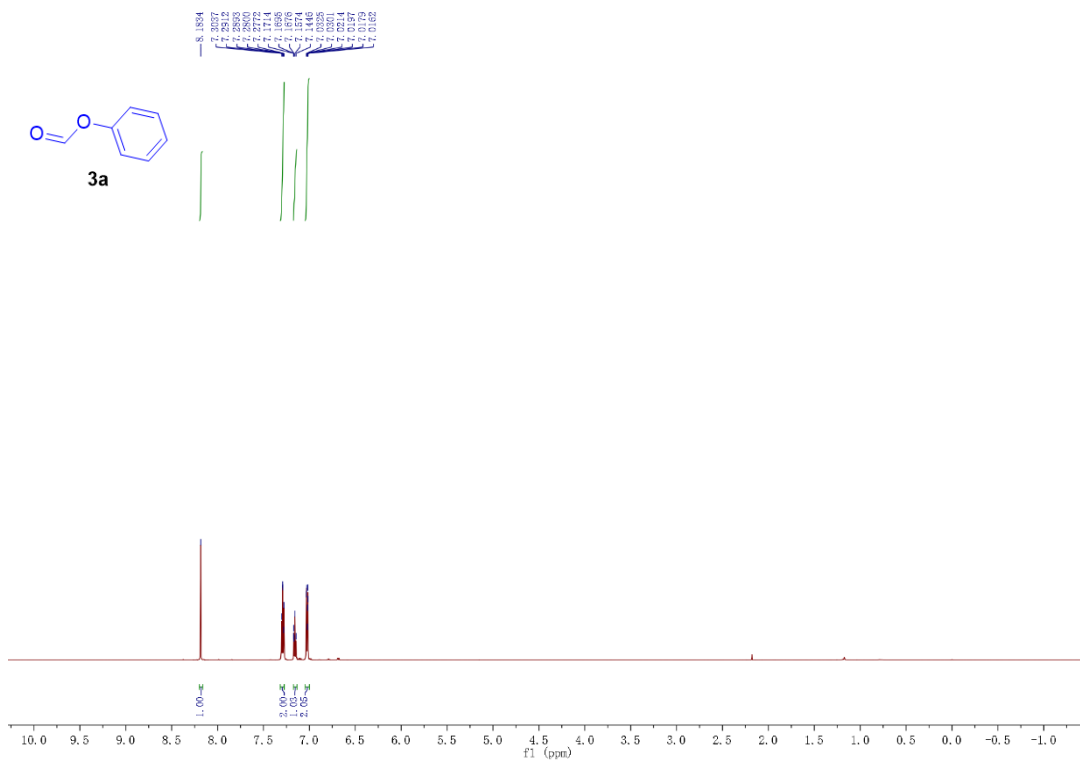
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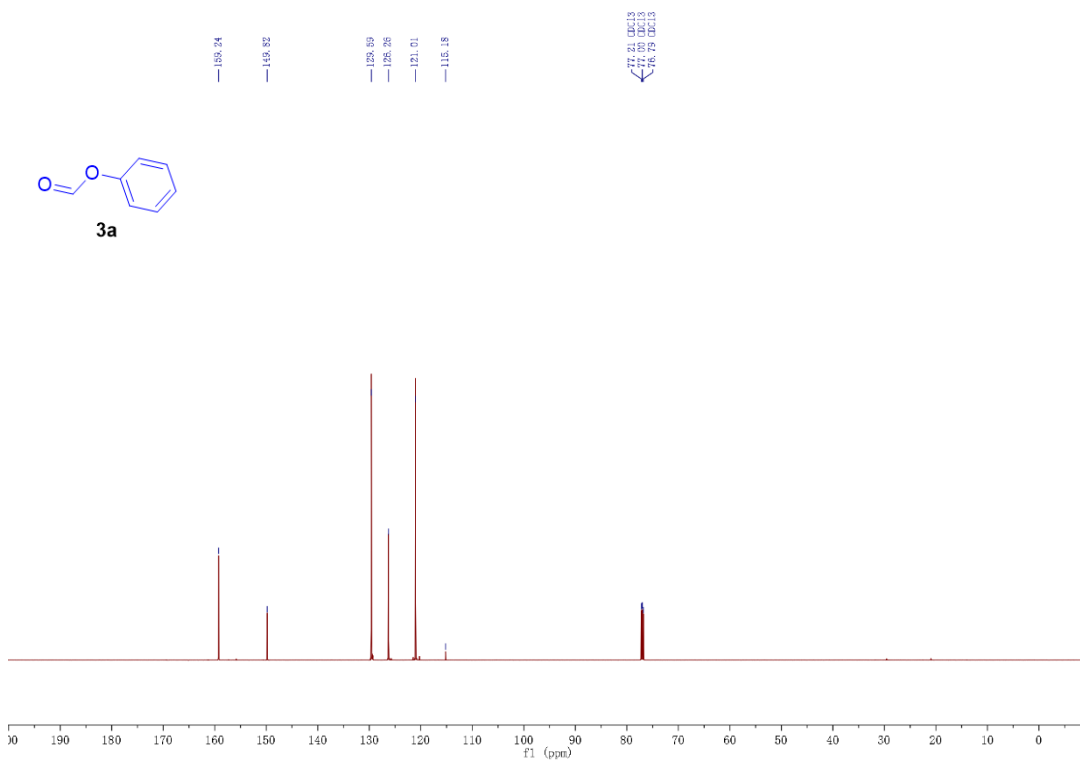
^1H NMR of **2f**



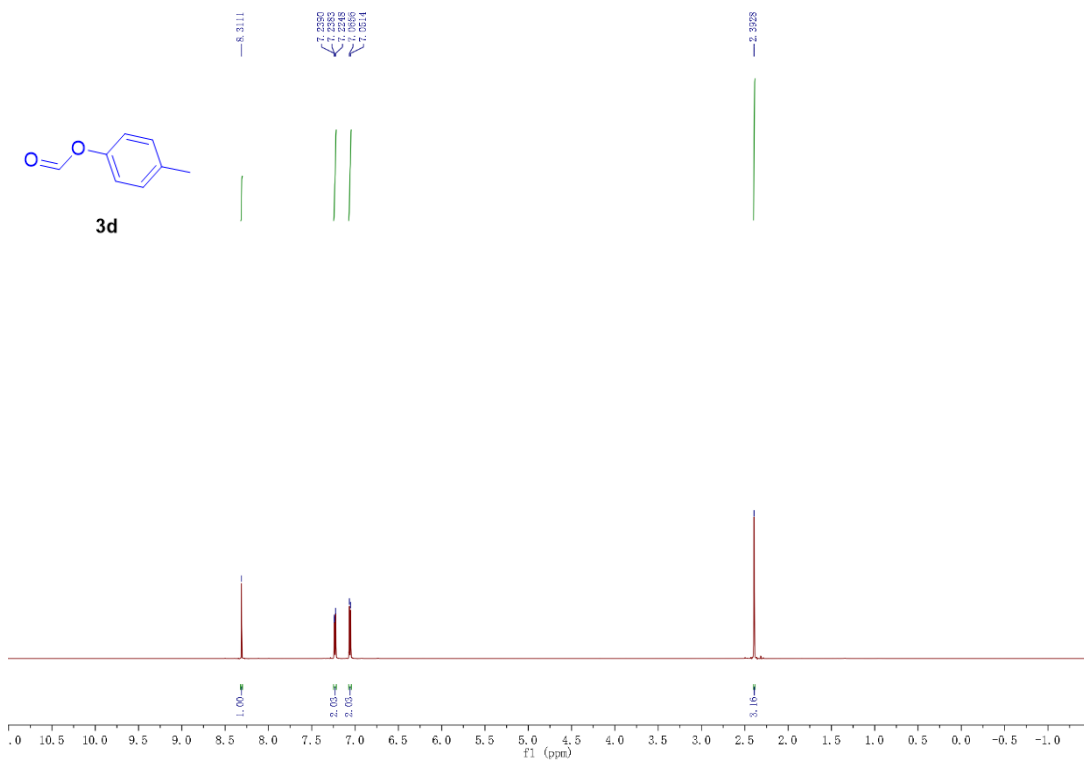
^{13}C NMR of **2f**



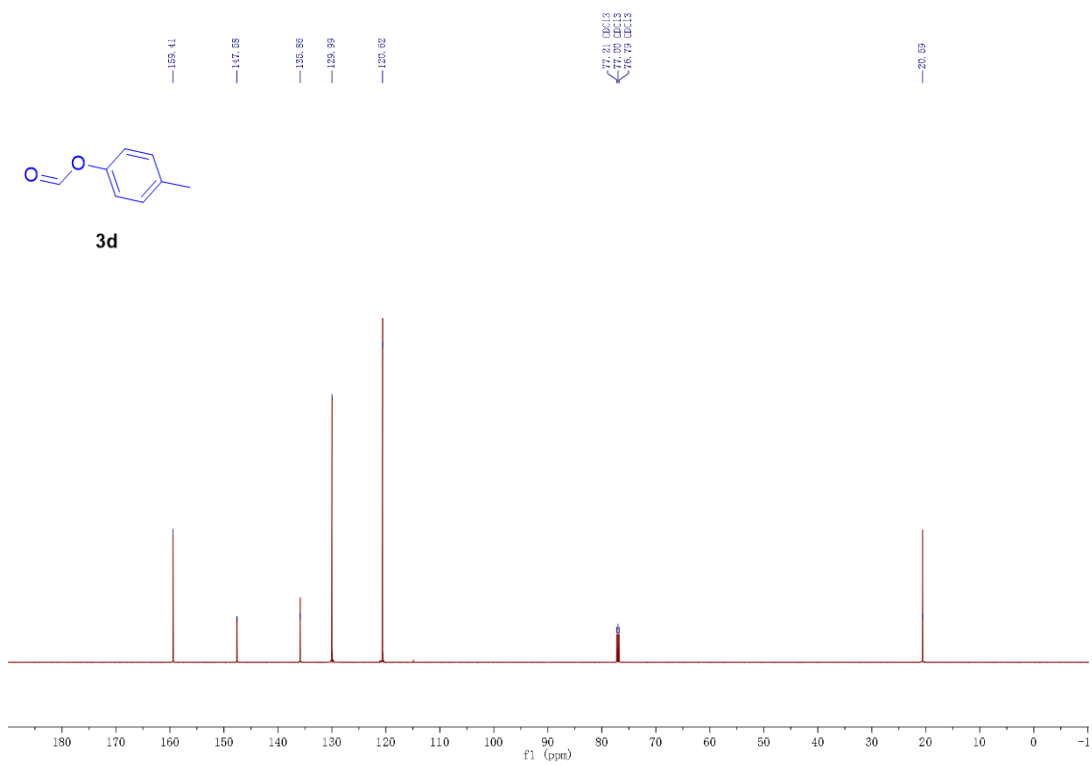
¹H NMR of 3a



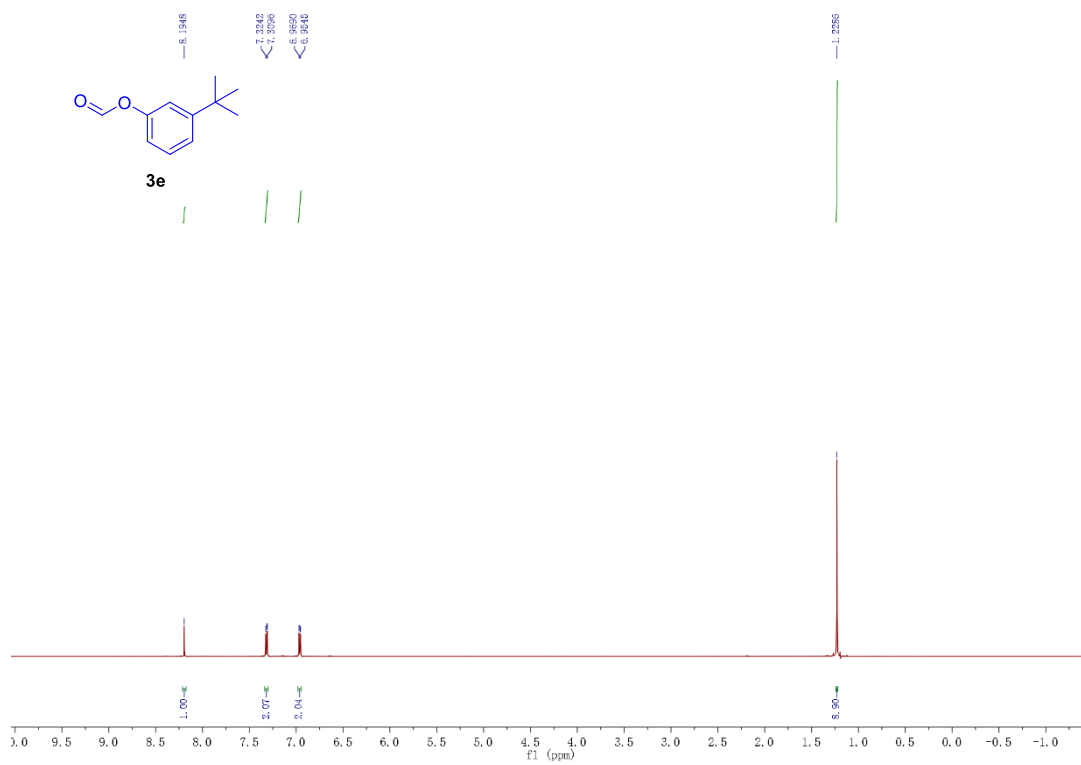
¹³C NMR of 3a



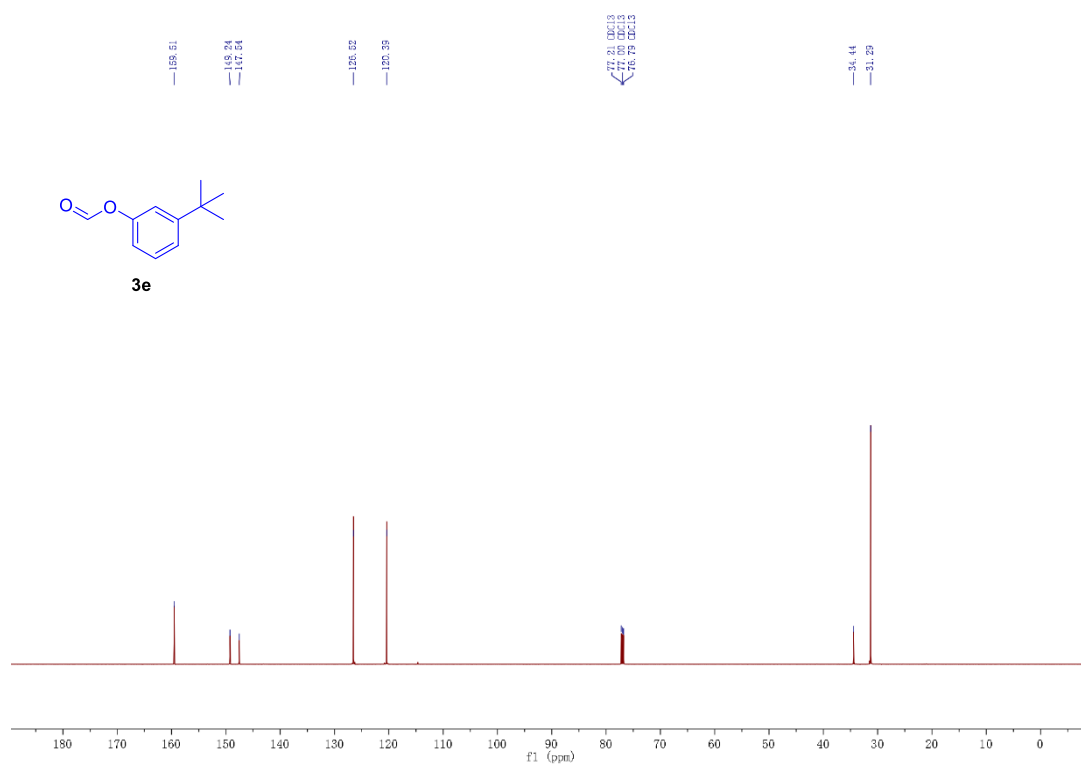
$^1\text{H NMR}$ of **3d**



$^{13}\text{C NMR}$ of **3d**



¹H NMR of **3e**



¹³C NMR of **3e**

